

من إصدارات

منصة أكاديمية الفيزياء التعليمية

# THERMODYNAMICS

## سلسلة محاضرات الديناميكا الحرارية

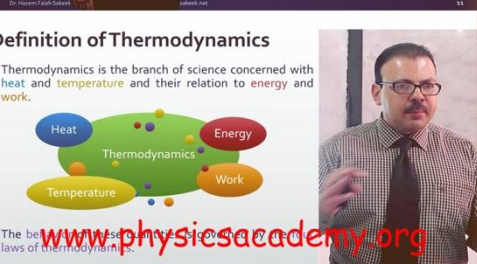
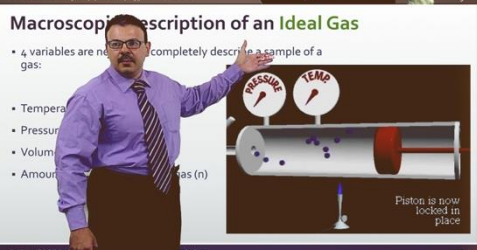
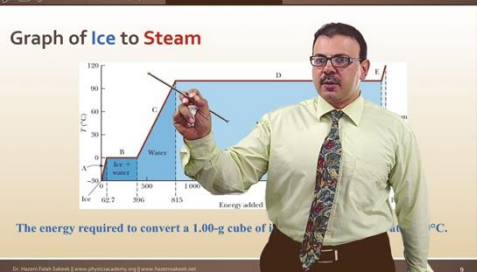
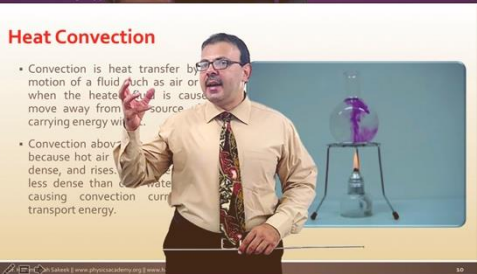
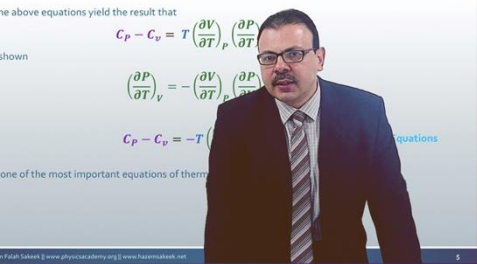
الدكتور حازم فلاح ستيبك

استاذ الفيزياء المشارك

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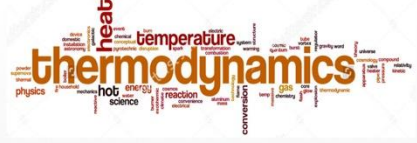
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كلية العلوم - قسم الفيزياء

**سلسلة محاضرات  
الديناميكا الحرارية  
Thermodynamics**

إعداد وشرح  
الدكتور حازم فلاح سكيك  
ديسمبر 2016

# المحتويات

## Thermodynamics Thermology



### System

- Homogeneous
- Heterogeneous

### System

- Isolated system
- Closed system
- Open system

### Surrounding

### Universe

### Process

- Isothermal process
- Isobaric process
- Isochoric process
- Adiabatic process
- Cyclic process
- Quasi-Static Process

### Process

- Reversible
- Irreversible

### Contact

### Thermal Equilibrium

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الوحدة الأولى: مفاهيم أساسية

الوحدة الثانية: الحرارة والقانون الأول للديناميكا الحرارية

الوحدة الثالثة: معادلة الحالة

الوحدة الرابعة: المحركات الحرارية والثلاجة والقانون الثاني للديناميكا الحرارية

الوحدة الخامسة: المواد النقية

## مقدمة

علم الفيزياء هو علم تجريبي يقوم على الملاحظة الواعية الدقيقة ثم التجربة لفهم الظواهر الطبيعية من ثم تسخيرها لما فيه فائدة الإنسان وراحته، هذا بالإضافة إلى أن علم الفيزياء يعد أساسا لا بد منه لجميع العلوم التطبيقية والتقنية وهذا ما سوف نلمسه من هذا الكتاب الذي يشرح موضوع الديناميكا الحرارية. ظهر علم الديناميكا الحرارية في أواخر القرن الثامن عشر - كعلم بدرس تحول الطاقة الحرارية إلى شغل ميكانيكي، واستنادا إلى ذلك وضعت الأسس النظرية لعمل الآلات الحرارية. غير أن التطور المستمر في المحركات الحرارية أعطى علم الديناميكا الحرارية أهمية كبيرة تحطت حدود الهندسة الحرارية لتلقى استخداما واسعا في فروع مختلفة من العلوم الأساسية كالفيزياء والكيمياء.

يهتم علم الديناميكا الحرارية بالحرارة أو الطاقة الحرارية بالدرجة الأولى وبكل الظواهر التي تظهر أو تتعلق بهذه الطاقة مثل عمليات انتقال الحرارة من جسم لآخر أو كيفية تخزين هذه الطاقة أو توليدها. يقوم علم الديناميكا الحرارية على أربعة قوانين أساسية وهي القانون صفر والقانون الأول والقانون الثاني والقانون الثالث. إلى جانب ذلك يدرس علم الديناميكا الحرارية علاقة الحرارة بالحركة الميكانيكية، مثلما ساعدنا في ذلك على اختراع الآلة البخارية ومحرك البنزين وطرق زيادة كفاءتهم، كما تدرس الديناميكا الحرارية العلاقة بين الحرارة و التفاعلات الكيميائية وتطبيقاتها العديدة التي تجمع بين اختراع البطاريات، وأخيرا علاقة الحرارة بالكهرباء حيث تساعدنا على توليد الطاقة الكهربائية من عدة وسائل مثل محطات تعمل بالفحم أو بالقوى المائية أو بالطاقة النووية كل تلك التقنيات تعتمد على تطويرها على علم الديناميكا الحرارية بهدف رفع كفاءتها.

## ما هو علم الديناميكا الحرارية؟

الديناميكا الحرارية هو العلم الذي يدرس خواص انتقال الشكل الحراري للطاقة وتحولاتها إلى أوجه أخرى، مثل تحول الطاقة الحرارية إلى طاقة ميكانيكية مثلما في محرك احتراق داخلي والآلة البخارية، أو تحول الطاقة الحرارية إلى طاقة كهربائية مثلما في محطات القوى، وتحول الطاقة الحركية إلى طاقة كهربائية كما في توليد الكهرباء من السدود والأنهار.

بدأت دراسات الحركة الحرارية مع اختراع الآلة البخارية وترتب عليها قوانين كثيرة تنطبق أيضا على جميع أنواع الآلات، وبصفة خاصة تلك التي تحول الطاقة الحرارية إلى شغل ميكانيكي مثل جميع أنواع المحركات أو عند تحول الطاقة الحركية إلى طاقة كهربائية مثلا أو العكس.



هذه السلسلة المتكاملة من محاضرات الديناميكا الحرارية موجهة لجميع الطلبة الدارسين لهذا المقرر، والذي حرصت على ان يكون مناسباً لكافة المستويات ومتناسقاً مع المنهاج المعتمد لمعظم الجامعات العربية والاجنبية في ٣٠ محاضرة اشتملت على الشرح والتوضيح لكل مفهوم ودعمت المحاضرات في معظمها بالأفلام الوثائقية والشروحات الفلاشية لتوضيح الفكرة. تم الاعتماد على أكثر من كتاب في تحضير هذه المحاضرات وجميعها مدرج في المحاضرة الصفيرية التعريفية بالمقرر.

آمل أن أكون قد قدمت لأبنائنا الدارسين من خلال هذا العمل المتواضع ما يعينهم على فهم واستيعاب هذا الفرع من فروع المعرفة. كما أتقدم بالشكر لكل من يقدم نصيحة حول هذه السلسلة من المحاضرات.

والله من وراء القصد

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على قناة شبكة الفيحاء التعليمية على اليوتيوب



### ٣٠ محاضرة تغطي كل مفردات المقرر

منصة أكاديمية الفيزياء التعليمية هي عبارة عن موقع الكتروني على شبكة الانترنت يتوفر عليها المادة المساندة للمحاضرات في صورة شرح فيديو للمحاضرة مع مجموعة من الوسائل التعليمية المساعدة للطالب على فهم المادة الدراسية. تشكل الاكاديمية وسيلة تفاعلية بين المحاضر والطلبة وتعمل بتقنية المودك MOOC.

موقع الأكاديمية  
www.physicsacademy.org

نبذة عن المحاضر

**د. حازم فلاح سكيك**

**استاذ الفيزياء المشارك بجامعة الازهر - غزة**



- ★ رئيس قسم الفيزياء بجامعة الازهر - غزة في الفترة 1993-1998
- ★ مؤسس وعميد كلية الدراسات المتوسطة بجامعة الازهر - غزة من الفترة 1996-2005
- ★ عميد القبول والتسجيل بجامعة الازهر - غزة في الفترتين 1998-2000 و 2007-2008
- ★ مدير الحاسب الالى بجامعة الازهر - غزة في الفترة من 1994-2000
- ★ رئيس وحدة تكنولوجيا المعلومات بجامعة الازهر - غزة في الفترة من 2000-2005
- ★ مؤسس شبكة الفيزياء التعليمي ومنتدى الفيزياء التعليمي.
- ★ مؤسس أكاديمية الفيزياء للتعليم الالكتروني.
- ★ مؤسس مركز الترجمة العلمي.
- ★ مؤسس قناة الفيزياء التعليمي على اليوتيوب.
- ★ رئيس تحرير مجلة الفيزياء العصرية.

لمزيد من المعلومات يرجى زيارة

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# Thermodynamics

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## Lecture 0: Introduction

About the Thermodynamics Course



# What is Thermodynamics

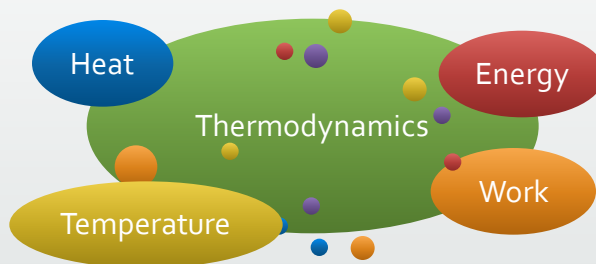
Definition ... History ... Importance

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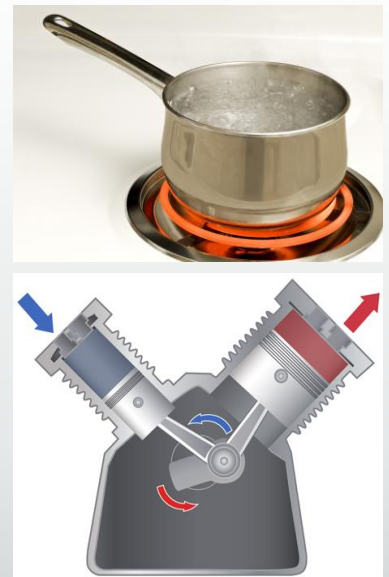
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## Definition of Thermodynamics

- Thermodynamics is the branch of science concerned with **heat** and **temperature** and their relation to **energy** and **work**.



- The **behavior** of these quantities is governed by the **four laws of thermodynamics**.



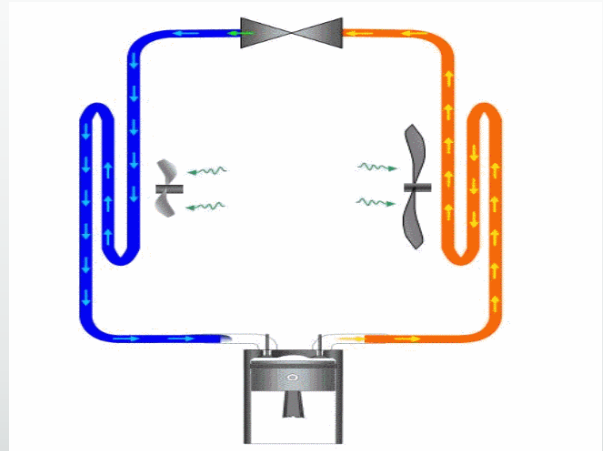
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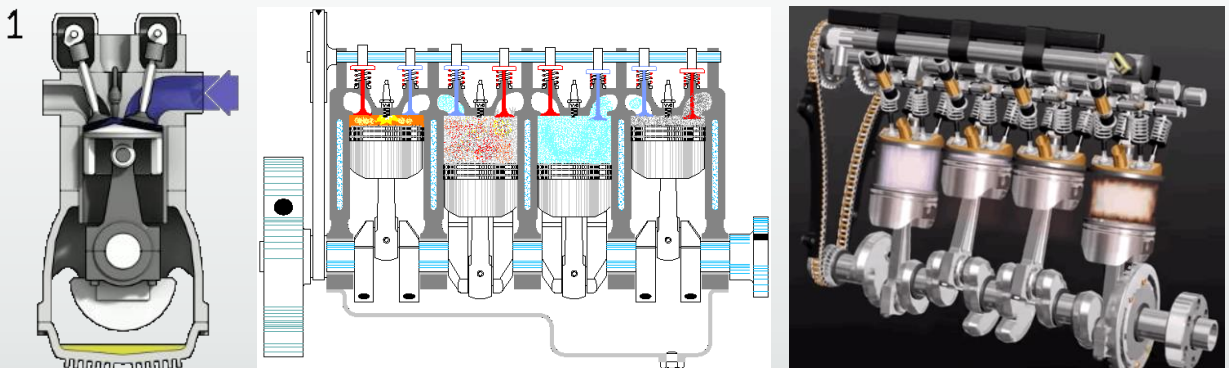
## Definition of Thermodynamics

Thermodynamics focuses largely on how a **heat transfer** is related to various **energy changes** within a **physical system** undergoing a **thermodynamic process**.

Such processes usually result in **work** being done by the **system** and are guided by the **laws of thermodynamics**.



## Car Engine as thermodynamic process



## تاريخ الديناميكا الحرارية

École Polytechnique	Glasgow school	Berlin school	Edinburgh school
			
Sadi Carnot (1796-1832)	William Thomson (1824-1907)	Rudolf Clausius (1822-1888)	James Maxwell (1831-1879)
Vienna school	Gibbsian school	Dresden school	Dutch school
			
Ludwig Boltzmann (1844-1906)	Willard Gibbs (1839-1903)	Gustav Zeuner (1828-1907)	Johannes der Waals (1837-1923)

يعتبر تاريخ الديناميكا الحرارية فرع رئيسي من أفرع تاريخ الفيزياء وتاريخ الكيمياء وتاريخ العلوم بشكل عام.

ارتبط تاريخ الديناميكا الحرارية ارتباطاً وثيقاً بتطور الميكانيكا الكلاسيكية، وميكانيكا الكم، والمغناطيسية، و علم الحركة الكيميائية.

كما ارتبط أيضاً بالتطور التكنولوجي للمحركات البخارية، ومحركات الاحتراق الداخلي، وفيزياء درجات الحرارة المتدنية، وتوليد الكهرباء.

كما أن تطور علم الديناميكا الحرارية قد أثر وتأثر بالنظرية الذرية.

## تاريخ الديناميكا الحرارية

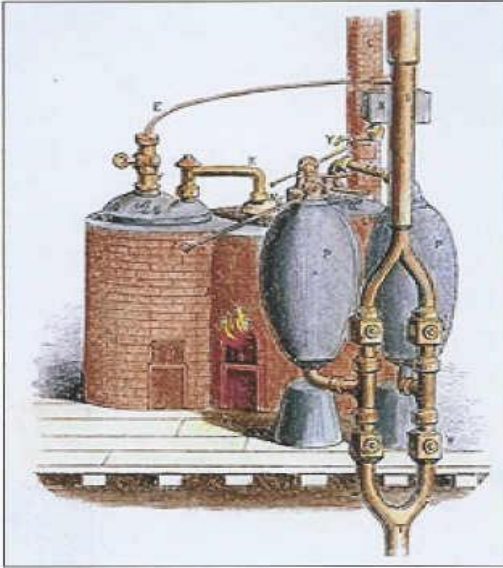


روبرت بويل. 1627-1691

▪ إن نشأة الديناميكا الحرارية ارتبطت بدراسة المحركات. فأول بشائر المحركات قام بتصميمها العالم الألماني **أوتو فون غريكه** في عام 1650.

▪ بعد ذلك بفترة وجيزة قام الفيزيائي والكيميائي الأيرلندي **روبرت بويل** بدراسة تصميمات أوتو، وفي عام 1656 وبالتعاون مع العالم الإنجليزي **روبرت هوك** قاموا ببناء مضخة هوائية. وباستخدام تلك المضخة قام كلا من بويل و **هوك** بفحص العلاقة بين الضغط والحجم والتي أظهرت أن **حاصل ضرب الضغط في الحجم تساوي مقدار ثابت**.

▪ بعد اختراع الترمومتر - أصبح من الممكن أن يتم دراسة خاصية درجة الحرارة دراسة كمية. و هذا الاختراع قد أتاح للعالم **لوساك** الفرصة لاستنباط قانونه، والذي أدى بعد ذلك بوقت قصير إلى معرفة **قانون الغاز المثالي**.

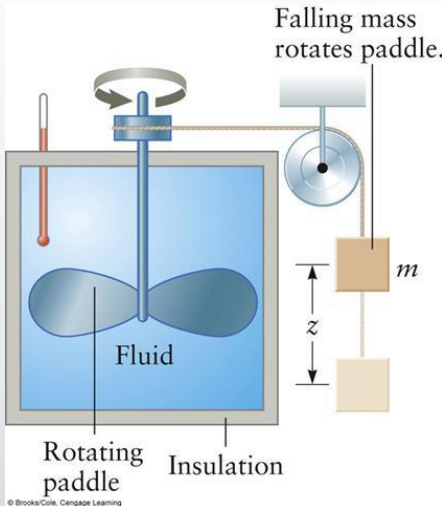


محرك سيفري لعام 1698 - أول محرك بخاري

## تاريخ الديناميكا الحرارية

- قام المهندس **توماس سيفري** في العام 1698 بتصميم أول محرك بخاري.
- مع أن هذه المحركات البدائية كانت بسيطة وكفاءتها متدنية إلا أنها قد جذبت انتباه العلماء الرواد في ذلك الوقت.
- ومن ضمن هؤلاء العلماء نجد **سادي كارنو** "أبو علم الديناميكا الحرارية" الذي قام في عام 1824 بنشر الورقة البحثية "انعكاسات القدرة الحركية للنار"، وهي كانت محاضرة عن الحرارة، والطاقة، وكفاءة المحركات. وهي تعتبر من العلامات الهامة في بداية تحول الديناميكا الحرارية إلى مادة من مواد العلوم الحديثة.

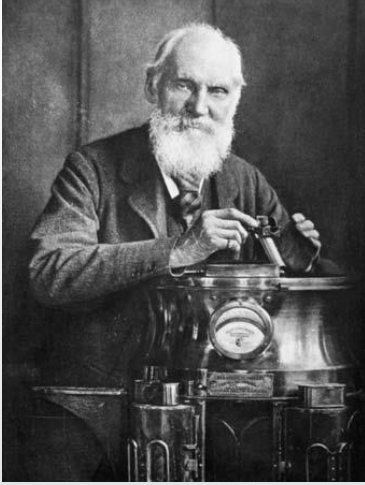
## تاريخ الديناميكا الحرارية



- لقد أسس **جيمس جول** بالتجارب لمبدأ القدرة الميكانيكية المكافئة للحرارة، وذلك في عام 1834. وفي عام 1845 قدم جول تقريراً عن أفضل تجربة معروفة قام بها، وهي تتضمن استخدام وزن يهبط من أعلى لإدارة عجلة ببدال داخل برميل من المياه، مما أتاح له تقدير القدرة الميكانيكية المكافئة للحرارة. وذلك أدى إلى ظهور نظرية بقاء الطاقة، وقامت بتفسير سبب إمكانية الحرارة لقيامها ببذل شغل.

- لقد قام الفيزيائي الرياضي المشهور **رودلف كلوسس** في عالم 1850 بتعريف مصطلح **الإنتروبي** S على أنه الحرارة المفقودة أو التي تحولت إلى عادم.

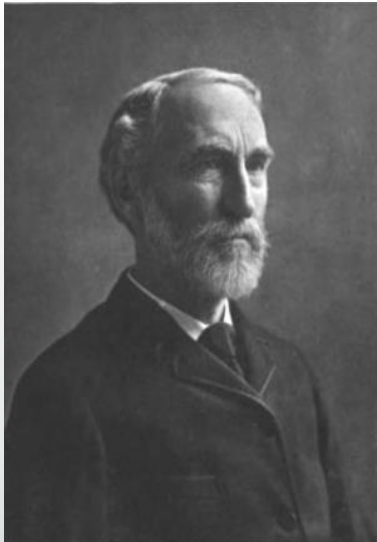
## تاريخ الديناميكا الحرارية



وليام طومسون، لورد كلفن  
(1907–1824)

- إلا أن كلمة "الديناميكا الحرارية" لم تكن معروفة حتى عام 1854، ففي ذلك العام صاغ الفيزيائي والرياضي البريطاني **وليام طومسون (اللورد كلفن)** مصطلح الديناميكا الحرارية في ورقته البحثية "حول النظرية الديناميكية للحرارة".
- قام الفيزيائي والرياضي الأسكتلندي **جيمس كلارك ماكسويل** في عام 1871 بالاشتراك مع كلوسس بصياغة فرع جديد من الديناميكا الحرارية يسمى الديناميكا الحرارية الإحصائية، وهي تقوم بتحليل عدد كبير من الجسيمات تحت حالة الاتزان.
- بعد ذلك بفترة وجيزة قام الفيزيائي النمساوي **لودفيغ بولتزمان** في عام 1875 بصياغة علاقة دقيقة بين **الإنتروبي S** والحركة الجزيئية.

## تاريخ الديناميكا الحرارية



ويلارد جيبس (1903–1839)

- في عام 1876 حدث نقطة هامة في تطور المفاهيم البشرية. فخلال هذه الفترة قام المهندس الكيميائي **ويلارد جيبس** (أول شخص في أمريكا يحصل على الدكتوراه في الهندسة (جامعة Yale) بنشر ورقة بحثية مكونة من 300 صفحة وعنوانها: **حول حالة الاتزان في المواد غير المتجانسة**، وقام فيها بصياغة إحدى المعادلات الكبرى، وهي **معادلة جيبس للطاقة الحرة**، والتي تعطي مقدار "الشغل المفيد" الذي من الممكن الحصول عليه من أنظمة التفاعلات الكيميائية.
- كما أن جيبس قد أنشأ المبدأ الذي نعرفه حالياً باسم **الإنثالبي H**، وأطلق عليه اسم "دالة الحرارة للضغط الثابت".

## افرع الديناميكا الحرارية

- |   |   |
|---|---|
| 1. الكيمياء الحرارية – 1780                       | 12. الديناميكا الحرارية النسبية – 1965                        |
| 2. الديناميكا الحرارية الكلاسيكية – 1824          | 13. الديناميكا الحرارية الكمومية – 1968                       |
| 3. الديناميكا الحرارية الكيميائية – 1876          | 14. الديناميكا الحرارية للثقوب السوداء – 1970                 |
| 4. الميكانيكا الإحصائية – 1880                    | 15. الديناميكا الحرارية للتطور البيولوجي – 1978               |
| 5. الديناميكا الحرارية في حالة الاتزان            | 16. الديناميكا الحرارية للجيولوجيا الكيميائية – 1980          |
| 6. الديناميكا الحرارية الهندسية                   | 17. الديناميكا الحرارية للهواء الجوي – 1980                   |
| 7. هندسة الديناميكا الحرارية الكيميائية - 1940    | 18. الديناميكا الحرارية للأنظمة الطبيعية – 1990               |
| 8. الديناميكا الحرارية في حالة عدم الاتزان - 1941 | 19. الديناميكا الحرارية للتركيبية الجزيئية – 1990             |
| 9. الديناميكا الحرارية في الأنظمة الصغيرة – 1960  | 20. الديناميكا الحرارية للزلازل الأرضية – 2000                |
| 10. الديناميكا الحرارية البيولوجية – 1957         | 21. الديناميكا الحرارية لمستقبلات الأدوية بالخلايا الحية 2001 |
| 11. الديناميكا الحرارية للنظم البيئية – 1959      | 22. الديناميكا الحرارية لأنظمة المستحضرات الدوائية – 2002     |

## Why study thermodynamics?

- Thermodynamics is essentially the study of the internal motions of many body systems (e.g., solids, liquids, gases, and light).
- Many people are drawn to Physics because they want to understand the world around us. It turns out that thermodynamics can explain more things about the world around us.

In this course we shall explain why heat flows from hot to cold bodies, why the air becomes thinner and colder at higher altitudes, why the Sun appears yellow whereas colder stars appear red and hotter stars appear bluish-white, why it is impossible to measure a temperature below  $-273^{\circ}\text{C}$ , why there is a maximum theoretical efficiency of a power generation unit which can never be exceeded no matter what the design, why high mass stars must ultimately collapse to form black-holes, and much more!



## Thermodynamics Course Objectives

- ❑ To be able to state the **First Law** and to define **heat**, **work**, **thermal efficiency** and the difference between various forms of energy.
- ❑ To be able to identify and describe **energy exchange** processes (in terms of various forms of energy, heat and work).
- ❑ To be able to explain how various **heat engines** work.
- ❑ To be able to explain the concepts of path dependence / independence and reversibility / irreversibility of various thermodynamic processes.
- ❑ To be able to apply ideal cycle analysis to simple heat engine cycles to estimate thermal efficiency and work as a function of pressures and temperatures at various points in the cycle.
- ❑ An understanding of the use of the **Gibbs** and **Helmholtz** free energies as equilibrium criteria, and the statement of the equilibrium condition for closed and open systems.



## Thermodynamics Course Outline



Unit 1	Fundamental Concepts	Unit 2	Heat and the first law of thermodynamics
Macroscopic and microscopic point of view, Scope of thermodynamics, Thermal equilibrium, Temperature concept, Comparison of thermometers, Comparison of temperature scale (Celsius, Fahrenheit, Kelvin) Gas thermometer, The Ideal gas.		Heat flow, Heat flow depends on the path, The mechanical equivalent of heat, Heat capacity and specific heat, Latent heat, Work in a volume change, Work depends on the path, PV diagram, The first law of thermodynamics, Internal energy. The energy equation, T and V independent, Gas equation during an adiabatic process, Adiabatic work.	



# Thermodynamics Course Outline

Unit 3	Equation of state	Unit 4	Engines, Refrigerators and the second law of thermodynamics
Equation of state of an ideal gas, equation of state of a real gas, PVT surfaces for a an ideal gas, PVT for a real substance, Phase diagrams, Triple point and critical point, Vapor pressure.		Conservation of work into heat and vice versa, the stirling engine, the steam engine, Internal-combustion engines, The second law of thermodynamics, The refrigerator, Reversibility and irreversibility.	
Unit 5	The entropy	Unit 6	Pure substances
The concept of entropy, Entropy of an ideal gas, Carnot cycle, Entropy and reversibility, Entropy and irreversibility.		Enthalpy, The Helmholtz and Gibbs functions, The Tds equations, Energy equations, Heat-capacity equations	

## Text Book

- (1) **Heat and thermodynamics** by M.W. Zemansky and R.H. Dittman
- (2) **Heat and thermodynamics** by Brij Lal and N. Subrahmanyam
- (3) **Thermodynamics, Kinetic theory and Statistical thermodynamics** By F.R.Sears and G.L. Salinger
- (4) **Physics for scientists and engineering with modern physics** by R.A. Serway
- (5) **University physics** by F.R. Sears and M.W. Zemansky



# إلى اللقاء مع المحاضرة (١) **Thermodynamics Terminology**



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# Thermodynamics

Dr. Hazem Falah Sakeek  
Al-Azhar University - Gaza

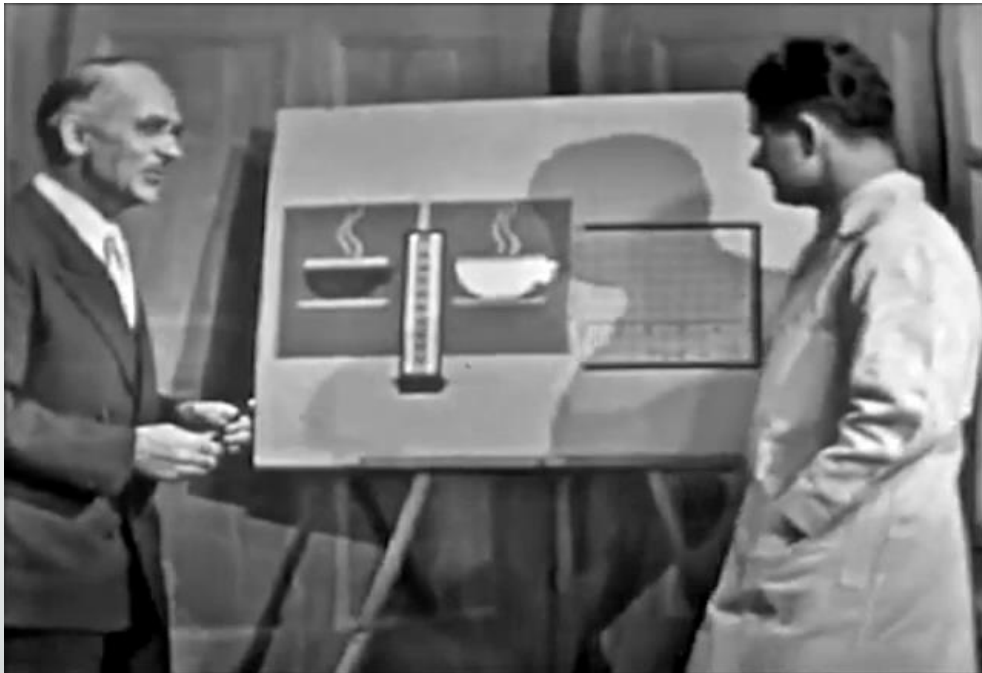
## Unit 1: Fundamental Concepts

### Lecture 1: Thermodynamics Terminology

## Unit 1: Fundamental Concepts

- ❑ Scope of Thermodynamics
- ❑ Thermodynamics Terminology
  - ❑ System
  - ❑ Process
  - ❑ Thermal Contact
  - ❑ Thermal Equilibrium
- ❑ The Zeroth Law of Thermodynamics
- ❑ Temperature and Temperature scale
- ❑ The Ideal Gas





## Scope of Thermodynamics

- The study of thermodynamics is an experimental science concern with the concept of **heat** and **temperature** at a **macroscopic scale**.



The principle of thermodynamics are used by engineers in the design of internal combustion engines, conventional and nuclear power stations, refrigeration and air-conditioning system and also rockets, missiles, aircraft, ships, submarine, and vehicles.



# Macroscopic and Microscopic Approaches?

Behavior of matter can be studied by these two approaches.

## Macroscopic Approaches الطرق الجاهرية

In **macroscopic approach**, certain quantity of matter is considered, **without a concern** on the events occurring at the molecular level. These effects can be perceived by human senses or measured by instruments.

### Macroscopic Properties

pressure, volume, temperature, *Entropy; Enthalpy; Internal energy*, composition, density, viscosity, surface tension, refractive index, colour etc.

## Microscopic Approaches الطرق الجوهريّة او الميكروسكوبية

In **microscopic approach**, the effect of molecular motion is considered. Most microscopic properties cannot be measured with common instruments nor can be perceived by human senses.

# Thermodynamics Terminology



The important parts of the study of thermodynamics are a few **terms and definitions**, which must be understood clearly, and these are as follows:

## (1) System النظام

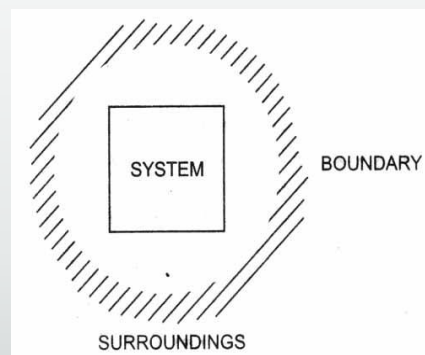
A thermodynamic system may be defined as any **specified portion of matter in the universe which is under study**. A system may consist of one or more substances.

## (2) Surrounding المحيط

The rest of the universe which **exchange energy and matter with the system** is called the surroundings. Thus, the system is separated from the surroundings by a **boundary** which may be real or imaginary.

## (3) Universe الكون

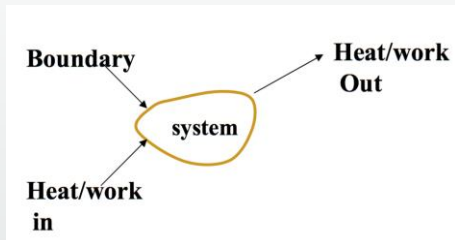
System + Surrounding



The diagram illustrates a thermodynamic system. It consists of a large circle representing the 'SYSTEM BOUNDARY'. Inside this circle is a U-shaped line representing the 'SYSTEM'. The area between the U-shaped line and the circle is labeled 'SURROUNDINGS'.

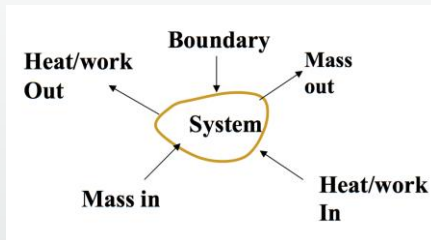
## 8

## Closed system



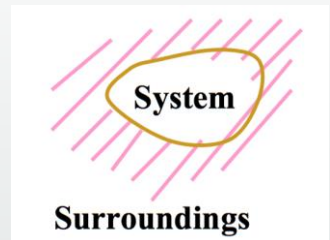
*cannot transfer matter but can transfer energy*

## Open system



*can transfer both energy and matter to and from its surroundings*

## Isolated System



*no interaction is possible with the surroundings*

# Thermodynamics Terminology



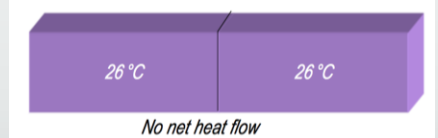
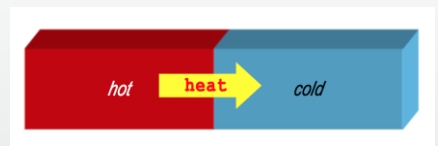
## (8) Thermal contact الاتصال الحراري

Two objects are in thermal contact with each other if the energy exchange can occur between them in the absence of work done by one on the other.

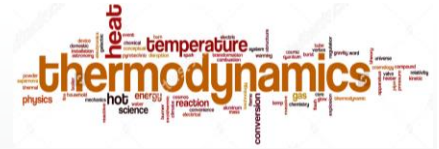
## (9) Thermal Equilibrium الاتزان الحراري

A system in which the macroscopic properties do not undergo any change with time is said to be in thermodynamic equilibrium.

A system is said to be in **thermal equilibrium** if there is no flow of heat from one position of the system to another. This is possible if the temperature remains the same throughout in all parts of the system.



# Thermodynamics Terminology

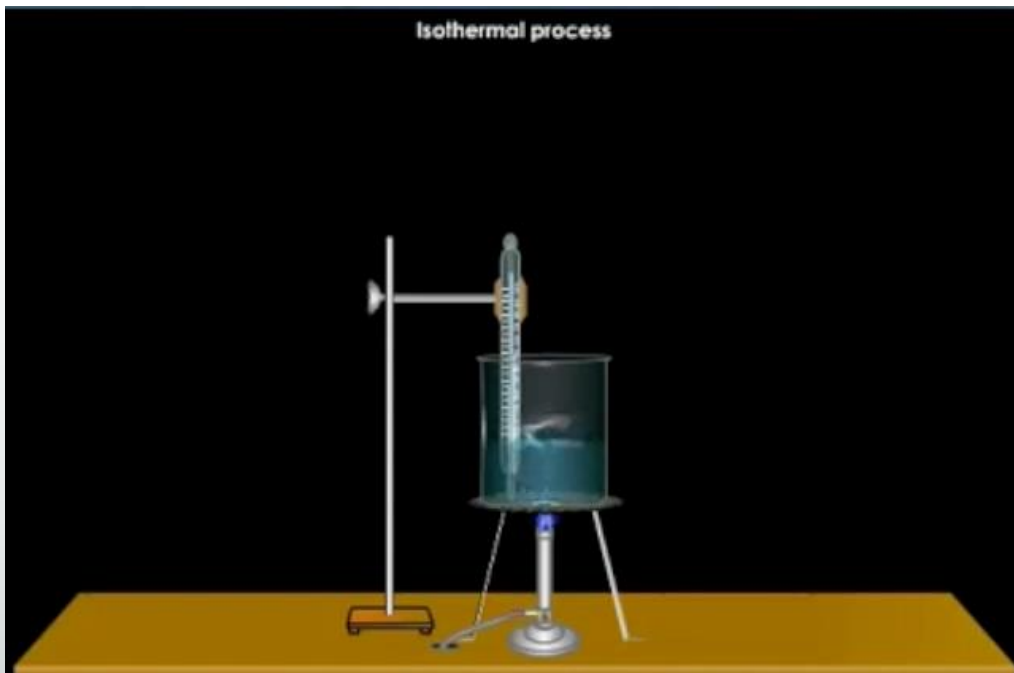
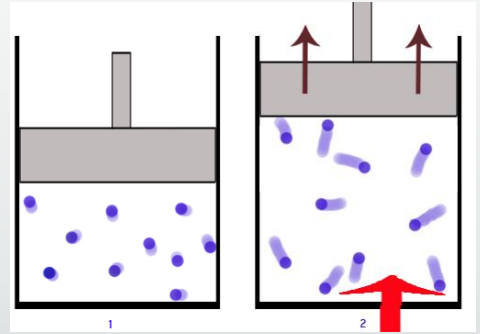


## (10) Process عملية

Whenever the state of a **system changes**, it is said to have undergone a process. *Thus a process may be defined as the operation by which a system changes from one state to another.*

In a process at least one of the properties of the system changes.

A change in state of the system is always accompanied by a change in energy. Therefore, a process may also be defined as *a path of change of a system from one equilibrium state to another which is usually accompanied by a change in energy or mass.*

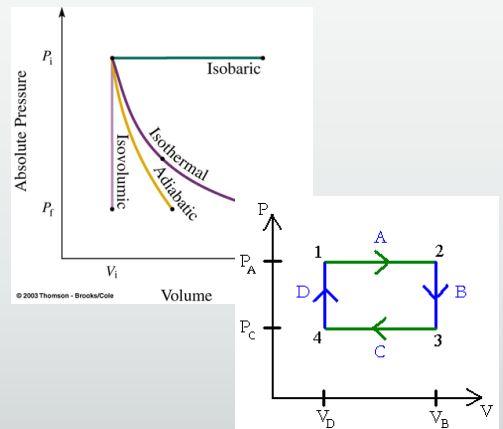


# Thermodynamics Terminology

## Types of Processes

Different types of processes connecting an initial state, in which, one of the properties to remain a constant during a process.

- Isothermal process** (T remains constant)
- Isobaric process** (P remains constant)
- Isochoric process** (V remains constant)
- Adiabatic process** (Thermally insulated from the surroundings).
- Cyclic process** (The process which brings back a system to its original state after a series of changes).
- Quasi-Static Process** The deviation from thermodynamic equilibrium is infinitesimal.



# Thermodynamics Terminology

## (11) Reversible and Irreversible Processes

**Reversible process:** A process that can be reversed without leaving any trace on the surroundings.

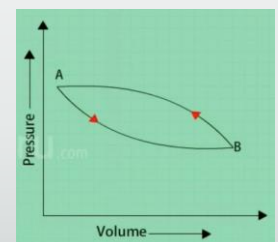
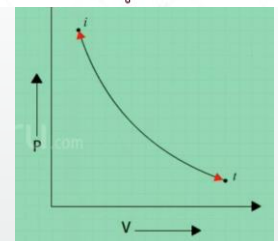
A thermodynamic reversible process is one that takes place **infinitesimally slowly** and its direction at any point can be reversed by an infinitesimally change in the state of the system.

**Irreversible process:** A process that is not reversible.

*All the processes occurring in nature are irreversible.*

**Why are we interested in reversible processes?**

(a) They are easy to analyze and (b) they serve as idealized models to which the actual processes can be compared.



# Thermodynamics Terminology



## System

- Homogeneous
- Heterogeneous

## System

- Isolated system
- Closed system
- Open system

Surrounding

Universe

## Process

- Isothermal process
- Isobaric process
- Isochoric process
- Adiabatic process
- Cyclic process
- Quasi-Static Process

## Process

- Reversible process
- Irreversible process

Thermal contact

Thermal Equilibrium

إلى اللقاء مع المحاضرة (٢)

## Definition of Temperature & Zeroth Law of Thermodynamics



## Unit 1: Fundamental Concepts

Lecture 2: Definition of Temperature and Zeroth Law of Thermodynamics

## Unit 1: Fundamental Concepts

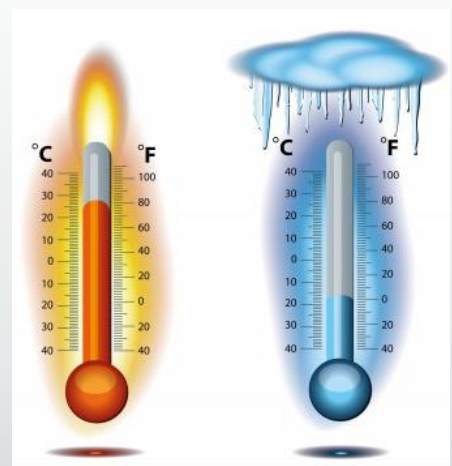
- ☐ Scope of Thermodynamics
- ☐ Thermodynamics Terminology
  - ☐ System
  - ☐ Process
  - ☐ Thermal Contact
  - ☐ Thermal Equilibrium
- ☐ **The Zeroth Law of Thermodynamics**
- ☐ **Temperature and Temperature scale**
- ☐ The Ideal Gas





## Definition of Temperature

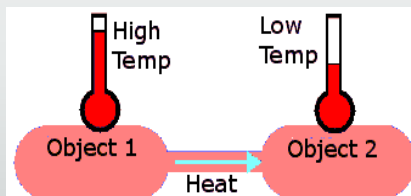
- **Temperature** is a property of a system which determines the degree of hotness. *Obviously, it is a relative term.*
- **For example:** A hot cup of coffee is at a higher temperature than a block of ice. On the other hand, *ice is hotter than liquid hydrogen.*
- Two systems are said to be equal in temperature, when there is **no change** in their respective observable properties when they are brought together. **In other words, "when two systems are at the same temperature they are in thermal equilibrium" (They will not exchange heat).**



# Definition of Temperature

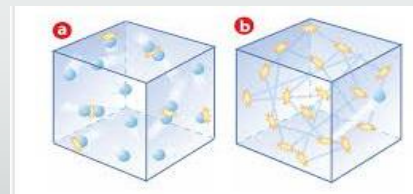
## Macroscopic definition

On the **macroscopic scale**, temperature is the unique physical property that determines the direction of heat flow between two objects placed in thermal contact.



## Microscopic definition

On the **microscopic scale**, temperature is defined as the average energy of microscopic motions of a single particle in the system per degree of freedom.

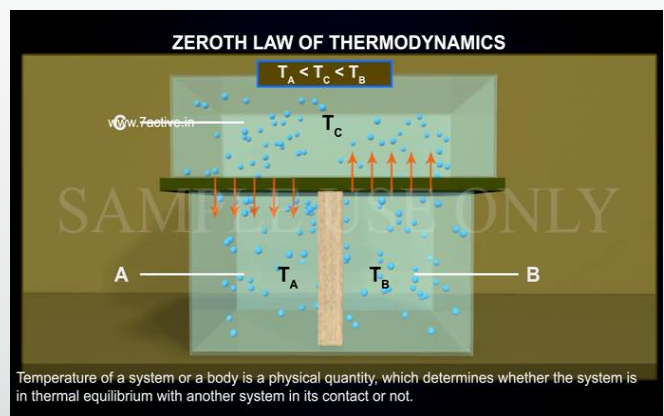


# Zeroth Law of Thermodynamics

If two systems (A and B) are in thermal equilibrium with a third system (C) separately

(that is A and C are in thermal equilibrium; B and C are in thermal equilibrium),

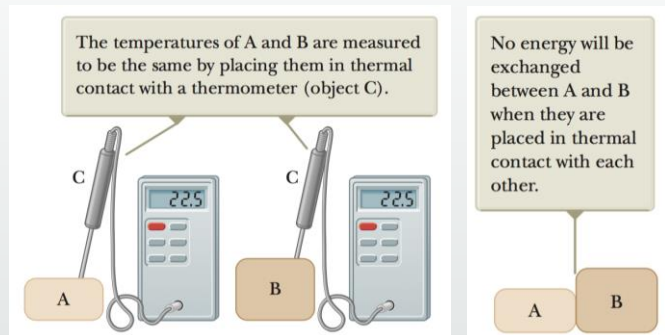
then they are in thermal equilibrium themselves (that is A and B will be in thermal equilibrium).



## Explanation of Zeroth Law

- Let us say  $T_A$ ,  $T_B$  and  $T_C$  are the temperatures of A, B and C respectively.
- A and C are in thermal equilibrium.
- B and C are in thermal equilibrium.
- A and B will also be in thermal equilibrium  $T_A = T_B$

**All temperature measurements are based on this LAW.**



### Zeroth law of thermodynamics

If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

## Quiz

Two objects, with different sizes, masses, and temperatures, are placed in thermal contact. In which direction does the energy travel?

- (a) Energy travels from the larger object to the smaller object.
- (b) Energy travels from the object with more mass to the one with less mass.
- (c) Energy travels from the object at higher temperature to the object at lower temperature.



## Thermometers

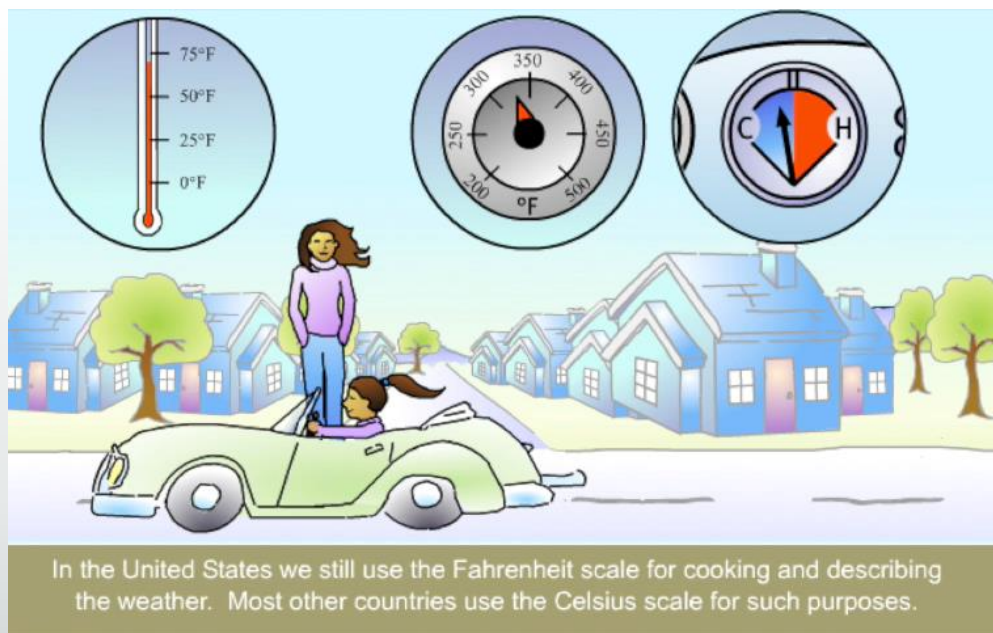
- Thermometers are devices used to measure the temperature of a system.
- All thermometers are based on the principle that some physical property of a system changes as the system's temperature changes.
- **Some physical properties that change with temperature are**
  - (1) the volume of a liquid,
  - (2) the dimensions of a solid,
  - (3) the pressure of a gas at constant volume,
  - (4) the volume of a gas at constant pressure,
  - (5) the electric resistance of a conductor,
  - (6) the color of an object.



## Types of Thermometers

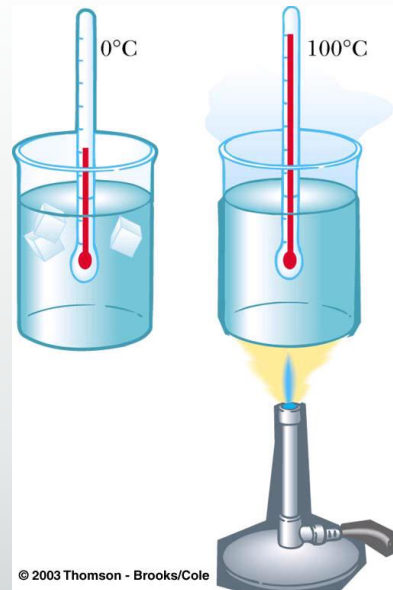
	Physical property	Material	Type of thermometer
1	Change in length	Mercury or Alcohol	Liquid thermometer
2	Change in pressure	Hydrogen	Gas Thermometer
3	Change in resistance	Platinum	Resistance thermometer
4	Change in electric potential	Chromel and Alumel	Thermocouple thermometer
5	Change in radiation color	Pyrometer	Radiation Thermometer
6	Change in susceptibility		Magnetic thermometer

- Temperature is measured with thermometers that may be **calibrated** to a variety of temperature scales.
- In most of the world (except for the United States and a few other countries), the **degree Celsius scale** is used for most temperature measuring purposes.
- The entire scientific world measures temperature using thermodynamic temperature using the **kelvin scale**.



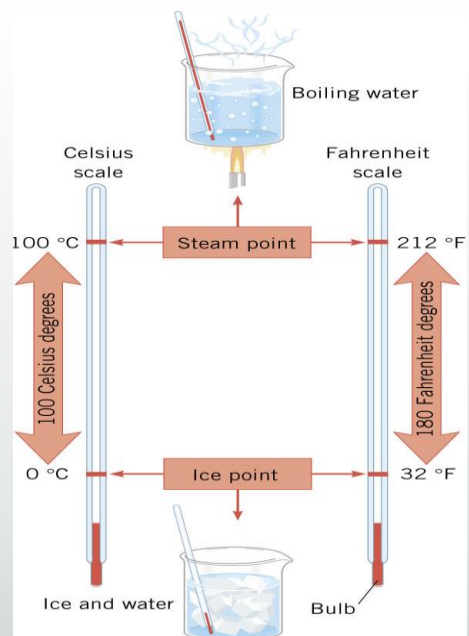
## (1) Celsius Temperature Scale

- The degree **Celsius** ( $^{\circ}\text{C}$ ) is a unit of temperature named for the Swedish astronomer Anders Celsius (1701-1744) who first proposed it.
- The Celsius temperature scale was designed so that the freezing point of water is 0 degrees and the boiling point is 100 degrees at standard atmospheric pressure.
- Since there are one hundred steps between these two reference points the original term for this system was Centigrade (100 parts).

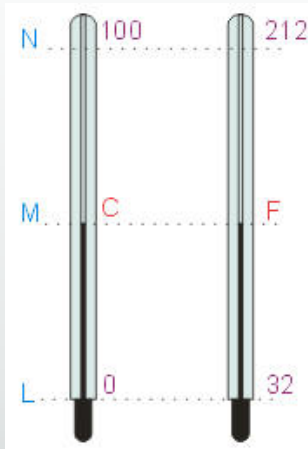


## Fahrenheit Temperature Scale

- The degree **Fahrenheit** ( $^{\circ}\text{F}$ ) is a unit of temperature named for the German physicist Gabriel Fahrenheit (1686 - 1736).
- In the Fahrenheit scale of temperature the freezing point of water is 32 degrees and the boiling point is 212 degrees placing the boiling and melting points of water 180 degrees apart.



## Temperature Conversions between Fahrenheit scale and Celsius scale



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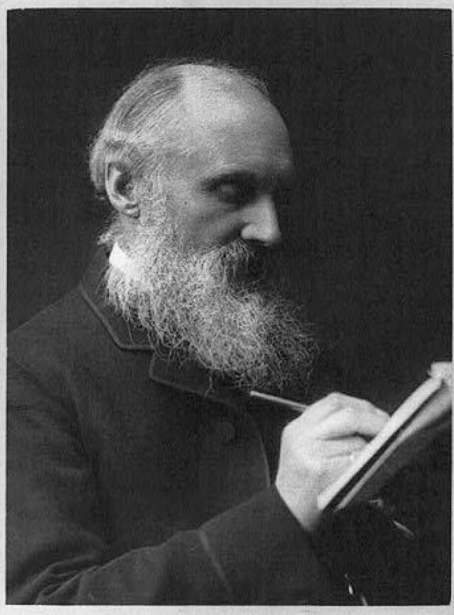
$$\frac{ML}{NL} = \frac{C - 0}{100 - 0} = \frac{F - 32}{212 - 32}$$

$$\therefore \frac{C}{100} = \frac{F - 32}{180}$$

$$F = \frac{9}{5}C + 32$$

$$T(\text{in } ^\circ\text{F}) = 32 + \frac{9}{5}T(\text{in } ^\circ\text{C})$$

$$T(\text{in } ^\circ\text{C}) = \frac{5}{9}[T(\text{in } ^\circ\text{F}) - 32]$$



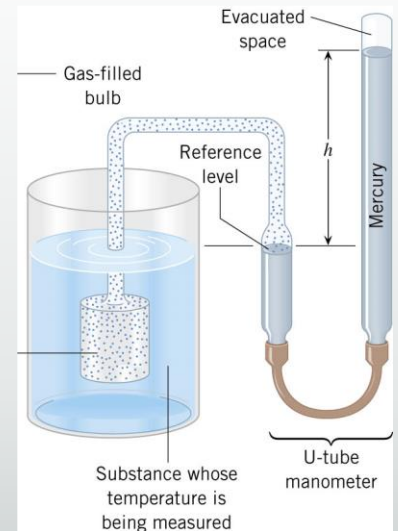
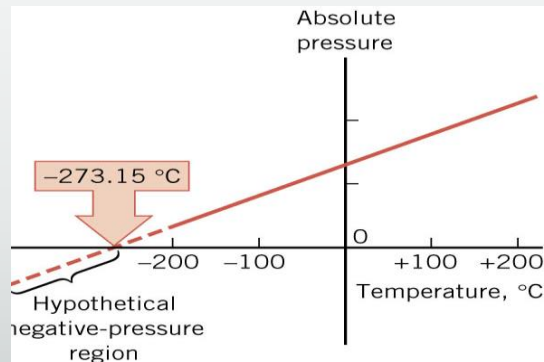
Lord Kelvin, 1824–1907

## Kelvin Temperature scale

- **Kelvin temperature scale** was introduced by the Scottish physicist William Thomson (Lord Kelvin, 1824–1907), and in his honor each degree on the scale is called a kelvin (K).
- By international agreement, the symbol K is not written with a degree sign (°), nor is the word “degrees” used when quoting temperatures.
- For example, a temperature of 300 K (not 300 °K) is read as “three hundred kelvins,” not “three hundred degrees kelvin.” The kelvin is the SI base unit for temperature.

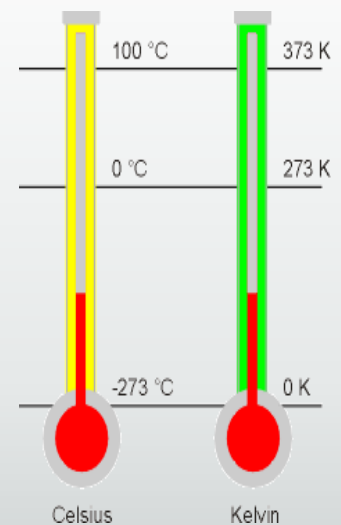
## Kelvin Experiment: *constant-volume gas thermometer*

- When a gas confined to a fixed volume is heated, its pressure increases. Conversely, when the gas is cooled, its pressure decreases. The change in gas pressure with temperature is the basis for the *constant-volume gas thermometer*.



## Temperature Conversions between Kelvin scale and Celsius scale

$$T(\text{in } ^\circ\text{C}) = T(\text{in K}) - 273.15$$



## Example 1

- On a day when the temperature reaches 50°F, what is the temperature in degrees Celsius and in kelvins?

$$T_C = \frac{5}{9}(T_F - 32) = \frac{5}{9}(50 - 32) = 10^\circ\text{C}$$

$$T = T_C + 273.15 = 10^\circ\text{C} + 273.15 = 283 \text{ K}$$

## Example 2

- A pan of water is heated from 25°C to 80°C. What is the change in its temperature on Kelvin scale and on the Fahrenheit scale?

$$\Delta T = \Delta T_C = 80^\circ\text{C} - 25^\circ\text{C} = 55^\circ\text{C} = 55 \text{ K}$$

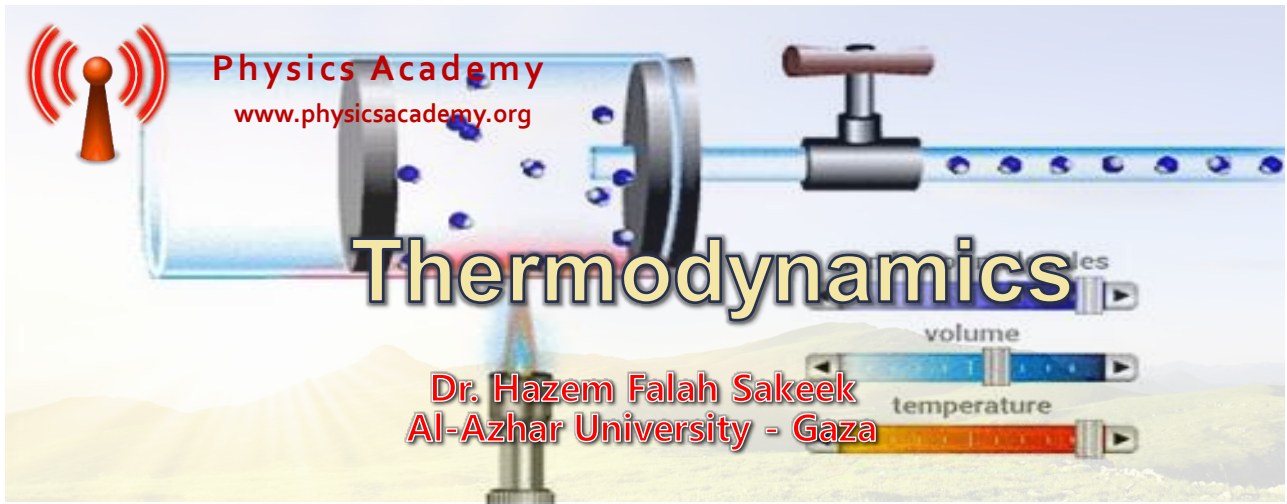
$$\Delta T_F = \frac{9}{5} \Delta T_C = \frac{9}{5}(55^\circ\text{C}) = 99^\circ\text{F}$$

## Problem to solve by yourself

- Convert the following temperatures to their values on the Fahrenheit and Kelvin scales: (a) the sublimation point of dry ice,  $-78.5^{\circ}\text{C}$ ; (b) human body temperature,  $37^{\circ}\text{C}$ .
- The temperature difference between the inside and the outside of a home on a cold winter day is  $57^{\circ}\text{F}$ . Express this difference on (a) the Celsius scale and (b) the Kelvin scale.
- Liquid nitrogen has a boiling point of  $-195.81^{\circ}\text{C}$  at atmospheric pressure. Express this temperature (a) in degrees Fahrenheit and (b) in kelvins.

إلى اللقاء مع المحاضرة (٣)

## The Ideal Gas



## Unit 1: Fundamental Concepts

### Lecture 3: The Ideal Gas




## Unit 1: Fundamental Concepts

- ☐ Scope of Thermodynamics
- ☐ Thermodynamics Terminology
  - ☐ System
  - ☐ Process
  - ☐ Thermal Contact
  - ☐ Thermal Equilibrium
- ☐ The Zeroth Law of Thermodynamics
- ☐ Temperature and Temperature scale
- ☐ **The Ideal Gas**





## The particles in **solids**, **liquids** and **gases**

	Solid	Liquid	Gas
Arrangement of particles	Close together Regular pattern	Close together Random arrangement	Far apart Random arrangement
Movement of particles	Vibrate on the spot	Move around each other	Move quickly in all directions
Diagram			

# Properties of **solids**, **liquids** and **gases**

Properties	Why they are like this
<b>Solids</b>	
They have a fixed shape and <b>cannot flow</b> . They cannot be compressed.	The particles cannot move from place to place. The particles are close together and have no space to move into.
<b>Liquids</b>	
They <b>flow</b> and take the shape of their container. They cannot be compressed.	The particles are free to move around each other. The particles are close together and have no space to move into.
<b>Gases</b>	
They <b>flow</b> and completely fill their container. They can be compressed.	The particles can move quickly in all directions. The particles are far apart and have space to move into.

## Temperature effect on matter **Thermal expansion**

- All three states of matter (**solid**, **liquid** and **gas**) **expand when heated**. The atoms themselves do not expand, but the **volume** they take up does.



## Thermal expansion of **solids**, **liquids** and **gases**

- When a **solid** is heated, its atoms vibrate faster about their fixed points. The **relative increase in the size of solids when heated is therefore small**. Metal railway tracks have small gaps so that when the sun heats them, the tracks expand into these gaps and don't buckle.
- **Liquids** expand for the same reason, but because the bonds between separate molecules are usually less tight **they expand more than solids**. This is the principle behind liquid-in-glass thermometers.
- Molecules within **gases** are further apart and weakly attracted to each other. Heat causes the molecules to **move faster**, which means that the **volume of a gas increases more than the volume of a solid or liquid**.
- However, gases that are contained in a **fixed volume** cannot expand - and so **increases in temperature** result in **increases in pressure**.

## Thermal expansion Law

### Thermal expansion in one dimension

$$\Delta L = \alpha L_i \Delta T$$

Where  $\Delta L$  is the change in length,  $\Delta T$  is the change in temperature,  $\alpha$  is the **coefficient of linear expansion** ( $^{\circ}\text{C}^{-1}$ ) or ( $\text{K}^{-1}$ )

### Thermal expansion in two dimensions

$$\Delta A = 2\alpha A_i \Delta T$$

Where  $\Delta A$  is the change in area.

### Thermal expansion in three dimensions

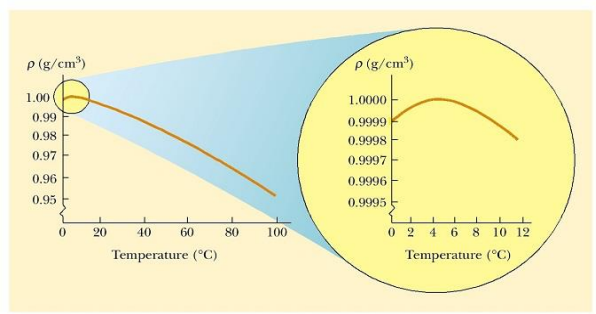
$$\Delta V = 3\alpha V_i \Delta T$$

$$\Delta V = \beta V_i \Delta T$$

Where  $\Delta V$  is the change in Volume,  $\beta$  is the **coefficient of volume expansion** ( $^{\circ}\text{C}^{-1}$ ) or ( $\text{K}^{-1}$ )

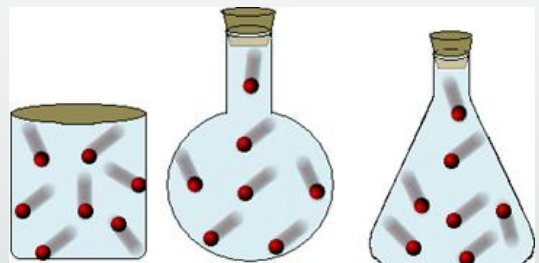
# The Unusual Behavior of Water

- Liquids generally increase in volume with increasing temperature. Cold water is an exception to this rule as you can see from its density-versus-temperature curve.
- As the temperature increases from  $0^{\circ}\text{C}$  to  $4^{\circ}\text{C}$ , water contracts and its density therefore increases.
- Above  $4^{\circ}\text{C}$ , water expands with increasing temperature and so its density decreases.
- Therefore, the density of water reaches a maximum value of  $1.000\text{ g/cm}^3$  at  $4^{\circ}\text{C}$ .
- As the water freezes, the ice remains on the surface because ice is less dense than water. The ice continues to build up at the surface, while water near the bottom remains at  $4^{\circ}\text{C}$ . If that were not the case, fish and other forms of marine life would not survive.



## Problem with the initial volume ( $V_i$ ) of the gas

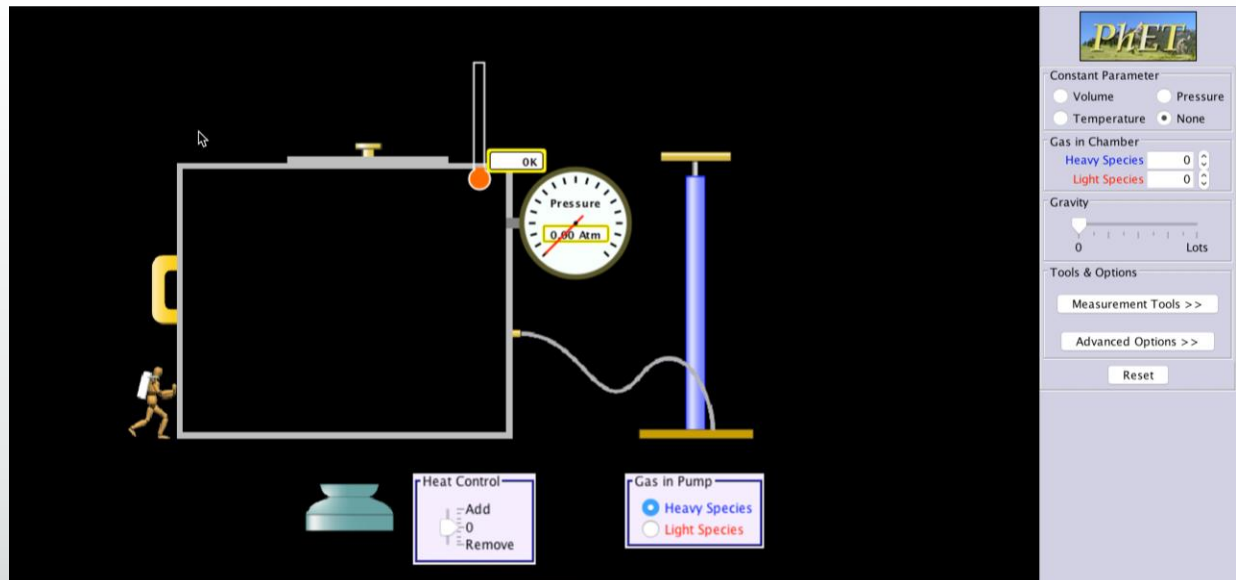
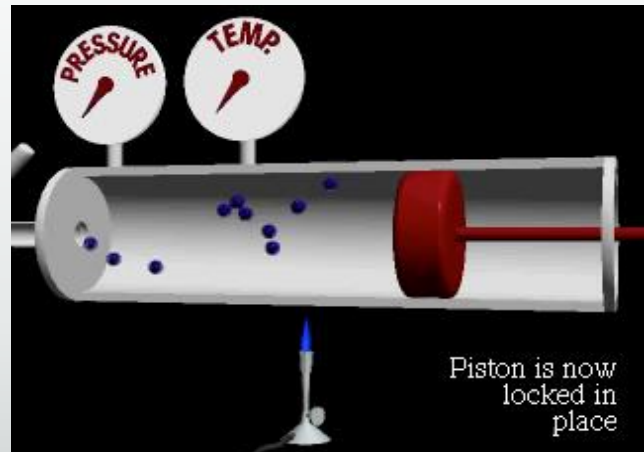
- The volume expansion equation  $\Delta V = \beta V_i \Delta T$  is based on the assumption that the material has an initial volume  $V_i$  before the temperature change occurs.
- The case for gases is completely different. There is no equilibrium separation for the atoms and no "standard" volume at a given temperature; the volume depends on the size of the container.
- As a result, we cannot express changes in volume  $\Delta V$  in a process on a gas with equation  $\Delta V = \beta V_i \Delta T$  because we have no defined volume  $V_i$  at the beginning of the process.



# Macroscopic Description of an Ideal Gas

- 4 variables are needed to completely describe a sample of a gas:

- Temperature ( $T$ )
- Pressure ( $P$ )
- Volume ( $V$ )
- Amount (number of moles) of gas ( $n$ )



Boyle's Law	Charles' Law	Avogadro's Law
$V \propto 1/P$	$V \propto T \text{ (Kelvin)}$	$V \propto n$
Constant T, n	Constant P, n	Constant T, P

So  $V \propto 1/P \times n \times T$

- To turn a proportionality into an equation, insert a constant:  $V = \frac{nRT}{P}$
- Or multiply both sides by P:

The diagram shows the equation  $PV = nRT$  with color-coded variables and labels in boxes connected by lines:

- P** (blue) is labeled "Pressure" (blue box).
- V** (green) is labeled "Volume" (green box).
- n** (pink) is labeled "No. of moles" (pink box).
- R** (purple) is labeled "Universal Gas Constant" (purple box).
- T** (yellow) is labeled "Temperature" (yellow box).

- The units of R depend on the units used for P, T, and V.
- If the pressure is in pascals ( $1 \text{ Pa} = 1 \text{ N/m}^2$ ) and volume in  $\text{m}^3$  then

$$R = 8.314 \text{ J/mol.K}$$

- If the pressure is in atmospheres and the volume in liters ( $1 \text{ L} = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3$ ) then

$$R = 0.0821 \text{ L.atm/mol.K}$$

Using value of  $R$  ( $0.0821 \text{ L.atm/mol.K}$ ) and Equation  $PV = nRT$  shows that the volume occupied by 1 mol of any gas at atmospheric pressure and at  $0^\circ\text{C}$  (273 K) is,

$$V = \frac{nRT}{P}$$

$$V = \frac{(1\text{mol})(0.0821 \text{ L atm/mol K})(273\text{K})}{1\text{atm}} = 22.4 \text{ L}$$

What is the mass of oxygen gas in a 500 L container at 1 atm and  $0^\circ\text{C}$  (273 K)?

The number of moles  $n$  of a substance is related to its mass  $m$  through the expression

$$n = \frac{m}{M} \quad \text{where } m \text{ is the mass in gram and } M \text{ is the molar mass in gram/mol}$$

$$m = \left( \frac{500\text{L}}{22.4\text{L/mol}} \right) 32\text{g/mol} = 71 \text{ g}$$

- The ideal gas law can be expressed in terms of the total number of molecules  $N$  where  $N = n N_A$
- where  $N_A$  is the Avogadro's number =  $6.022 \times 10^{23}$  molecules/mole.
- One mole of substance is that mass of the substance that contains Avogadro's number of molecules

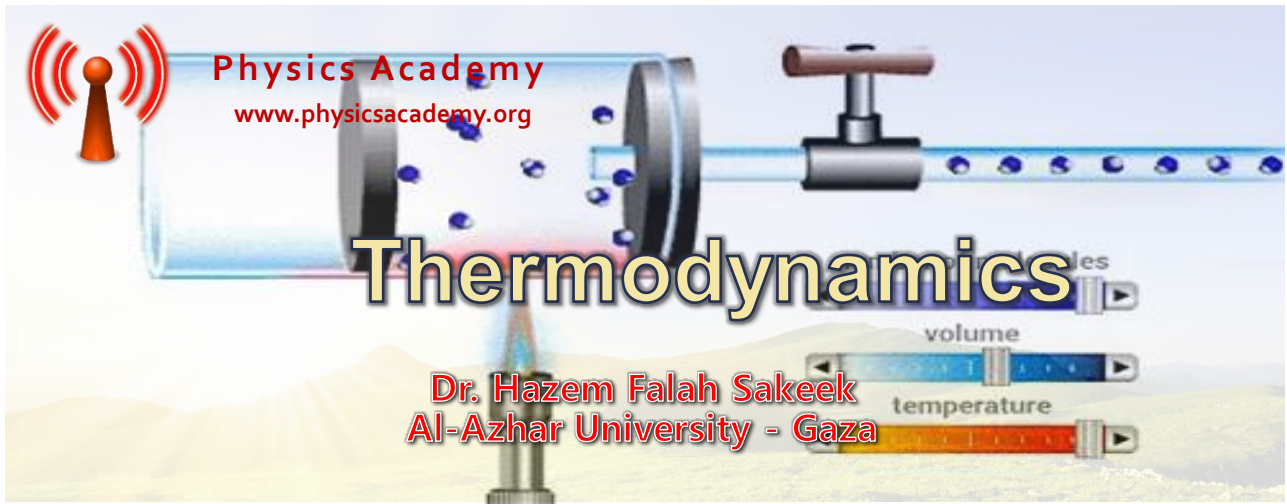
$$PV = nRT = \frac{N}{N_A} RT$$

- the value  $\frac{R}{N_A}$  is called Boltzmann's constant  $K$ ,

$$K = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$$

$$PV = nRT = NK T$$

Ideal Gas Equation



## Unit 1: Fundamental Concepts

### Lecture 3a: Examples on the Ideal Gas equation

#### Example 1

A spray can containing a gas at twice atmospheric pressure (202 kPa) and having a volume of 125.00 cm<sup>3</sup> is at 22°C. It is then heated into an open fire. When the temperature of the gas in the can reaches 195°C, **what is the pressure inside the can?**

**Solution**

$$PV = nRT \longrightarrow \frac{PV}{T} = nR$$

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \longrightarrow \frac{P_i}{T_i} = \frac{P_f}{T_f}$$

$$P_f = \left( \frac{T_f}{T_i} \right) P_i = \left( \frac{468 \text{ K}}{295 \text{ K}} \right) (202 \text{ kPa}) = 320 \text{ kPa}$$

## Example 2

Pure helium gas is admitted into a tank containing a movable piston. The initial volume, pressure and temperature of the gas are 15 L, 2atm and 300K respectively. If the volume is decreased to 12 L and the pressure is increased to 3.5atm, find the final temperature of the gas.

### Solution

Since the gas can not escape from the tank then the number of moles is constant, therefore,  $PV = nRT$  at the initial and final points of the process

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \longrightarrow T_2 = \left( \frac{p_2 V_2}{p_1 V_1} \right) T_1 = \frac{3.5 \text{ atm} \cdot 12 \text{ liters}}{2 \text{ atm} \cdot 15 \text{ liters}} (300 \text{ K}) = 420 \text{ K}$$

## Example 3

One mole of oxygen gas is at a pressure of 6 atm and a temperature of 7°C. (a) If the gas is heated at constant volume until the pressure triples, (a) what is the final temperature? (b) If the gas is heated until both the pressure and the volume are doubled, what is the final temperature?

$$(a) T_1 = 273 + 7 = 280 \text{ K}, \quad p_2 = 3p_1 \Rightarrow \frac{p_1}{T_1} = \frac{3p_1}{T_2} \Rightarrow \frac{1}{T_1} = \frac{3}{T_2}$$

$$\text{So } T_2 = 3T_1 = 280 \times 3 = 840 \text{ K}$$

$$(b) p_2 = 2p_1, V_2 = 2V_1$$

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \Rightarrow \frac{p_1 V_1}{T_1} = \frac{4p_1 V_1}{T_2}$$

$$T_2 = 4T_1 = 4 \times 280 = 1120 \text{ K}$$

## Problem to solve by yourself

1. Gas is confined in a tank at a pressure of 11.0 atm and a temperature of 25.0°C. If two-thirds of the gas is withdrawn and the temperature is raised to 75.0°C, what is the pressure of the gas remaining in the tank?
2. (a) Find the number of moles in one cubic meter of an ideal gas at 20.0°C and atmospheric pressure. (b) For air, Avogadro's number of molecules has mass 28.9 g. Calculate the mass of one cubic meter of air. (c) State how this result compares with the tabulated density of air at 20.0°C.
3. An automobile tire is inflated with air originally at 10.0°C and normal atmospheric pressure. During the process, the air is compressed to 28.0% of its original volume and the temperature is increased to 40.0°C. (a) What is the tire pressure? (b) After the car is driven at high speed, the tire's air temperature rises to 85.0°C and the tire's interior volume increases by 2.00%. What is the new tire pressure?

إلى اللقاء مع المحاضرة (٤)

## Heat and the first law of thermodynamics



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# Thermodynamics

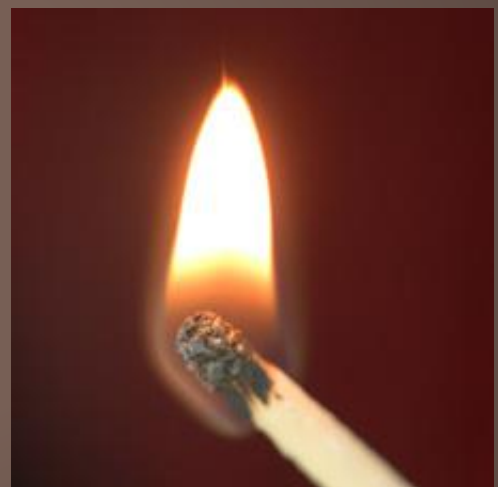
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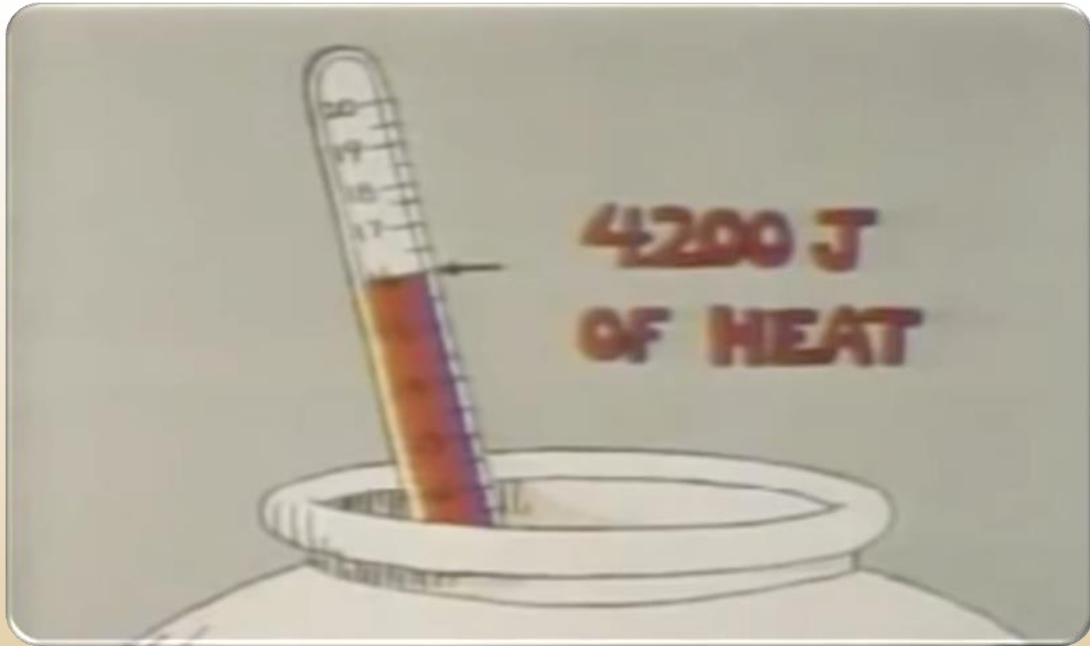
## Unit 2: Heat and the first law of thermodynamics

### Lecture 4: Heat and Internal Energy

## Unit 2: Heat and the first law of thermodynamics

- ❑ Heat and Internal Energy
- ❑ Specific Heat and Calorimetry
- ❑ Latent Heat
- ❑ Work and Heat in Thermodynamic Processes
- ❑ The First Law of Thermodynamics
- ❑ Some Applications of the First Law of Thermodynamics
- ❑ Energy Transfer Mechanisms in Thermal Processes





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## Thermodynamics – Historical Background

- ❖ Thermodynamics and mechanics were considered to be distinct branches of physics.
  - ❖ Until about 1850
  - ❖ Experiments by **James Joule** and others showed a connection between them.
- ❖ A connection was found between the **transfer of energy by heat in thermal processes** and the **transfer of energy by work in mechanical processes**.
- ❖ The concept of energy was generalized to include **internal energy**.
- ❖ The principle of conservation of energy emerged as a universal law of nature.



**James Prescott Joule**

1818 – 1889  
British physicist

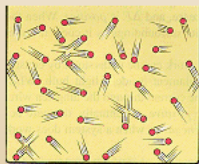
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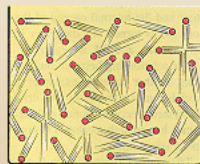
# Heat and Internal Energy

## Internal Energy

**Internal Energy** is all the energy of a system that is associated with its microscopic components —atoms and molecules— when viewed from a reference frame at rest with respect to the center of mass of the system.



Low Temperature



High Temperature



## Heat

**Heat** is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings. We also use the term *heat* to represent the amount of energy transferred ( $Q$ ).

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# Heat and Internal Energy

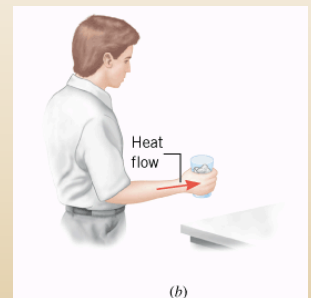
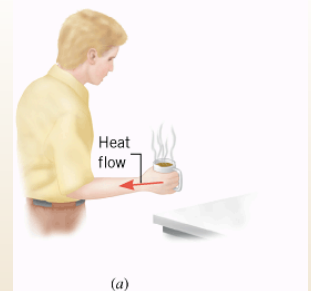
Heat is *not* in the following common quotes.

- (1) Heat is *not* energy in a hot substance.
- (2) Heat is *not* radiation.
- (3) Heat is *not* warmth of an environment.

### Note:

Heat, internal energy, and temperature are all different quantities.

- Be sure to use the correct definition of heat.
- You cannot talk about the "heat of a system," you can refer to heat only when energy has been transferred as a result of a temperature difference.

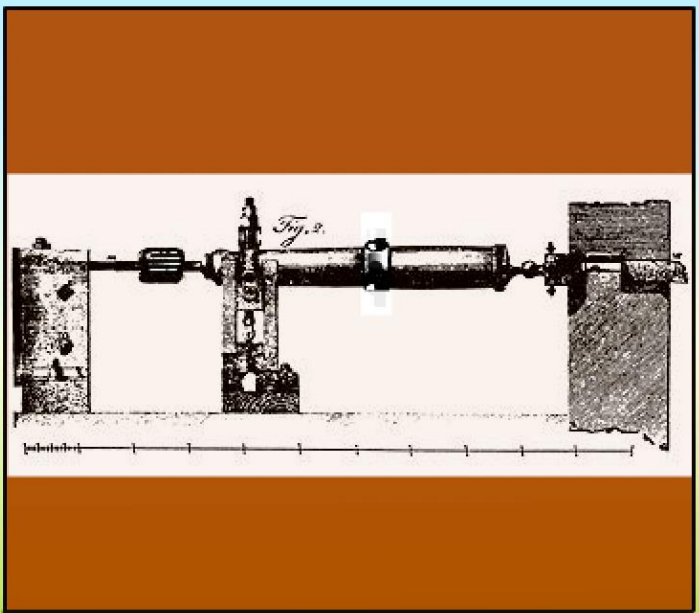
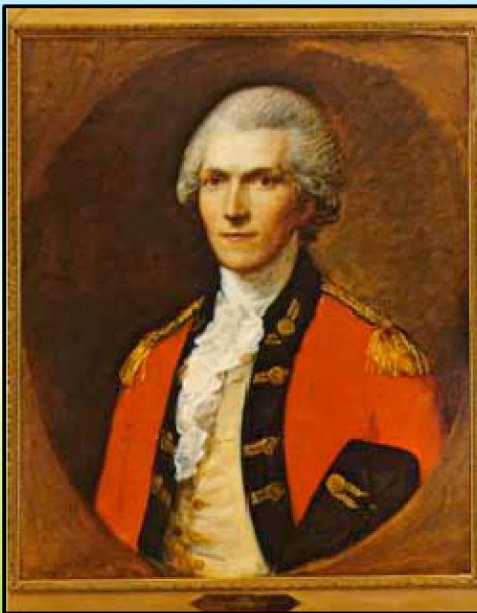
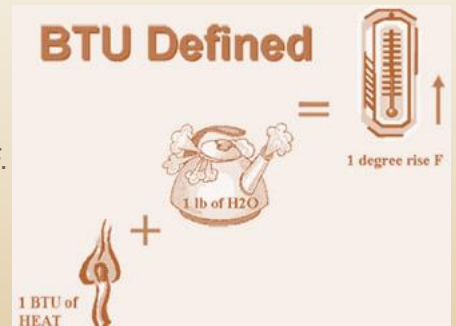


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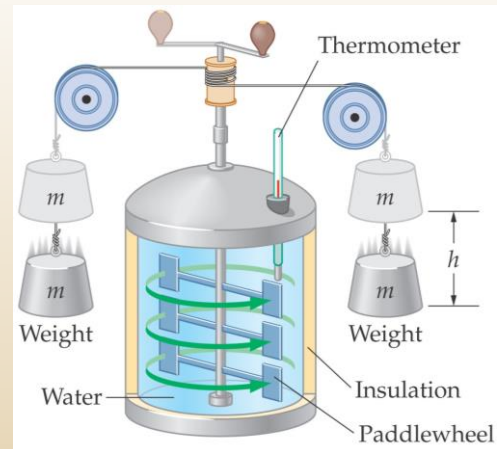
# Units of Heat

- Historically, the **calorie** was the unit used for heat.
  - One calorie is the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.
  - The "Calorie" used for food is actually 1 kilocalorie.
- In the US Customary system, the unit is a BTU (British Thermal Unit).
  - One BTU is the amount of energy transfer necessary to raise the temperature of 1 lb of water from 63°F to 64°F. (1 BTU = 1 055 joules).
- The standard unit for **heat**, **work**, and **internal energy** are measured in joules.



## Mechanical Equivalent of Heat

- Joule established the equivalence between mechanical energy and internal energy.
- His experimental setup is shown at right.
- The decrease in potential energy associated of the system as the blocks fall equals the work done by the paddle wheel on the water.

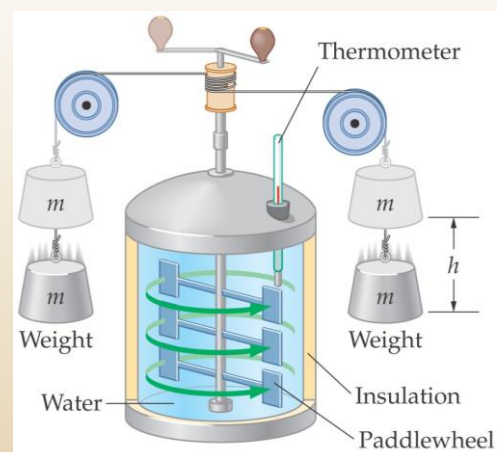


## Mechanical Equivalent of Heat

- Joule found that it took approximately 4.18 J of mechanical energy to raise the water 1°C.
- Later, more precise, measurements determined the amount of mechanical energy needed to raise the temperature of water from 14.5°C to 15.5°C.

$$1 \text{ cal} = 4.186 \text{ J}$$

- This is known as the **mechanical equivalent of heat**.
  - A more proper name would be **the equivalence between mechanical energy and internal energy**, but the historical name is well entrenched.



## Example

A student eats a dinner rated at 2000 (food) Calories. He wishes to do an equivalent amount of work in the gymnasium by lifting 50Kg mass. How many times must he raise the weight to expend this much energy? Assume that he raises the weight a distance of 2m each time and no work is done when the weight is dropped to the floor.

## Solution

$$1 \text{ (food) Calories} = 1000 \text{ cal}$$

then the work required is  $2000 \times 1000 \text{ cal} = 2 \times 10^6 \text{ cal}$ .

Converting this to joule, then the work required is

$$W = 2 \times 10^6 \text{ cal} \times 4.186 \text{ J/cal} = 8.37 \times 10^6 \text{ J}$$

الشغل المبذول لرفع الاثقال لمسافة  $h$  يساوي  $mgh$  والشغل الكلي لرفع الأثقال عدة مرات يعطي بالعلاقة  $nmgh$  وعليه فإن عدد مرات رفع الأثقال هو:

$$W = nmgh = 8.37 \times 10^6 \text{ J}$$

Since  $m = 50 \text{ Kg}$ , and  $h = 2\text{m}$

$$n = 8.54 \times 10^3 \text{ times}$$



اي انه يلزم الطالب رفع الثقل ما يقارب 8500 مرة لحرق السعرات الحرارية المطلوبة ولو كان يؤدي كل رفعة في زمن مقداره 5 ثواني فهذا يعني انه يلزمه 12 ساعة لإنجاز المهمة!!

## Problem to solve by yourself

1. A 55.0-kg woman cheats on her diet and eats a 540 Calorie (540 kcal) jelly doughnut for breakfast.
  - (a) How many joules of energy are the equivalent of one jelly doughnut?
  - (b) How many steps must the woman climb on a very tall stairway to change the gravitational potential energy of the woman–Earth system by a value equivalent to the food energy in one jelly doughnut? Assume the height of a single stair is 15.0 cm.
  - (c) If the human body is only 25.0% efficient in converting chemical potential energy to mechanical energy, how many steps must the woman climb to work off her breakfast?

إلى اللقاء مع المحاضرة (٥)

## Specific Heat and Calorimetry

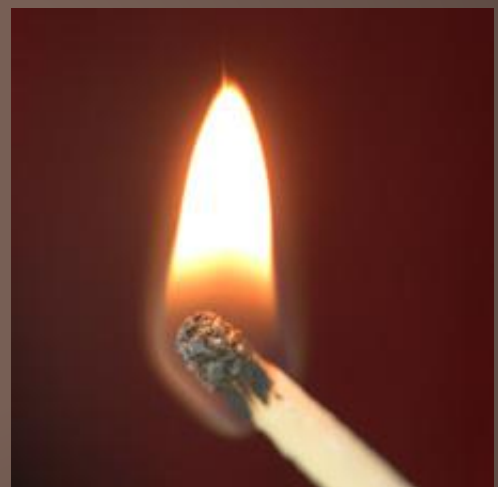


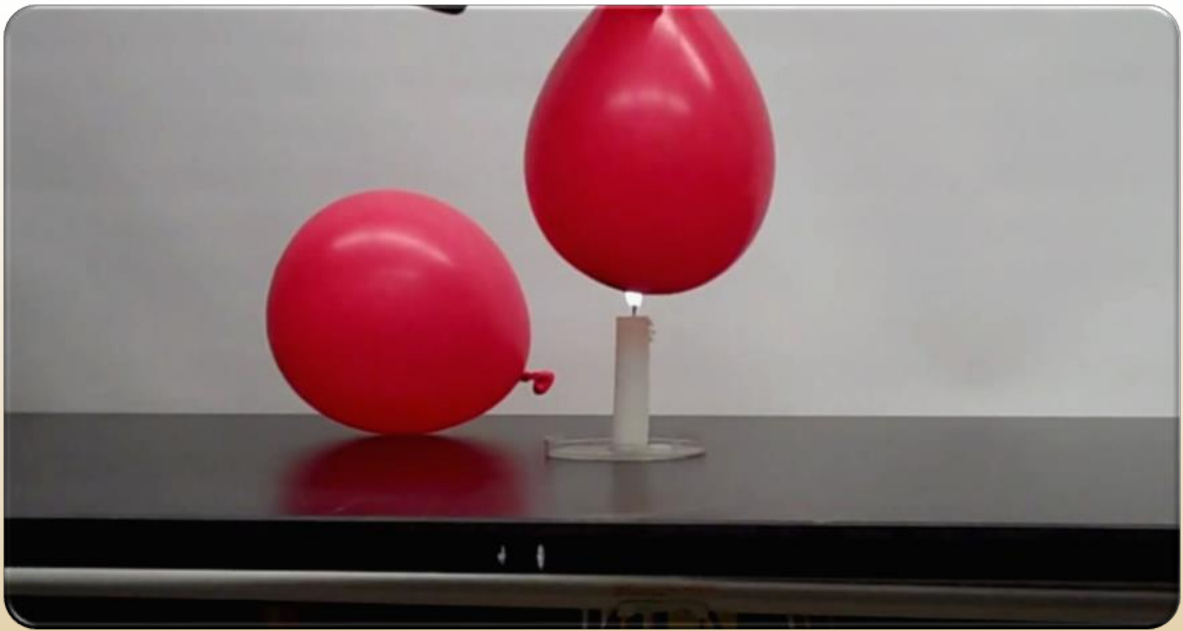
## Unit 2: Heat and the first law of thermodynamics

### Lecture 5: Specific Heat and Calorimetry

## Unit 2: Heat and the first law of thermodynamics

- ☐ Heat and Internal Energy
- ☒ **Specific Heat and Calorimetry**
- ☐ Latent Heat
- ☐ Work and Heat in Thermodynamic Processes
- ☐ The First Law of Thermodynamics
- ☐ Some Applications of the First Law of
- ☐ Thermodynamics
- ☐ Energy Transfer Mechanisms in Thermal Processes





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## The effect of Heat on substance

- When energy is added to a system and there is **no change in the kinetic or potential energy of the system**, the temperature of the system **usually** rises.

(An exception to this statement is the case in which a system undergoes a *phase transition*—as discussed in the next lecture.)

- The **quantity of energy** required to **raise the temperature** of a given mass of the substance by some amount **varies** from one substance to another.

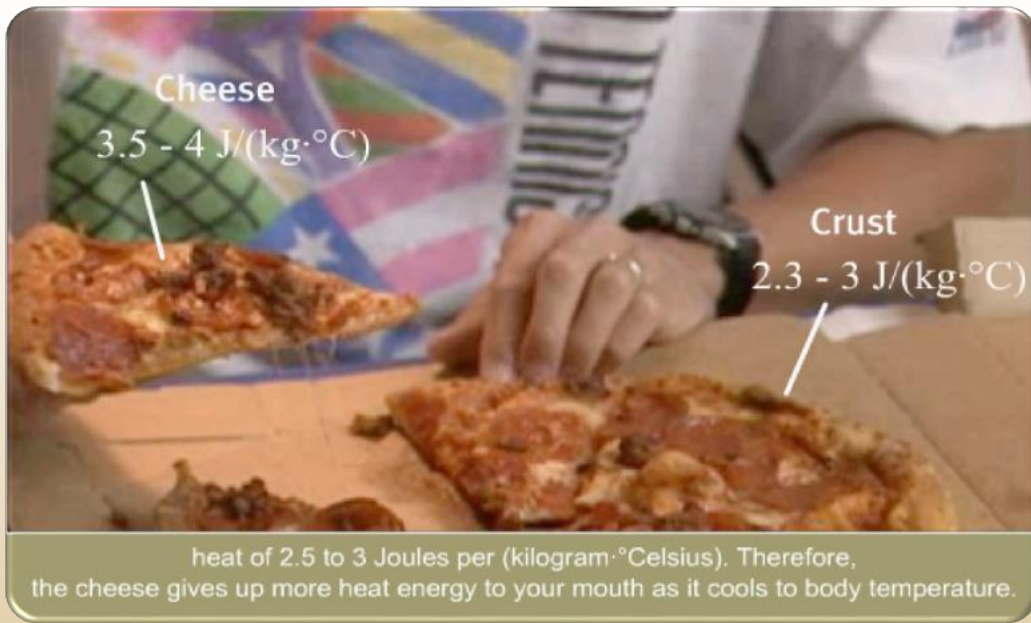
### For example

The **quantity of energy** required to raise the temperature of 1 kg of **water** by  $1^{\circ}\text{C}$  is **4 186 J**

The **quantity of energy** required to raise the temperature of 1 kg of **copper** by  $1^{\circ}\text{C}$  is **387 J**

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## Heat Capacity

Suppose that several objects composed of different materials are heated in the same manner. **Will the objects warm up at equal rates?**

**The answer:** most likely not. Different materials would warm up at different rates because each material has its own **heat capacity**.

$$Q \propto \Delta T \quad \longrightarrow \quad Q = C\Delta T \quad \longrightarrow \quad C = \frac{Q}{\Delta T}$$

The **heat capacity,  $C$** , of a particular sample is defined as **the amount of energy** needed to **raise the temperature** of that sample by  $1^\circ\text{C}$ .

▪ If **energy  $Q$**  produces a change of temperature of  $\Delta T$ , then  **$Q = C\Delta T$** .

## Specific Heat Capacity (Specific Heat)

- **Specific heat,  $c$ ,** is the heat capacity per unit mass.
- If **energy  $Q$**  transfers to a sample of a substance of **mass  $m$**  and the temperature changes by  **$\Delta T$** , then the specific heat is

$$c = \frac{Q}{m\Delta T}$$

- The specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy.
  - The greater the substance's specific heat, the more energy that must be added to a given mass to cause a particular temperature change.
- The equation is often written in terms of  $Q$ :  **$Q = mc\Delta T$**

## Some Specific Heat Values

**TABLE 20.1** Specific Heats of Some Substances at 25°C and Atmospheric Pressure

Substance	Specific Heat (J/kg · °C)	Substance	Specific Heat (J/kg · °C)
<i>Elemental solids</i>		<i>Other solids</i>	
Aluminum	900	Brass	380
Beryllium	1 830	Glass	837
Cadmium	230	Ice (−5°C)	2 090
Copper	387	Marble	860
Germanium	322	Wood	1 700
Gold	129	<i>Liquids</i>	
Iron	448	Alcohol (ethyl)	2 400
Lead	128	Mercury	140
Silicon	703	Water (15°C)	4 186
Silver	234	<i>Gas</i>	
		Steam (100°C)	2 010

*Note:* To convert values to units of cal/g · °C, divide by 4 186.

## Example 1

Calculate the energy required to raise the temperature of 0.500 kg of water by 3.00°C.

**Solution**

$$Q = mc\Delta T$$

$$Q = (0.500 \text{ kg})(4186 \text{ J/kg} \cdot ^\circ\text{C})(3.00 ^\circ\text{C}) = 6.3 \times 10^3 \text{ J}.$$

**Notice that:**

- When the **temperature increases**,  $Q$  and  $\Delta T$  are taken to be **positive** and **energy transfers into the system**.
- When the temperature decreases,  $Q$  and  $\Delta T$  are **negative** and **energy transfers out of the system**.

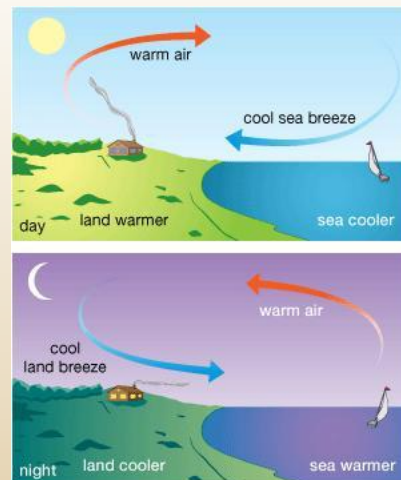
## Quiz

Imagine you have 1 kg each of iron, glass, and water, and all three samples are at 10°C.

- (a) Rank the samples from highest to lowest temperature after 100 J of energy is added to each sample.
- (b) Rank the samples from greatest to least amount of energy transferred by heat if each sample increases in temperature by 20°C.

## Specific Heat of Water

- ❖ Water has the highest specific heat of common materials.
- ❖ This is in part responsible for many weather phenomena:
  - Moderate climates near large bodies of water
  - Global wind systems
  - Land and sea breezes



## Calorimetry

One technique for **measuring specific heat** involves heating a material, adding it to a sample of water, and recording the final temperature.

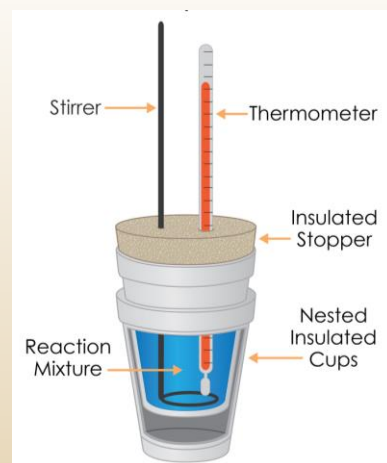
- This technique is known as **calorimetry**.
  - A calorimeter is a device in which this energy transfer takes place.
- The system of the sample and the water is isolated.

Conservation of energy requires that the amount of energy that leaves the sample equals the amount of energy that enters the water.

$$Q_{cold} = -Q_{hot}$$

or

$$Q_{gain} = -Q_{lost}$$

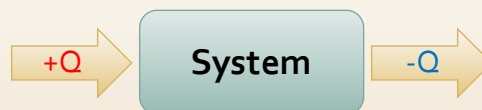


**calorimeters**

## Sign Conventions

If the temperature increases:

- $Q$  and  $\Delta T$  are positive
- Energy transfers into the system



If the temperature decreases:

- $Q$  and  $\Delta T$  are negative
- Energy transfers out of the system

The negative sign in the calorimetry equation is critical for consistency with the sign convention.

$$Q_{\text{cold}} = -Q_{\text{hot}}$$

## Calorimetry

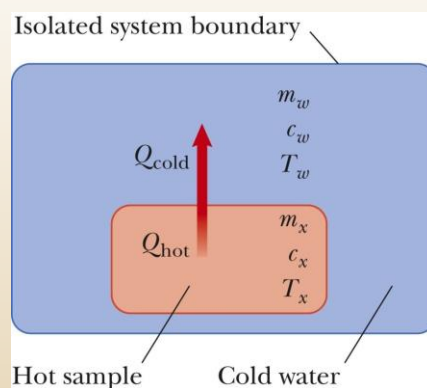
$T_f$  is the final temperature after the system comes to equilibrium.

The subscript  $w$  represent values for water and  $x$  represents the values for the sample whose specific heat is to be determined.

▪ Since each  $Q = m c \Delta T$ , the calorimetry equation can be expressed as

$$m_w c_w (T_f - T_w) = -m_x c_x (T_f - T_x)$$

- This can be solved for the unknown specific heat.



## Example 2

A 0.05kg of metal is heated to 200°C and then dropped into a beaker containing 0.4kg of water initially at 20°C. If the final equilibrium temperature of the mixed system is 22.4°C (a) find the specific heat of the metal. (b) What is the total heat transferred to water in cooling the metal?

(a) **Heat lost by the metal = heat gained by water**

$$- m_x c_x (T_f - T_i) = m_w c_w (T_f - T_i)$$

$$+ m_x c_x (T_i - T_f) = m_w c_w (T_f - T_i)$$

$$(0.05\text{Kg}) c_x (200^\circ\text{C} - 22.4^\circ\text{C}) = (0.4\text{kg})(4186\text{J/kg}\cdot\text{C}^\circ)(22.4^\circ\text{C} - 20^\circ\text{C})$$

$$c_x = 453\text{J/kg}\cdot\text{C}^\circ$$

(b) total heat transferred to water is  $Q = m_x c_x (T_i - T_f) = 0.05 \times 453 \times (200 - 22.4) = 4020\text{J}$

## Example 3

A man fires a silver bullet of mass 2g with a velocity of 200m/sec into a wall. What is the temperature change of the bullet?

The kinetic energy of the bullet  $E_k = 1/2 m v^2 = 40 \text{ J} =$  the heat transferee to the bullet

$$Q = mc\Delta T$$

where c for silver is 234J/kg.C°

$$\Delta T = \frac{Q}{mc} = \frac{40\text{J}}{(2 \times 10^{-3}\text{kg})(234\text{J/kg}\cdot\text{C}^\circ)} = 85.5\text{C}^\circ$$

## Problem to solve by yourself

1. A quantity of hot water at  $91^{\circ}\text{C}$  and another cold one at  $12^{\circ}\text{C}$ . How much kilogram of each one is needed to make an 800 liter of water bath at temperature of  $35^{\circ}\text{C}$ .
2. Consider Joule's apparatus. The mass of each of the two blocks is 1.50 kg, and the insulated tank is filled with 200 g of water. What is the increase in the water's temperature after the blocks fall through a distance of 3.00 m?
3. What mass of water at  $25.0^{\circ}\text{C}$  must be allowed to come to thermal equilibrium with a 1.85-kg cube of aluminum initially at  $150^{\circ}\text{C}$  to lower the temperature of the aluminum to  $65.0^{\circ}\text{C}$ ?

إلى اللقاء مع المحاضرة (٦)

## Latent Heat



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# Thermodynamics

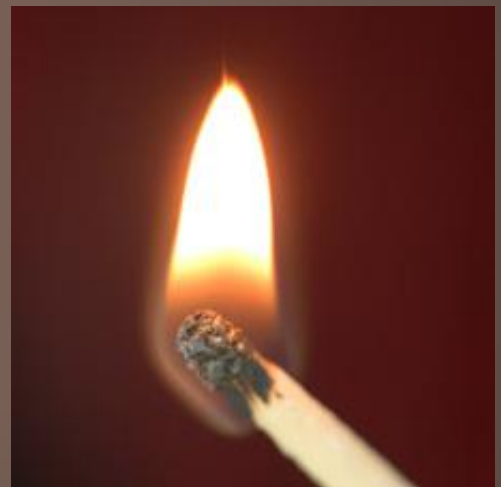
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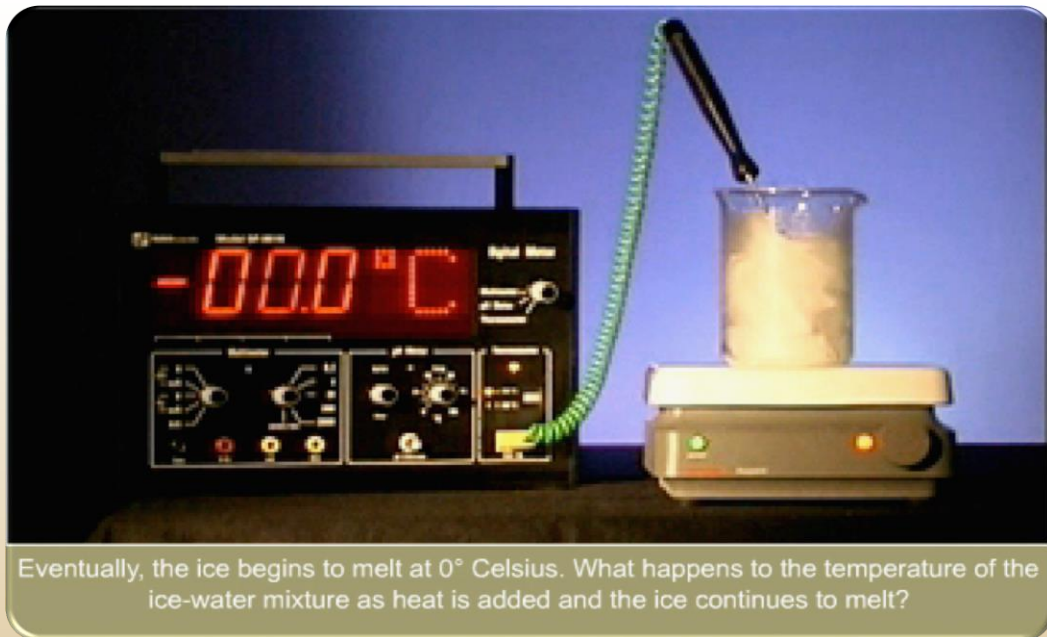
## Unit 2: Heat and the first law of thermodynamics

### Lecture 6: Latent Heat

## Unit 2: Heat and the first law of thermodynamics

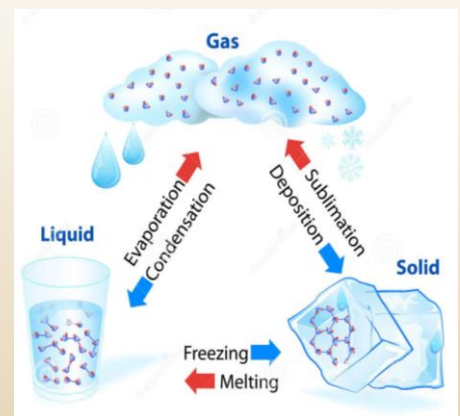
- ❑ Heat and Internal Energy
- ❑ Specific Heat and Calorimetry
- ❑ **Latent Heat**
- ❑ Work and Heat in Thermodynamic Processes
- ❑ The First Law of Thermodynamics
- ❑ Some Applications of the First Law of Thermodynamics
- ❑ Energy Transfer Mechanisms in Thermal Processes





## Phase Changes

- ❖ A **phase change** is when a substance changes from one form to another.
  - ❖ Two common phase changes are
    - ❖ Solid to liquid (**melting**)
    - ❖ Liquid to gas (**boiling**)
- ❖ During a phase change, there is **no change** in **temperature** of the substance.
  - ❖ For example, in boiling the **increase in internal energy** is represented by the breaking of the bonds between molecules, giving the molecules of the gas a higher **intermolecular potential energy**.



# Latent Heat

- ❖ Different substances react differently to the energy added or removed during a phase change.
  - ❖ Due to their different internal molecular arrangements
- ❖ The amount of energy also depends on the mass of the sample.
  - ❖ The higher-phase material is the material existing at the higher temperature.  
Example, water is the higher-phase material in an ice-water mixture
  - ❖ The initial amount of the higher-phase material in a system is  $m_i$ .
- ❖ If an amount of energy  $Q$  is required to change the phase of a sample is

$$Q \propto \Delta m \quad \Rightarrow \quad Q = L \Delta m \quad \Rightarrow \quad L = \frac{Q}{\Delta m}$$

$\Delta m = m_f - m_i$  is the change in mass of the higher-phase material

## Latent Heat and mass of substance

$$Q = L \Delta m$$

- The quantity  $L$  is called the **latent heat** of the material.
  - Latent means “hidden”.
  - The value of  $L$  depends on the substance as well as the actual phase change.
- The quantity  $\Delta m$  refers to the higher-phase material.
  - If the entire amount of the lower-phase material undergoes a phase change, the change in mass of the higher-phase material is equal to initial mass of the lower-phase material.

**For example,** if an ice cube of mass  $m$  on a plate melts completely, the change in mass of the water is

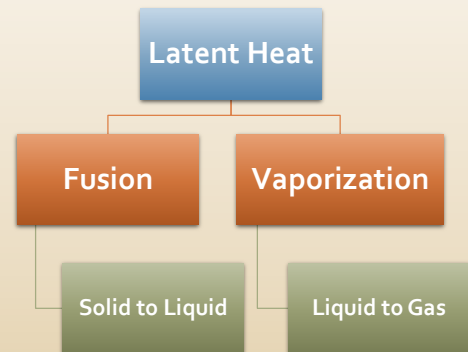
$$m_f - 0 = m$$

which is the mass of new water and is also equal to the initial mass of the ice cube.



## Latent Heat and type of phase change

- The **latent heat of fusion** is used when the phase change is from solid to liquid.
- The **latent heat of vaporization** is used when the phase change is from liquid to gas.
- If energy is enters the system:
  - This will result in melting or vaporization
  - The amount of the higher-phase material will increase
  - $\Delta m$  and  $Q$  are positive
- If energy is extracted from the system:
  - This will result in freezing or condensation
  - The amount of the higher-phase material will decrease
  - $\Delta m$  and  $Q$  are negative

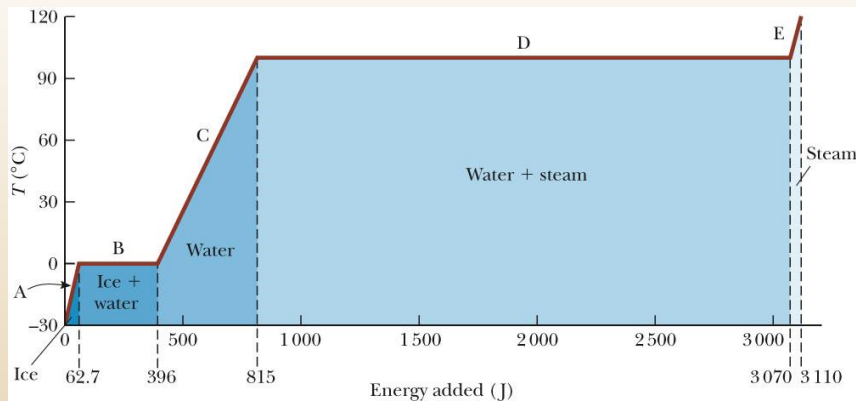


## Sample Latent Heat Values

**TABLE 20.2** Latent Heats of Fusion and Vaporization

Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	-269.65	$5.23 \times 10^3$	-268.93	$2.09 \times 10^4$
Oxygen	-218.79	$1.38 \times 10^4$	-182.97	$2.13 \times 10^5$
Nitrogen	-209.97	$2.55 \times 10^4$	-195.81	$2.01 \times 10^5$
Ethyl alcohol	-114	$1.04 \times 10^5$	78	$8.54 \times 10^5$
Water	0.00	$3.33 \times 10^5$	100.00	$2.26 \times 10^6$
Sulfur	119	$3.81 \times 10^4$	444.60	$3.26 \times 10^5$
Lead	327.3	$2.45 \times 10^4$	1 750	$8.70 \times 10^5$
Aluminum	660	$3.97 \times 10^5$	2 450	$1.14 \times 10^7$
Silver	960.80	$8.82 \times 10^4$	2 193	$2.33 \times 10^6$
Gold	1 063.00	$6.44 \times 10^4$	2 660	$1.58 \times 10^6$
Copper	1 083	$1.34 \times 10^5$	1 187	$5.06 \times 10^6$

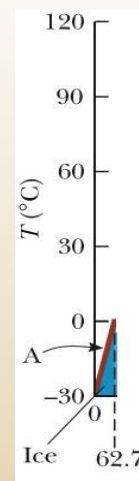
## Graph of Ice to Steam



The energy required to convert a 1.00-g cube of ice at  $-30.0^\circ\text{C}$  to steam at  $120.0^\circ\text{C}$ .

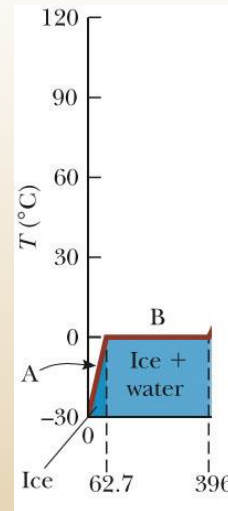
## Warming Ice, Graph Part A

- Start with one gram of ice at  $-30.0^\circ\text{C}$ .
- During phase A, the temperature of the ice changes from  $-30.0^\circ\text{C}$  to  $0^\circ\text{C}$ .
- Use  $Q = m_i c_i \Delta T$ 
  - In this case, **62.7 J** of energy are added.



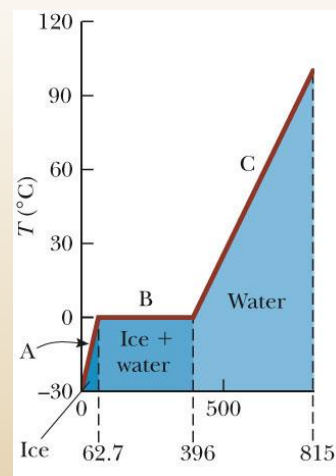
## Melting Ice, Graph Part B

- Once at 0°C, the phase change (melting) starts.
- The temperature stays the same although energy is still being added.
- Use  $Q = L_f \Delta m_w = L_f m_i$ 
  - The energy required is **333 J**.
  - On the graph, the values move from 62.7 J to 396 J.



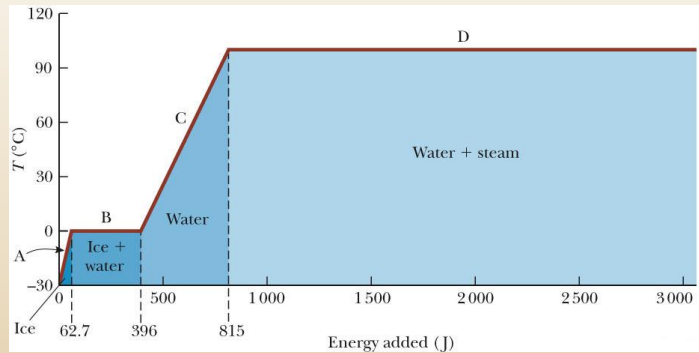
## Warming Water, Graph Part C

- Between 0°C and 100°C, the material is liquid and no phase changes take place.
- Energy added increases the temperature.
- Use  $Q = m_w c_w \Delta T$ 
  - **419 J** are added
  - The total is now 815 J



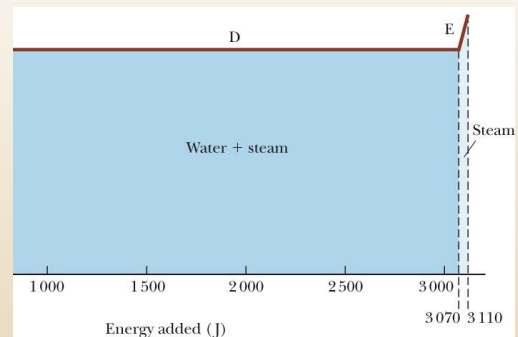
## Boiling Water, Graph Part D

- At 100°C, a phase change occurs (boiling).
- Temperature does not change.
- Use  $Q = L_v \Delta m_s = L_v m_w$ 
  - This requires **2260 J**
  - The total is now 3070 J



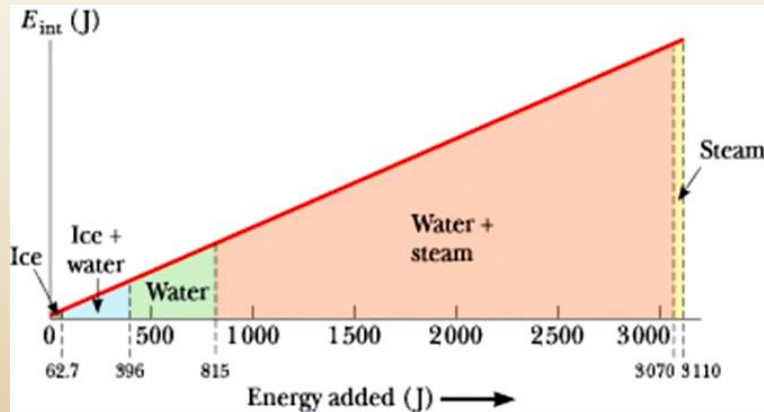
## Heating Steam, Graph Part E

- After all the water is converted to steam, the steam will heat up.
- No phase change occurs.
- The added energy goes to increasing the temperature.
- Use  $Q = m_s c_s \Delta T$ 
  - In this case, **40.2 J** are needed.
  - The temperature is increasing from 100°C to 120°C.
  - **The total is now 3110 J.**



## Quiz

Suppose the same process of adding energy to the ice cube is performed as discussed above, but instead we graph the **internal energy of the system as a function of energy input**. What would this graph look like?



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## Example 1

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

**Solution**

**The steam undergoes three processes:** first a decrease in temperature to 100°C,

$$Q_1 = m_s c_s \Delta T_s$$

then condensation into liquid water,

$$Q_2 = L_v \Delta m_s = L_v(0 - m_s) = -m_s L_v$$

finally a decrease in temperature of the water to 50.0°C.

$$Q_3 = m_s c_w \Delta T_{\text{hot water}}$$

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- the energy transfers in these three stages

$$Q_{\text{hot}} = Q_1 + Q_2 + Q_3 = m_s(c_s \Delta T_s - L_v + c_w \Delta T_{\text{hot water}})$$

- The 20.0°C water and the glass undergo only one process, an increase in temperature to 50.0°C.

$$Q_{\text{cold}} = m_w c_w \Delta T_{\text{cold water}} + m_g c_g \Delta T_{\text{glass}}$$

$$Q_{\text{cold}} = -Q_{\text{hot}}$$

$$m_w c_w \Delta T_{\text{cold water}} + m_g c_g \Delta T_{\text{glass}} = -m_s(c_s \Delta T_s - L_v + c_w \Delta T_{\text{hot water}})$$

$$m_s = - \frac{(0.200 \text{ kg})(4186 \text{ J/kg} \cdot ^\circ\text{C})(50.0^\circ\text{C} - 20.0^\circ\text{C}) + (0.100 \text{ kg})(837 \text{ J/kg} \cdot ^\circ\text{C})(50.0^\circ\text{C} - 20.0^\circ\text{C})}{(2010 \text{ J/kg} \cdot ^\circ\text{C})(100^\circ\text{C} - 130^\circ\text{C}) - (2.26 \times 10^6 \text{ J/kg}) + (4186 \text{ J/kg} \cdot ^\circ\text{C})(50.0^\circ\text{C} - 100^\circ\text{C})}$$

$$= 1.09 \times 10^{-2} \text{ kg} = 10.9 \text{ g}$$

## Problem to solve by yourself

- How much energy is required to change a 40.0-g ice cube from ice at 210.0°C to steam at 110°C?
- A 75.0-g ice cube at 0°C is placed in 825 g of water at 25.0°C. What is the final temperature of the mixture?
- A 3.00-g lead bullet at 30.0°C is fired at a speed of 240 m/s into a large block of ice at 0°C, in which it becomes embedded. What quantity of ice melts?
- Steam at 100°C is added to ice at 0°C. (a) Find the amount of ice melted and the final temperature when the mass of steam is 10.0 g and the mass of ice is 50.0 g. (b) What If? Repeat when the mass of steam is 1.00 g and the mass of ice is 50.0 g.
- In an insulated vessel, 250 g of ice at 0°C is added to 600 g of water at 18.0°C. (a) What is the final temperature of the system? (b) How much ice remains when the system reaches equilibrium?

إلى اللقاء مع المحاضرة (V)

## Work and Heat in Thermodynamic Processes



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# Thermodynamics

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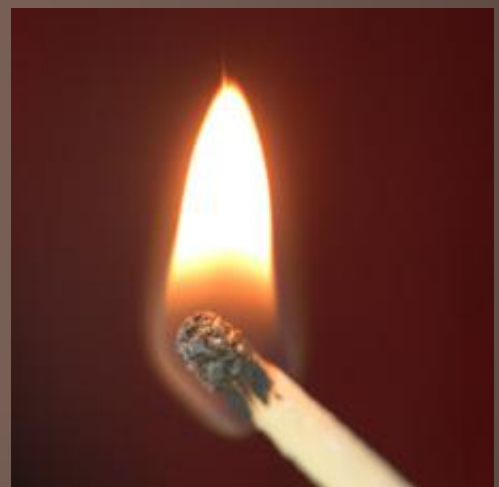


## Unit 2: Heat and the first law of thermodynamics

### Lecture 7: Work and Heat in Thermodynamic Processes

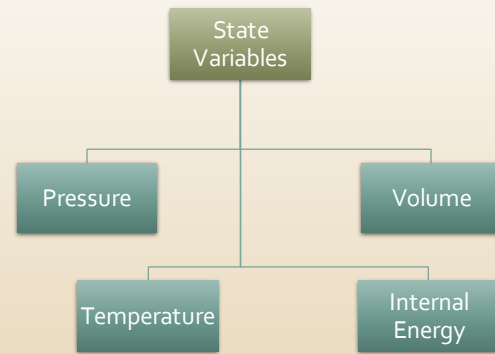
## Unit 2: Heat and the first law of thermodynamics

- ❑ Heat and Internal Energy
- ❑ Specific Heat and Calorimetry
- ❑ Latent Heat
- ❑ **Work and Heat in Thermodynamic Processes**
- ❑ The First Law of Thermodynamics
- ❑ Some Applications of the First Law of Thermodynamics
- ❑ Energy Transfer Mechanisms in Thermal Processes



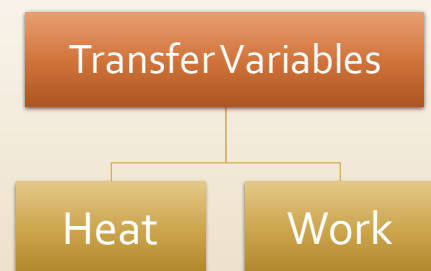
## State Variables

- **State variables** describe the state of a system.
- **Variables** may include:
  - Pressure, temperature, volume, internal energy
- The state of an **isolated system** can be specified only if the system is in **thermal equilibrium internally**.
  - For a gas in a container, this means every part of the gas must be at the **same pressure and temperature**.



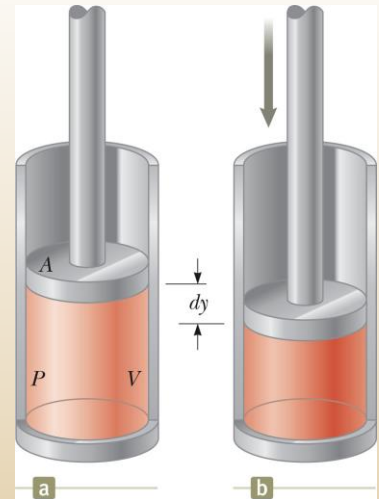
## Transfer Variables

- **Transfer variables** are zero **unless** a **process** occurs in which **energy is transferred** across the boundary of a system.
- **Transfer variables** are not associated with any given state of the system, **only with changes in the state**.
  - Heat and work are transfer variables.
- **Transfer variable** can be positive or negative, depending on whether energy is entering or leaving the system.



## Work in Thermodynamics

- **Work** can be done on a deformable system, such as a gas.
- Consider a cylinder with a moveable piston.
- A force is applied to **slowly** compress the gas.
  - The compression is slow enough for all the system to remain essentially in **thermal equilibrium**.
  - This is said to occur **quasi-statically**.



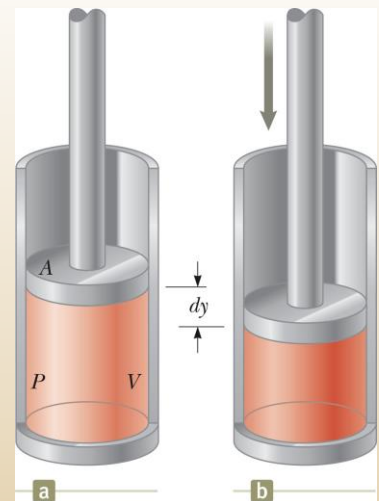
## Work in Thermodynamics

- The force exerted by the gas on the piston is  $F = PA$
- The piston is pushed downward by a force  $\vec{F} = -F\hat{j}$
- through a displacement of  $d\vec{r} = dy\hat{j}$
- the work done on the gas is

$$dW = \vec{F} \cdot d\vec{r} = -F\hat{j} \cdot dy\hat{j} = -Fdy = -PA dy$$

- $Ady$  is the change in volume of the gas,  $dV$ .
- Therefore, the work done on the gas is

$$dW = -PdV$$



# Work in Thermodynamics

## Interpreting $dW = -PdV$

- If the gas is **compressed**,  $dV$  is **negative** and the **work done on the gas is positive**.
- If the gas **expands**,  $dV$  is **positive** and the **work done on the gas is negative**.
- If the volume remains constant, the work done is zero.

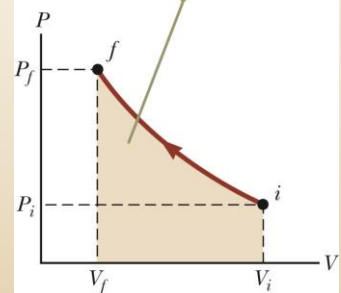
## The total work done is:

$$W = - \int_{V_i}^{V_f} P dV$$

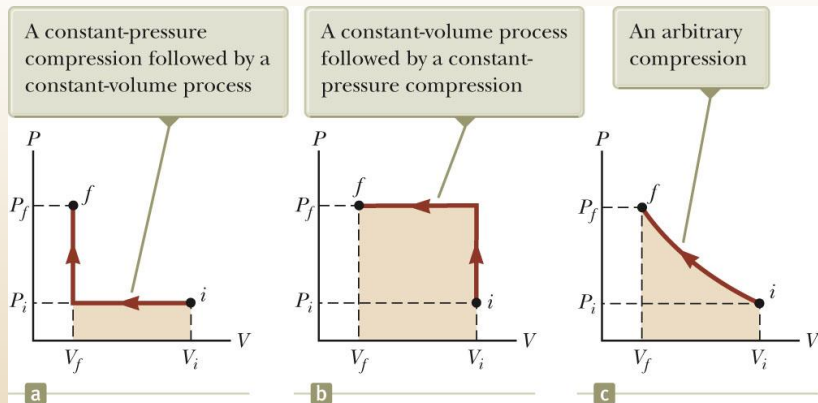
## PV Diagrams

- Used when the pressure and volume are known at each step of the process.
- The state of the gas at each step can be plotted on a graph called a **PV diagram**.
  - This allows us to visualize the process through which the gas is progressing.
- The curve is called the **path**.
- The **work done on a gas** in a quasi-static process that takes the gas from an **initial state** to a **final state** is the **negative of the area under the curve on the PV diagram**, evaluated between the initial and final states.
  - This is true whether or not the pressure stays constant.
  - The work done does depend on the path taken.

The work done on a gas equals the negative of the area under the PV curve. The area is negative here because the volume is decreasing, resulting in positive work.



## Work Done By Various Paths



- Each of these processes has the same initial and final states.
- The work done differs in each process.
- The work done depends on the path.

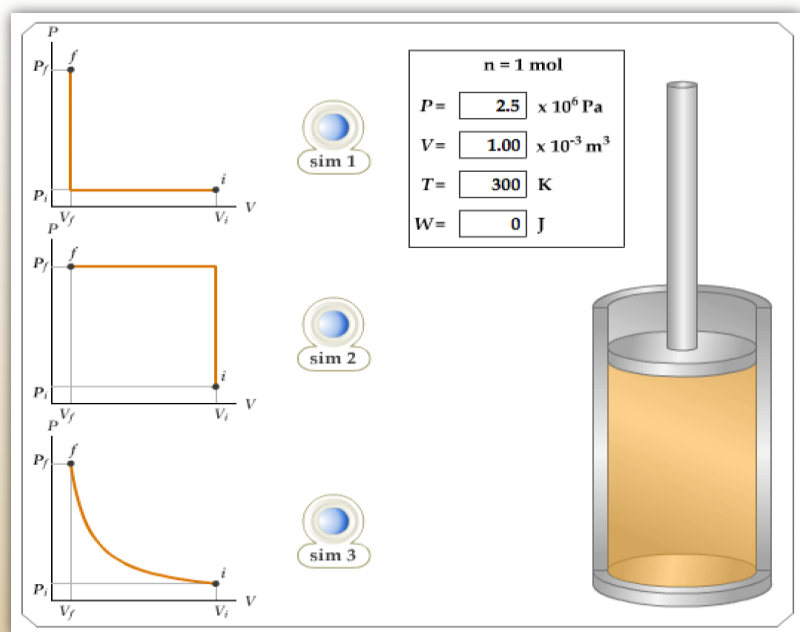
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**Constant Volume then  
constant Pressure**

**Constant Pressure then  
constant Volume**

**Constant Temperature**



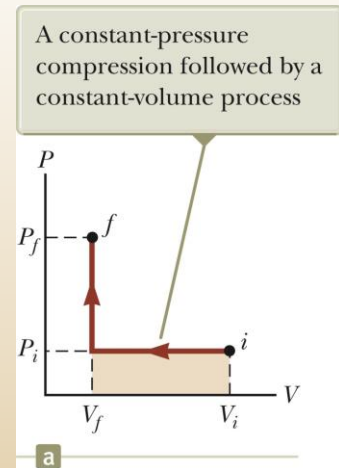
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## Work From a $PV$ Diagram, Example 1

- The volume of the gas is first reduced from  $V_i$  to  $V_f$  at constant pressure  $P_i$
- Next, the pressure increases from  $P_i$  to  $P_f$  by heating at constant volume  $V_f$ .

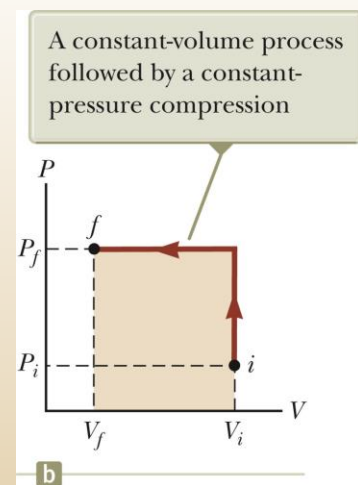
$$W = -P_i (V_f - V_i)$$



## Work From a $PV$ Diagram, Example 2

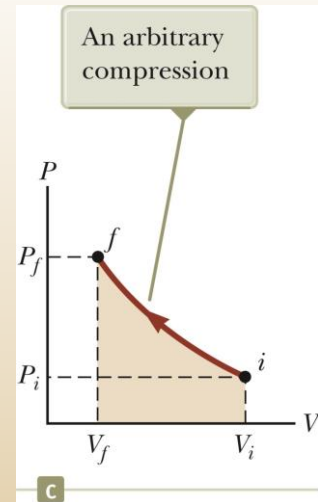
- The pressure of the gas is increased from  $P_i$  to  $P_f$  at a constant volume.
- The volume is decreased from  $V_i$  to  $V_f$ .

$$W = -P_f (V_f - V_i)$$



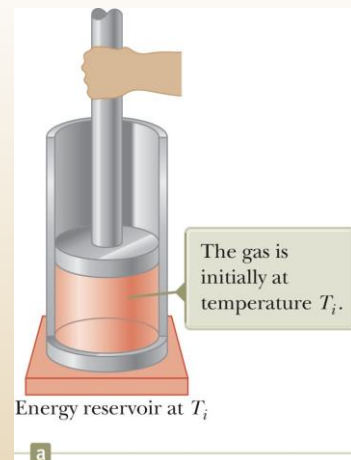
## Work From a $PV$ Diagram, Example 3

- The pressure and the volume continually change.
- The work is some intermediate value between  $-P_f(V_f - V_i)$  and  $-P_i(V_f - V_i)$
- To evaluate the actual amount of work, the function  $P(V)$  must be known.



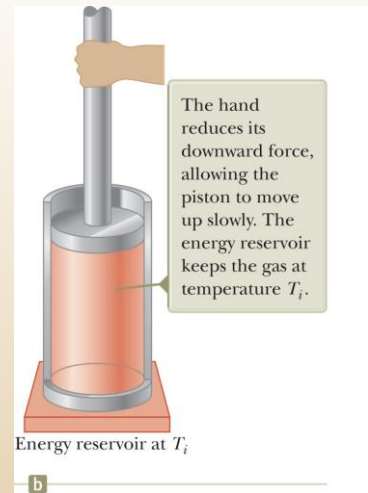
## Energy Transfer

- The energy transfer,  $Q$ , into or out of a system also depends on the process.
- The **energy reservoir** is a source of energy that is considered to be so great that a finite transfer of energy does not change its temperature.
- The piston is held at its internal position by an external agent.



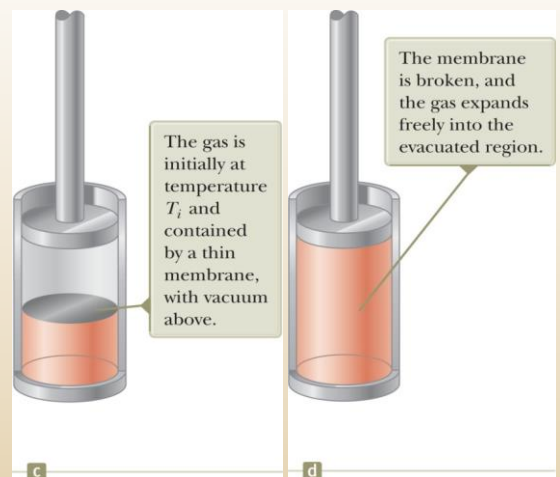
## Energy Transfer

- The external force is reduced.
- The piston is moving **upward** and the gas is doing work on the piston.
- During this **expansion**, just enough energy is transferred by heat from the reservoir to the gas to maintain a constant temperature.



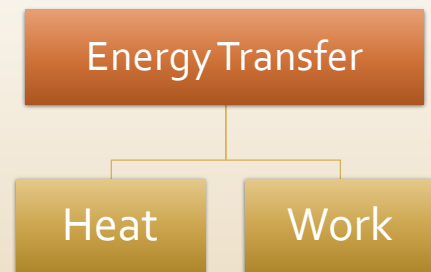
## Energy Transfer, **Isolated System**

- The system is completely thermally insulated.
- When the **membrane is broken**, the gas expands rapidly into the vacuum until it comprises the final volume.
- The gas does **no work** because it does not apply a force.
- **No energy** is transferred by heat through the insulating wall.



## Energy Transfer, Summary

- Energy transfers by heat, like the work done, depend on the initial, final, and intermediate states of the system.
- Both work and heat depend on the path taken.
- Neither can be determined only by the end points of a thermodynamic process.



## Example 1

An ideal gas is enclosed in a cylinder with a movable piston on top of it. The piston has a mass of 8000 g and an area of 5.00 cm<sup>2</sup> and is free to slide up and down, keeping the pressure of the gas constant. **How much work is done on the gas as the temperature of 0.200 mol of the gas is raised from 20.0°C to 300°C?**

**Solution:**

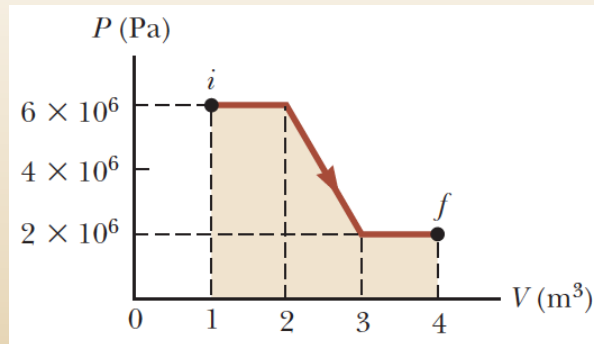
For constant pressure 
$$W = - \int_{V_i}^{V_f} P dV = -P\Delta V = -P(V_f - V_i)$$

$$W = -P \left( \frac{nRT_h}{P} - \frac{nRT_c}{P} \right) = -nR(T_h - T_c)$$

$$W = -nR\Delta T = -(0.200 \text{ mol})(8.314 \text{ J mol} \cdot \text{K})(280 \text{ K}) = -466 \text{ J}$$

## Problem to solve by yourself

1. Determine the work done on a gas that expands from  $i$  to  $f$  as indicated in the Figure.



إلى اللقاء مع المحاضرة (V)

*The First Law of Thermodynamics  
and Some Applications*

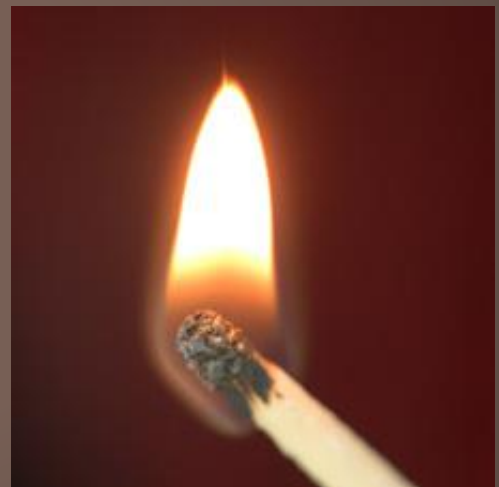


## Unit 2: Heat and the first law of thermodynamics

### Lecture 8: The First Law of Thermodynamics

## Unit 2: Heat and the first law of thermodynamics

- ❑ Heat and Internal Energy
- ❑ Specific Heat and Calorimetry
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- ❑ Energy Transfer Mechanisms in Thermal Processes



# The First Law of Thermodynamics

- The First Law of Thermodynamics is a special case of the Law of Conservation of Energy.
  - It is a special cases when only the internal energy changes and the only energy transfers are by heat and work.
- The First Law of Thermodynamics states that

$$\Delta E_{int} = Q + W$$

- All quantities must have the same units of measure of energy (Joule).
- The internal energy is a state variable.

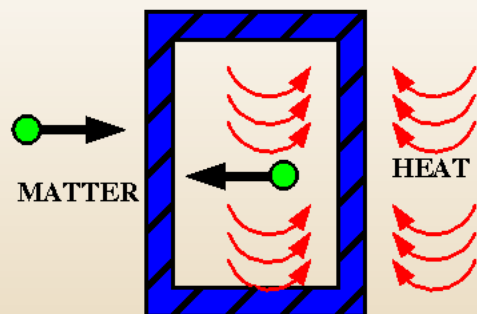
## Case 1: Isolated Systems

- An isolated system is one that does not interact with its surroundings.
  - No energy transfer by heat takes place.
  - The work done on the system is zero.

$$Q = W = 0,$$

$$\therefore \Delta E_{int} = 0$$

The internal energy of an isolated system remains constant.



## Case 2: Cyclic Processes

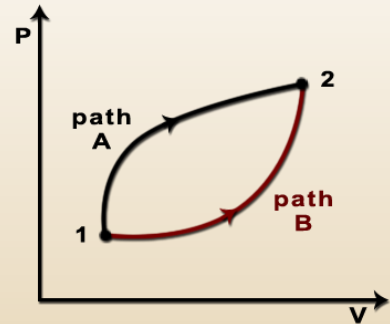
- A cyclic process is one that **starts and ends in the same state**.
  - This process would not be isolated.
  - On a  $PV$  diagram, a cyclic process appears as a closed curve.

- The internal energy must be zero

$$\therefore \Delta E_{int} = 0$$

$$\therefore Q = -W$$

- In a cyclic process, the **net work done on the system per cycle** equals the **area enclosed by the path** representing the process on a  $PV$  diagram.



## Some Applications of the First Law of Thermodynamics



## (1) Adiabatic Process

- An adiabatic process is one during which **no energy enters or leaves** the system by heat. i.e.  $Q = 0$
- This is achieved by:
  - Thermally **insulating** the walls of the system.
  - Having the process proceed so **quickly** that **no heat** can be exchanged.
- Since  $Q = 0$ ,  

$$\therefore \Delta E_{int} = W$$

- If the gas is **compressed adiabatically**,  $W$  is **positive** so  $\Delta E_{int}$  is **positive** and the **temperature of the gas increases**.
- If the gas **expands adiabatically**, the **temperature of the gas decreases**.
- Some important examples of adiabatic processes related to engineering are:**
  - The expansion of hot gases in an internal combustion engine
  - The liquefaction of gases in a cooling system
  - The compression stroke in a diesel engine

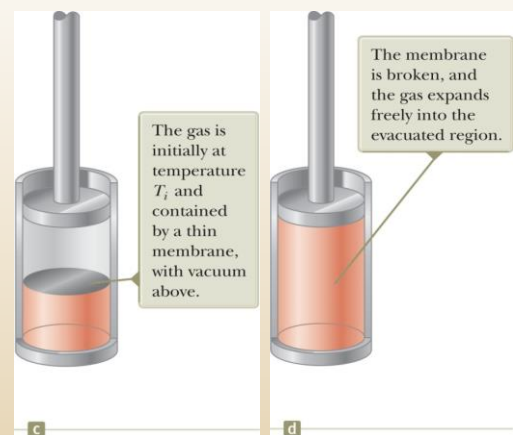
## (2) Adiabatic Free Expansion

- The process is adiabatic because it takes place in an insulated container.
- Because the gas expands into a vacuum, it does not apply a force on a piston and  $W = 0$ .
- Since  $Q = 0$  and  $W = 0$ ,

$$\Delta E_{int} = 0$$

and the initial and final states are the same.

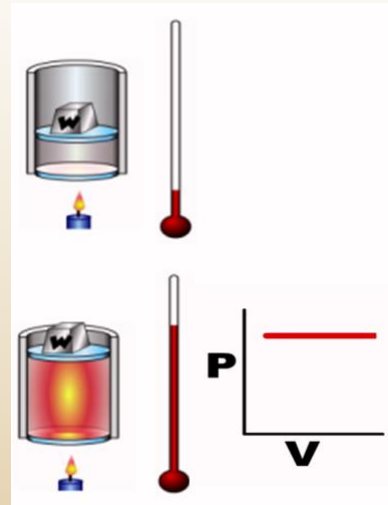
**No change in temperature is expected.**



### (3) Isobaric Processes

- An isobaric process is one that occurs at a constant pressure.
  - May be accomplished by allowing the piston to **move freely** so that it is always in **equilibrium** between the **net force from the gas pushing upward** and **the weight of the piston plus the force due to atmospheric pressure pushing downward**.
- The values of the **heat** and the **work** are generally both **nonzero**.

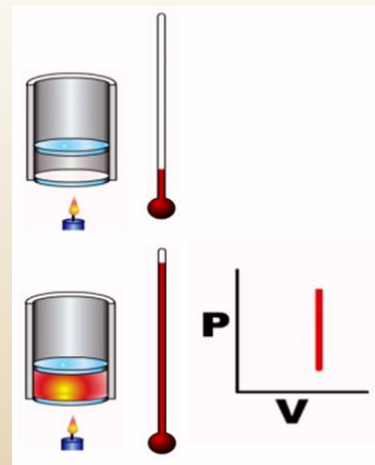
The work done is  $W = -P (V_f - V_i)$   
where  $P$  is the constant pressure.



### (4) Isovolumetric (isochoric) Processes

- An isovolumetric process is one in which there is no change in the volume.
  - This may be accomplished by clamping the piston at a fixed position.
- Since the volume does not change,  $W = 0$ .
- From the first law,  $\Delta E_{int} = Q$

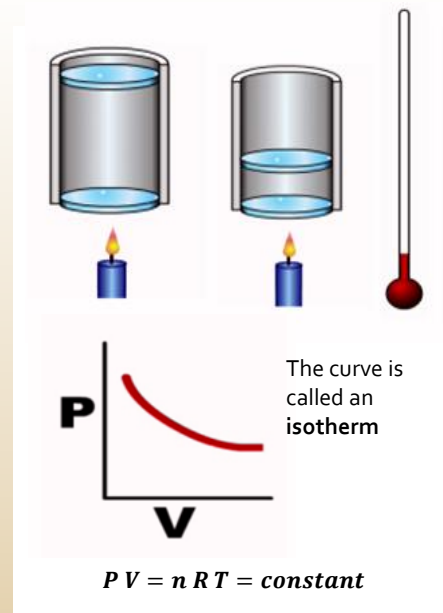
If energy is added by heat to a system kept at constant volume, **all of the transferred energy remains in the system as an increase in its internal energy**.



## (5) Isothermal Process

- An isothermal process is one that occurs at a constant temperature.
  - This can be accomplished by putting the cylinder in contact with some **constant-temperature reservoir**.
- Since there is no change in temperature,  $\Delta E_{int} = 0$ .
- Therefore,  $Q = -W$

**Any energy that enters the system by heat must leave the system by work.**



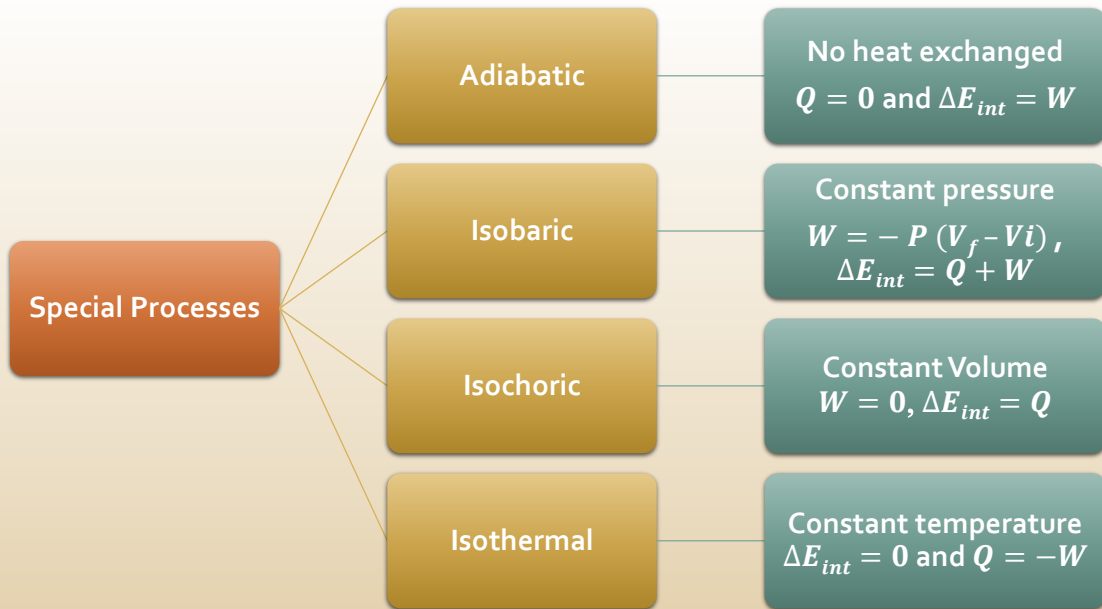
## Isothermal Expansion

- Because it is an ideal gas and the process is **quasi-static**, the ideal gas law is valid for each point on the path.

$$W = -\int_{V_i}^{V_f} P dV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$W = nRT \ln\left(\frac{V_i}{V_f}\right)$$

- Numerically, the work equals the negative of the area under the PV diagram.
- If the gas **expands**,  $V_f > V_i$  and the value of the **work done on the gas is negative**.
- If the gas is **compressed**,  $V_f < V_i$  and the value of the **work done on the gas is positive**.

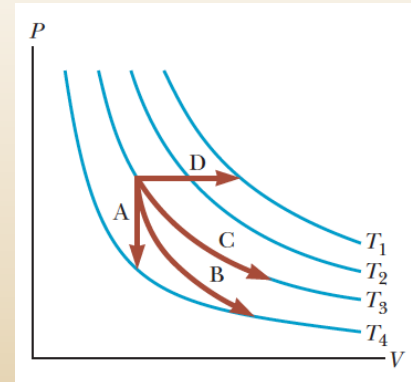


## Examples and Discussion

## Quiz 1

Characterize the paths in the Figure as isobaric, isovolumetric, isothermal, or adiabatic. For path B,  $Q = 0$ . The blue curves are isotherms.

- A → Isochoric
- B → Adiabatic
- C → Isothermal
- D → Isobaric



## Quiz 2

- In the last three columns of the following table, fill in the boxes with the correct signs ( $-$ ,  $+$ , or  $0$ ) for  $Q$ ,  $W$ , and  $\Delta E_{\text{int}}$ . For each situation, the system to be considered is identified.

Situation	System	$Q$	$W$	$\Delta E_{\text{int}}$
Rapidly pumping up a bicycle tire	Air in the pump			
Pan of room-temperature water sitting on a hot stove	Water in the pan			
Air quickly leaking out of a balloon	Air originally in the balloon			

## Example 1

A 1.0-mol sample of an ideal gas is kept at 0.0°C during an expansion from 3.0 to 10.0 L. **(A)** How much work is done on the gas during the expansion? **(B)** How much energy transfer by heat occurs between the gas and its surroundings in this process? **(C)** If the gas is returned to the original volume by means of an isobaric process, how much work is done on the gas?

**(A) How much work is done on the gas during the expansion?** Imagine a cylinder is immersed in an ice–water bath, and the piston moves outward so that the volume of the gas increases.

$$W = nRT \ln \left( \frac{V_i}{V_f} \right)$$

$$\begin{aligned} &= (1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K}) \ln \left( \frac{3.0 \text{ L}}{10.0 \text{ L}} \right) \\ &= -2.7 \times 10^3 \text{ J} \end{aligned}$$

**(B)** How much energy transfer by heat occurs between the gas and its surroundings in this process?

$$\Delta E_{\text{int}} = Q + W$$

$$0 = Q + W$$

$$Q = -W = 2.7 \times 10^3 \text{ J}$$

**(C)** If the gas is returned to the original volume by means of an isobaric process, how much work is done on the gas?

$$W = -P(V_f - V_i) = -\frac{nRT_i}{V_i}(V_f - V_i)$$

$$\begin{aligned} &= -\frac{(1.0 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K})}{10.0 \times 10^{-3} \text{ m}^3}(3.0 \times 10^{-3} \text{ m}^3 - 10.0 \times 10^{-3} \text{ m}^3) \\ &= 1.6 \times 10^3 \text{ J} \end{aligned}$$

The work done on the gas is positive because the gas is being compressed.

إلى اللقاء مع المحاضرة (٩)

*Example on the first law of  
thermodynamics*



## Unit 2: Heat and the first law of thermodynamics

### Lecture 9: Examples on the First Law of Thermodynamics

$$\Delta E_{int} = Q + W$$

Special Processes

Adiabatic

No heat exchanged  
 $Q = 0$  and  $\Delta E_{int} = W$

Isobaric

Constant pressure  
 $W = -P(V_f - V_i)$ ,  $\Delta E_{int} = Q + W$

Isochoric

Constant Volume  
 $W = 0$ ,  $\Delta E_{int} = Q$

Isothermal

Constant temperature  
 $\Delta E_{int} = 0$  and  $Q = -W$

## Example 1

A thermodynamic system undergoes a process in which its internal energy decreases by 500 J. Over the same time interval, 220 J of work is done on the system. Find the energy transferred from it by heat.

$$\Delta E_{int} = Q + W$$

$$\Delta E_{int} = -500 \text{ Joule} \quad \text{internal energy decreases}$$

$$W = +220 \text{ Joule} \quad \text{work is done on the system}$$

$$Q = \Delta E_{int} - W$$

$$Q = -500 \text{ J} - 220 \text{ J} = -720 \text{ J}$$

## Example 2

Suppose 1.00 g of water vaporizes **isobarically** at atmospheric pressure ( $1.013 \times 10^5 \text{ Pa}$ ). Its volume in the **liquid state** is  $V_i = V_{\text{liquid}} = 1.00 \text{ cm}^3$ , and its volume in the **vapor state** is  $V_f = V_{\text{vapor}} = 1671 \text{ cm}^3$ . Find the **work** done in the expansion and the **change in internal energy** of the system. Ignore any mixing of the steam and the surrounding air; imagine that the steam simply pushes the surrounding air out of the way.

**Solution:** Notice that the temperature of the system **does not change**. There is a phase change occurring as the water evaporates to steam.

the expansion takes place at constant pressure

$$\begin{aligned} W &= -P(V_f - V_i) \\ &= -(1.013 \times 10^5 \text{ Pa})(1671 \times 10^{-6} \text{ m}^3 - 1.00 \times 10^{-6} \text{ m}^3) \\ &= -169 \text{ J} \end{aligned}$$

The energy transferred into the system by heat we use the latent heat of vaporization

$$Q = L_v \Delta m_s = m_s L_v = (1.00 \times 10^{-3} \text{ kg})(2.26 \times 10^6 \text{ J/kg})$$

$$= 2\,260 \text{ J}$$

From the first law we can find the change in internal energy of the system:

$$\Delta E_{\text{int}} = Q + W = 2\,260 \text{ J} + (-169 \text{ J}) = 2.09 \text{ kJ}$$

- The **positive** value for  $\Delta E_{\text{int}}$  indicates that the internal energy of the system **increases**.
- The largest fraction of the energy (2090 J/ 2260 J = **93%**) goes into increasing the internal energy of the system.
- The remaining **7%** of the energy transferred leaves the system by work done by the steam on the surrounding atmosphere.

## Example 3

- **A 1.0-kg bar of copper is heated at atmospheric pressure so that its temperature increases from 20°C to 50°C.**
  - (A) What is the **work** done on the copper bar by the surrounding atmosphere?
  - (B) How much **energy** is transferred to the copper bar by heat?
  - (C) What is the increase in **internal energy** of the copper bar?

## Example 3 solution

Because the expansion takes place at **constant atmospheric pressure**, we categorize the process as isobaric.

(A) What is the work done on the copper bar by the surrounding atmosphere?

$$W = -P \Delta V$$

$$W = -P(\beta V_i \Delta T) = -P(3\alpha V_i \Delta T) = -3\alpha P V_i \Delta T$$

$$W = -3\alpha P \left( \frac{m}{\rho} \right) \Delta T$$

$$\begin{aligned} W &= -3[1.7 \times 10^{-5} (\text{°C})^{-1}](1.013 \times 10^5 \text{ N/m}^2) \left( \frac{1.0 \text{ kg}}{8.92 \times 10^3 \text{ kg/m}^3} \right) (50\text{°C} - 20\text{°C}) \\ &= -1.7 \times 10^{-2} \text{ J} \end{aligned}$$

Because this work is negative, work is done by the copper bar on the atmosphere.

(B) How much energy is transferred to the copper bar by heat?

$$\begin{aligned} Q &= mc \Delta T = (1.0 \text{ kg})(387 \text{ J/kg} \cdot \text{°C})(50\text{°C} - 20\text{°C}) \\ &= 1.2 \times 10^4 \text{ J} \end{aligned}$$

(C) What is the increase in internal energy of the copper bar?

$$\begin{aligned} \Delta E_{\text{int}} &= Q + W = 1.2 \times 10^4 \text{ J} + (-1.7 \times 10^{-2} \text{ J}) \\ &= 1.2 \times 10^4 \text{ J} \end{aligned}$$

- Most of the energy transferred into the system by heat goes into **increasing the internal energy** of the copper bar.
- Hence, when the thermal expansion of a solid or a liquid is analyzed, the small amount of work done on or by the system is usually **ignored**.

## Example 4

An ideal gas initially at 300 K undergoes an isobaric expansion at 2.50 kPa. If the volume increases from 1.00 m<sup>3</sup> to 3.00 m<sup>3</sup> and 12.5 kJ is transferred to the gas by heat, what are (a) the change in its internal energy and (b) its final temperature?

(A) the change in its internal energy

$$\Delta E_{int} = Q + W$$

$$W = -P\Delta V \quad \text{for a constant-pressure process}$$

$$\therefore \Delta E_{int} = Q - P\Delta V$$

$$\Delta E = 12.5 \times 10^3 J - (2.50 \times 10^3 N/m^2)(3.00 m^3 - 1.00 m^3) = 7500 J$$

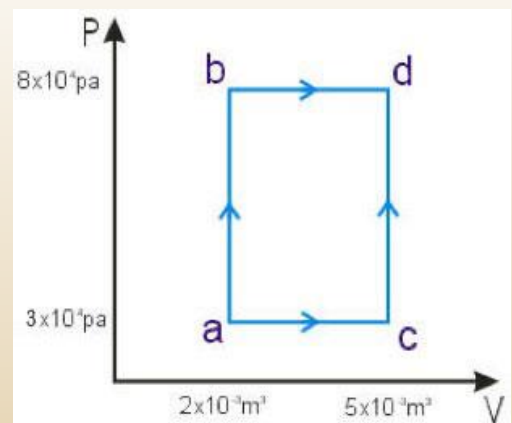
(B) Since pressure and quantity of gas are constant, we have from the ideal gas equation

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \rightarrow T_2 = \left(\frac{V_2}{V_1}\right)T_1 \rightarrow T_2 = \left(\frac{3.00 m^3}{1.00 m^3}\right)300 K = 900 K$$

## Example 5

A thermodynamic process is shown in Figure. In process ab, 600J of heat are added, and in process bd 200J of heat are added. Find

- the internal energy change in process ab
- the internal energy change in process abd
- the total heat added in process acd



## Example 5 solution

(a) in ab  $W = 0$  (لأنه على هذا المسار الحجم ثابت) and  $\Delta E_{\text{int}(ab)} = Q = 600\text{J}$

(b) in bd pressure is constant

$$W = -P(V_2 - V_1) = -[8 \times 10^4 \times (5 \times 10^{-3} - 2 \times 10^{-3})] = -240\text{J}$$

$$W_{\text{abd}} = -240 + 0 = -240\text{J}$$

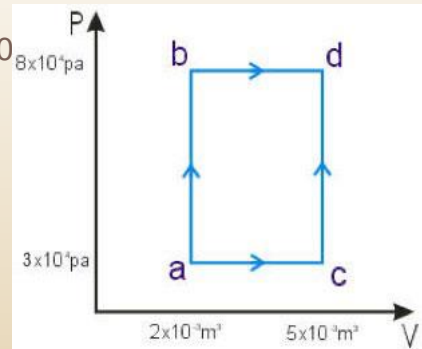
$$Q_{\text{abd}} = 600 + 200 = 800\text{J}$$

$$\Delta E_{\text{int}(abd)} = 800 + (-240) = 560\text{J}$$

(c) in acd  $\Delta E_{\text{int}(acd)} = 560\text{J}$  as well!

$$W_{\text{acd}} = -[3 \times 10^4 \times (5 \times 10^{-3} - 2 \times 10^{-3})] = -90\text{J}$$

$$Q_{\text{acd}} = \Delta E_{\text{int}(acd)} - W = 560 - (-90) = 650\text{J}$$



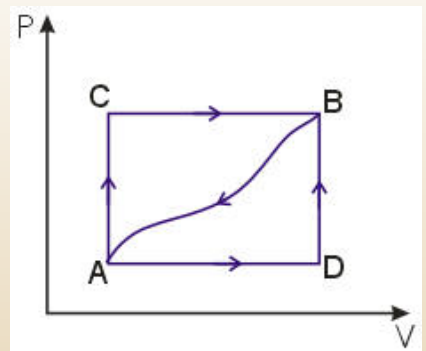
## Example 6

When a system is taken from state A to state B along the path ACB, **80J** of heat flow into the system and the system does **30J** of work,

(a) How much heat flow into the system along the path ADB if the work done by the system is 10J.

(b) The system is returned from the state B to A along the curved path. the work done on the system is 20J

(c) If  $E_{\text{int}A}=0$ ,  $E_{\text{int}D}=40\text{J}$ , find the heat absorbed in the process AD and DB.



## Example 6 solution

(a) How much heat flow into the system along the path ADB if the work done is 10J.

$$\therefore \Delta E_{\text{int}}(\text{ACB}) = \Delta E_{\text{int}}(\text{ADB})$$

Along the path ACB

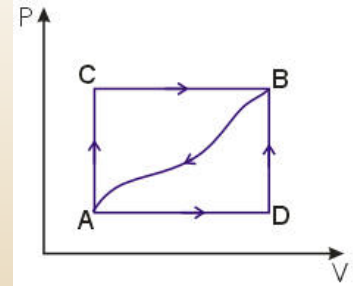
$$\begin{aligned}\Delta E_{\text{int}}(\text{ACB}) &= Q_{\text{ACB}} + W \\ &= 80 + (-30) = 50\text{J}\end{aligned}$$

$$\text{Hence } \Delta E_{\text{int}}(\text{ACB}) = \Delta E_{\text{int}}(\text{ADB}) = Q_{\text{ADB}} + W = 50\text{J}$$

$$Q_{\text{ADB}} = 50\text{J} - W$$

$$Q_{\text{ADB}} = 50 - (-10) = 60\text{J}$$

(Note: the negative sign for the work because work done by the system.)



(b) The system is returned from the state B to A along the curved path. the work done on the system is 20J

$$W = +20 \quad (\text{شغل خارجي بذل على النظام})$$

$$Q = \Delta E_{\text{int}}(\text{BA}) - W$$

$$= -50 - 20 = -70\text{J}$$

(The negative sign show that heat is liberated by the system)

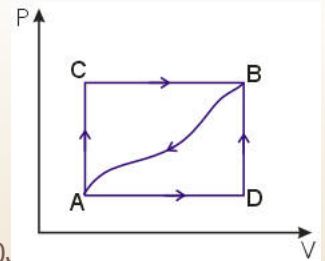
(c)  $E_{\text{intA}} = 0$  &  $E_{\text{intD}} = 40\text{J}$  &  $\Delta E_{\text{int}}(\text{AB}) = 50\text{J}$  then  $E_{\text{intB}} = 50$ .

$$Q_{\text{AD}} = (E_{\text{intD}} - E_{\text{intA}}) - W$$

In the process ADB, 10J of work is done = work done from A to D is 10J and from D to B is zero (at constant volume)

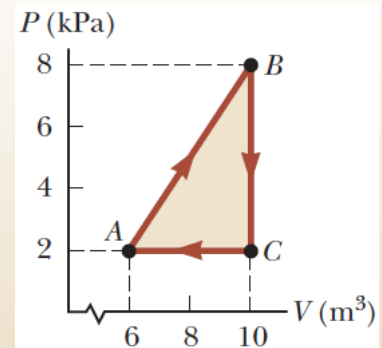
$$\text{for AD} \quad Q_{\text{AD}} = (40 - 0) - (-10) = 50\text{J}$$

$$\begin{aligned}\text{for DB} \quad Q_{\text{DB}} &= (E_{\text{intB}} - E_{\text{intD}}) - W \\ &= (50 - 40) - 0 = 10\text{J}\end{aligned}$$

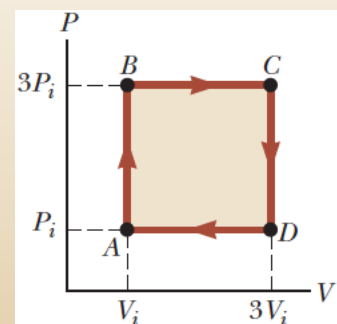


## Problem to solve by yourself

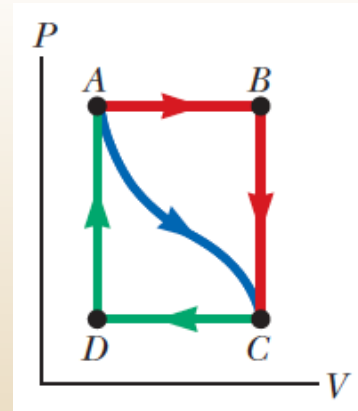
1. A gas is taken through the cyclic process described in the Figure. (a) Find the net energy transferred to the system by heat during one complete cycle. (b) **What If?** If the cycle is reversed—that is, the process follows the path *ACBA*—what is the net energy input per cycle by heat?
2. A 1.00-kg block of aluminum is warmed at atmospheric pressure so that its temperature increases from 22.0°C to 40.0°C. Find (a) the work done on the aluminum, (b) the energy added to it by heat, and (c) the change in its internal energy.



3. (a) How much work is done on the steam when 1.00 mol of water at 100°C boils and becomes 1.00 mol of steam at 100°C at 1.00 atm pressure? Assume the steam to behave as an ideal gas. (b) Determine the change in internal energy of the system of the water and steam as the water vaporizes.
4. One mole of an ideal gas does 3000 J of work on its surroundings as it expands isothermally to a final pressure of 1.00 atm and volume of 25.0 L. Determine (a) the initial volume and (b) the temperature of the gas.
5. An ideal gas initially at  $P_i$ ,  $V_i$ , and  $T_i$  is taken through a cycle as shown in the Figure. (a) Find the net work done on the gas per cycle for 1.00 mol of gas initially at 0°C. (b) What is the net energy added by heat to the gas per cycle?



6. In the Figure, the change in internal energy of a gas that is taken from  $A$  to  $C$  along the blue path is  $+800$  J. The work done on the gas along the red path  $ABC$  is  $-500$  J. (a) How much energy must be added to the system by heat as it goes from  $A$  through  $B$  to  $C$ ? (b) If the pressure at point  $A$  is five times that of point  $C$ , what is the work done on the system in going from  $C$  to  $D$ ? (c) What is the energy exchanged with the surroundings by heat as the gas goes from  $C$  to  $A$  along the green path? (d) If the change in internal energy in going from point  $D$  to point  $A$  is  $+500$  J, how much energy must be added to the system by heat as it goes from point  $C$  to point  $D$ ?



## إلى اللقاء مع المحاضرة (١٠)

## *Energy Transfer Mechanisms in Thermal Processes*

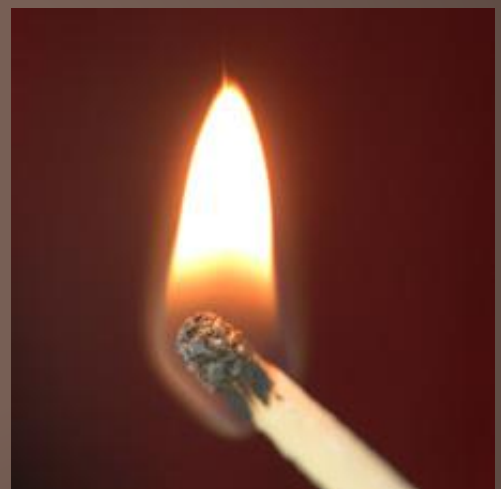


## Unit 2: Heat and the first law of thermodynamics

### Lecture 10: Energy Transfer Mechanisms in Thermal Processes

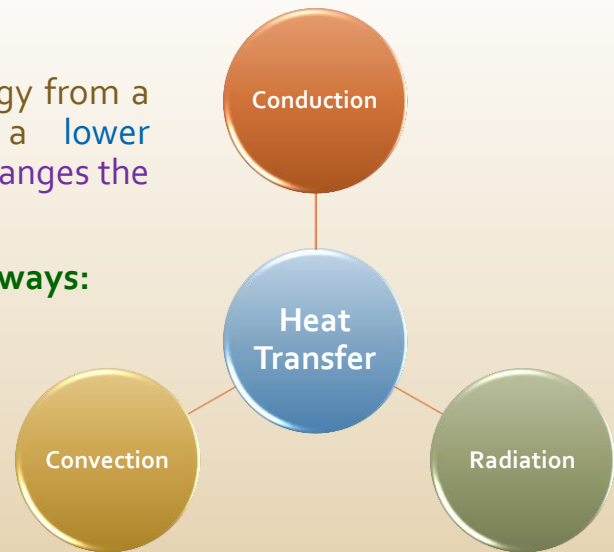
## Unit 2: Heat and the first law of thermodynamics

- ❑ Heat and Internal Energy
- ❑ Specific Heat and Calorimetry
- ❑ Latent Heat
- ❑ Work and Heat in Thermodynamic Processes
- ❑ The First Law of Thermodynamics
- ❑ Some Applications of the First Law of Thermodynamics
- ❑ **Energy Transfer Mechanisms in Thermal Processes**



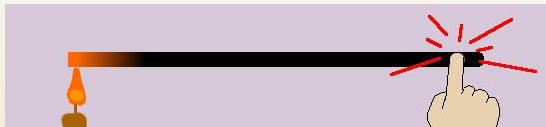
# Heat Transfer

- The heat is a transfer of the energy from a **high temperature** object to a **lower temperature** one. Heat transfer changes the internal energy of both systems
- **Heat can be transferred by three ways:**



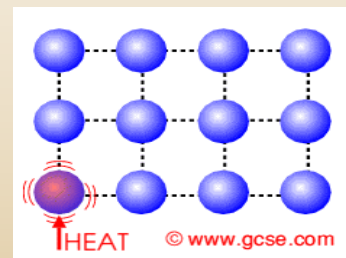
## Heat conduction

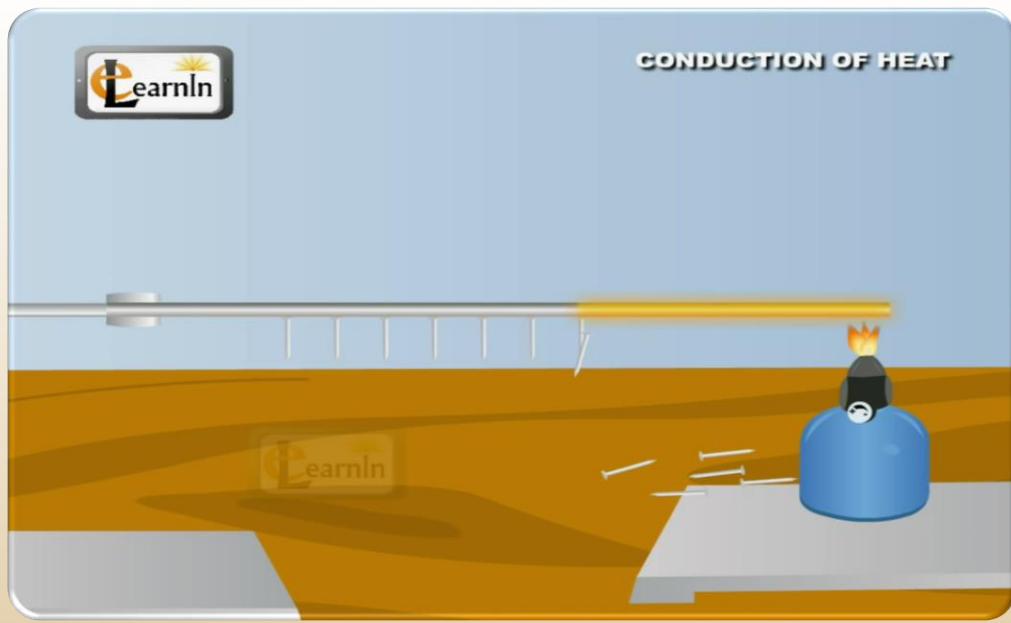
Conduction is heat transfer by means of molecular agitation within a material without any motion of the material as a whole.



**Conduction** is the transfer of heat within a substance, molecule by molecule.

If you put one end of a metal rod over a fire, that end will absorb the energy from the flame. The molecules at this end of the rod will gain energy and begin to vibrate faster. As they do their temperature increases and they begin to bump into the molecules next to them. The heat is being transferred from the warm end to the cold end.

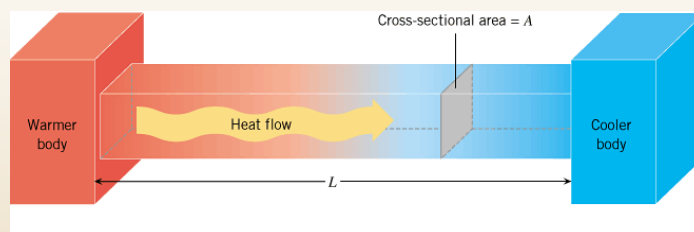


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## Heat conduction

Conduction – when two objects are in physical contact.



$$H = \frac{Q}{t} = kA \left( \frac{\Delta T}{L} \right)$$

$H$  = rate of conduction heat transfer (Watt)

$k$  = thermal conductivity (W/m.K)

$Q$  = heat transferred

$A$  = cross sectional area

$t$  = duration of heat transfer

$L$  = length

$\Delta T$  = temperature difference between two ends

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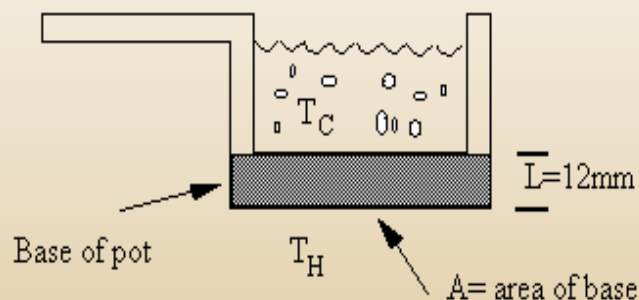
## The thermal conductivity coefficient

Substance	(W m <sup>-1</sup> K <sup>-1</sup> )	Substance	(W m <sup>-1</sup> K <sup>-1</sup> )
Silver	427	Ice	2
Copper	397	Water	0.6
Aluminum	238	Wood	0.08
Gold	314	Air	0.023
Concrete	0.8	Hydrogen	0.1
Glass	0.8	Helium	0.138

Why metals are good conductors? Find the answer in your reference book!

## Example 1

An aluminum pot contains water that is kept steadily boiling (100°C). The bottom surface of the pot, which is 12 mm thick and  $1.5 \times 10^4 \text{ mm}^2$  in area, is maintained at a temperature of 102°C by an electric heating unit. Find the rate at which heat is transferred through the bottom surface. Compare this with a copper based pot.



## Solution

$$H = kA \left( \frac{\Delta T}{L} \right)$$

- For the aluminum base:  $T_H = 102^\circ\text{C}$ ,  $T_C = 100^\circ\text{C}$ ,  $L = 12\text{ mm} = 0.012\text{ m}$ ,  $K_{Al} = 238\text{ Wm}^{-1}\text{K}^{-1}$ , Base area  $A = 1.5 \times 10^4\text{ mm}^2 = 0.015\text{ m}^2$ .

$$H_{Al} = 238 (0.015) \frac{(102 - 100)}{0.012} = 588\text{ W}$$

- For the copper base  $K_{Cu} = 397\text{ Wm}^{-1}\text{K}^{-1}$ .

$$H_{Cu} = 397 (0.015) \frac{(102 - 100)}{0.012} = 1003\text{ W}$$

## Heat Convection

- Convection is heat transfer by mass motion of a fluid such as air or water when the heated fluid is caused to move away from the source of heat, carrying energy with it.
- Convection above a hot surface occurs because hot air expands, becomes less dense, and rises. Hot water is likewise less dense than cold water and rises, causing convection currents which transport energy.

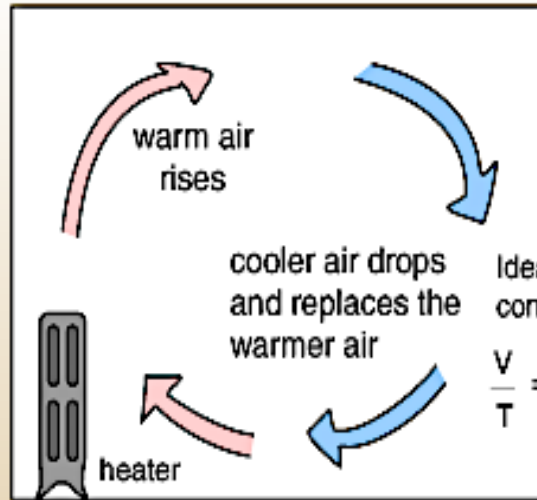


If volume increases,  
then density decreases,  
making it buoyant.

$$\rho = \frac{m}{V}$$

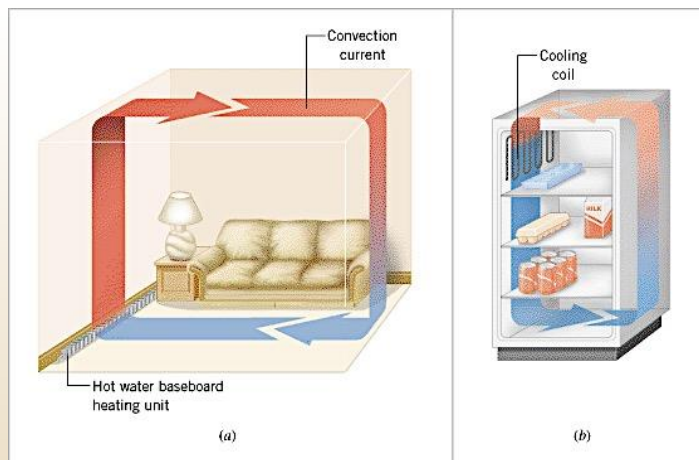
$$\frac{V}{T} = \text{constant}$$

If the temperature  
of a given mass of  
air increases, the  
volume must increase  
by the same factor.



Ideal gas law for  
constant pressure

$$\frac{V}{T} = \frac{nR}{P} = \text{constant}$$



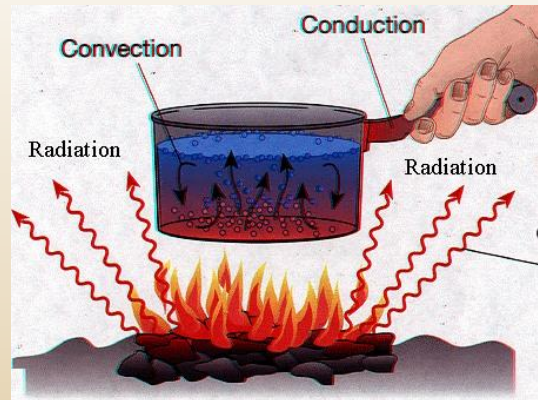
**Q:** In the living room, the heating unit is placed in the floor but the refrigerator has a top-mounted cooling coil. Why?

**A:** Air warmed by the baseboard heating unit is pushed to the top of the room by the cooler and denser air. Air cooled by the cooling coil sinks to the bottom of the refrigerator.

# Heat Radiation

- Energy is transferred by electromagnetic radiation. All of the earth's energy is transferred from the Sun by radiation.

- Our bodies radiate electromagnetic waves in a part of the spectrum that we can't see called the infra-red. However, there are some cameras that can actually see this radiation.

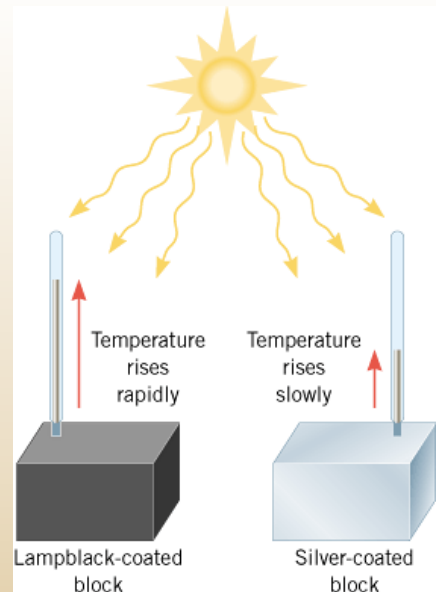


# Heat Radiation

- The color and texture of different surfaces determines how well they absorb the radiation.

(1) Black objects absorb more radiation than white objects.

(2) Matt and rough surfaces absorb more than shiny and smooth surfaces.



## Heat Radiation

The relationship governing radiation from hot objects is called the **Stefan-Boltzmann Law**:

$$P = e \sigma A (T^4 - T_s^4)$$

**P** is the net radiated power measured in Watt,

**e** is the emissivity (=1 for ideal radiator),

**A** is the radiation area in m<sup>2</sup>,

**T** is the temperature of the radiator in Kelvin,

**T<sub>s</sub>** is the temperature of the surroundings in Kelvin,

$\sigma = 5.67 \times 10^{-8} \text{ Watt/m}^2 \text{ K}^4$  is a constant called Stefan-Boltzmann constant.

## Example 2

- A student tries to decide what to wear is staying in a room that is at 20°C. If the skin temperature is 37°C, how much heat is lost from the body in 10 minutes? Assume that the emissivity of the body is 0.9 and the surface area of the student is 1.5 m<sup>2</sup>.

### Solution

- Using the Stefan-Boltzmann's law

$$P_{net} = e \sigma A (T^4 - T_s^4) = (5.67 \times 10^{-8})(0.9)(1.5)(310^4 - 293^4) = 143 \text{ watt}.$$

- The total energy lost during 10 min is

$$Q = P_{net} \Delta t = 143 \times 600 = 85.8 \text{ kJ}$$

## Problem to solve by yourself

1. A glass windowpane in a home is 0.620 cm thick and has dimensions of 1.00 m  $\times$  2.00 m. On a certain day, the temperature of the interior surface of the glass is 25.0°C and the exterior surface temperature is 0°C. (a) What is the rate at which energy is transferred by heat through the glass? (b) How much energy is transferred through the window in one day, assuming the temperatures on the surfaces remain constant?
2. The surface of the Sun has a temperature of about 5 800 K. The radius of the Sun is  $6.96 \times 10^8$  m. Calculate the total energy radiated by the Sun each second. Assume the emissivity of the Sun is 0.986.

إلى اللقاء مع المحاضرة (١١)

***The kinetic theory of gases***



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# Thermodynamics

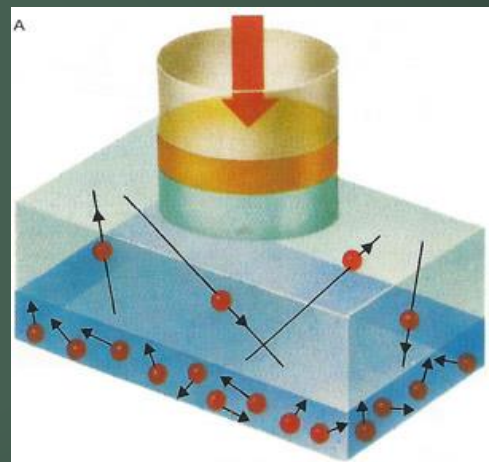
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Al-Azhar University - Gaza

## Unit 3: The kinetic theory of gases and the Equation of state

### Lecture 11: Molecular Model of an Ideal Gas

## Unit 3: The kinetic theory of gases and the Equation of state

- ❑ **Molecular Model of an Ideal Gas**
  - ❑ Pressure and Kinetic Energy
  - ❑ Molecular Interpretation of Temperature
- ❑ Equation of state of an ideal and real gas
  - ❑ Molar Specific Heat of an Ideal Gas
  - ❑ Adiabatic Processes for an Ideal Gas
- ❑ PVT surfaces for an ideal and real gas
- ❑ Phase diagrams, Triple point, critical point and Vapor pressure.



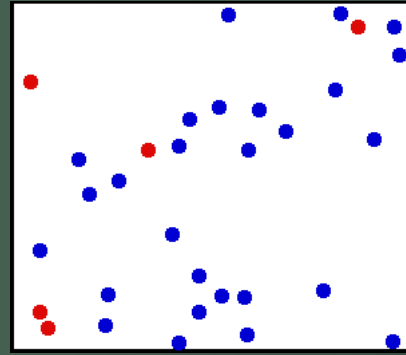
## Macroscopic vs. Macroscopic Descriptions

- So far we have dealt with **macroscopic variables**:
  - Pressure
  - Volume
  - Temperature
- These can be related to a description on a **microscopic level**.
  - Matter is treated as a collection of molecules.
  - Applying Newton's laws of motion in a statistical manner to a collection of particles provides a reasonable description of thermodynamic processes.
- **Pressure and temperature relate directly to molecular motion in a sample of gas.**

## Ideal Gas Assumptions

- ❑ The **number of molecules** in the gas is large, and the **average separation** between the molecules is large compared with their dimensions. The **molecules occupy** a negligible volume within the container.
- ❑ The **molecules obey** Newton's laws of motion, but as a whole they move randomly, i.e. any molecule can move in any direction with any speed.
- ❑ The **molecules interact** only by short-range forces during elastic collisions.
- ❑ The **molecules make** elastic collisions with the walls. **These collisions lead to the macroscopic pressure on the walls of the container.**
- ❑ The gas under consideration is a **pure substance**. i.e. all molecules are identical.

# Pressure and Kinetic Energy



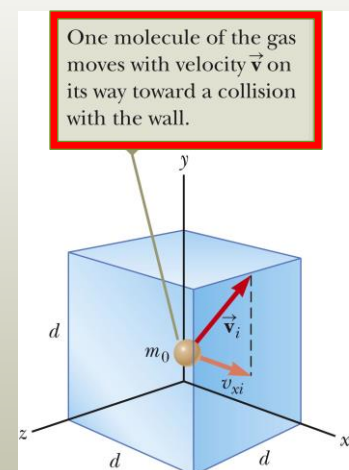
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## Pressure and Kinetic Energy

To relate the **macroscopic** variable of pressure  $P$  to **microscopic** quantities.

- Consider a collection of  $N$  molecules of an ideal gas in a container of volume  $V$ .
- Assume the container is a cube with edges are length  $d$
- Look at the motion of the molecule in terms of its velocity components.
- Look at its momentum and the average force.

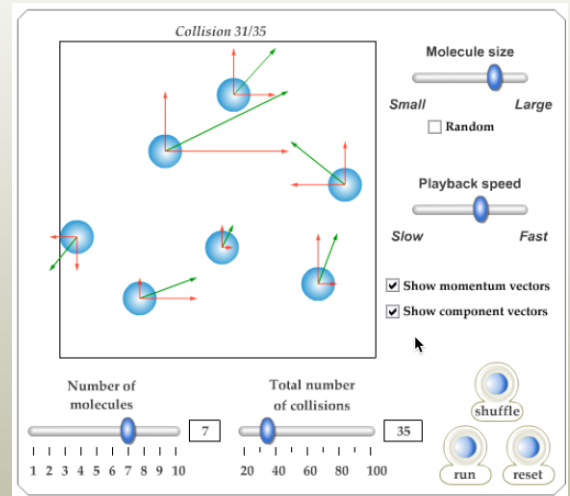


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## Pressure and Kinetic Energy, 2

- Assume perfectly **elastic collisions** with the walls of the container.
- The molecule's velocity component perpendicular to the wall is **reversed**, because the mass of the wall is much greater than the mass of the molecule.
- The molecule is modeled as a non-isolated system for which the **impulse from the wall causes a change in the molecule's momentum**.



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## Pressure and Kinetic Energy, 3

- The momentum component  $p_{xi}$  of the molecule is  $m_0 v_{xi}$  before the collision and  $-m_0 v_{xi}$  after the collision, the change in the x component of the momentum of the molecule is

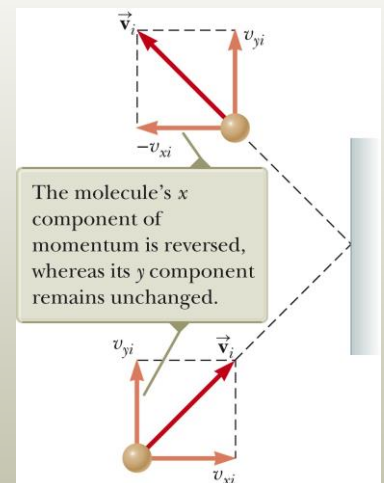
$$\Delta p_{xi} = -m_0 v_{xi} - (m_0 v_{xi}) = -2m_0 v_{xi}$$

- Because the molecules obey Newton's laws, we can apply the impulse-momentum theorem

$$F = m a \rightarrow F = m \frac{\Delta v}{t} \rightarrow F t = m \Delta v$$

Impulse = Change in momentum

$$\bar{F}_i \Delta t = \Delta p_{xi} = -2m_0 v_{xi}$$



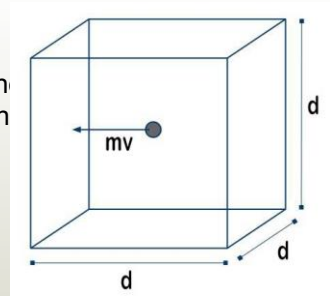
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The **time interval** between two collisions with the same wall is

$$\Delta t = \frac{2d}{v_{xi}}$$

$2d$  is the distance for the molecule to make another collision with the same wall after this first collision



The **average force** exerted **by the wall** on the molecule

$$\bar{F}_i = -\frac{2m_0 v_{xi}}{\Delta t} = -\frac{2m_0 v_{xi}^2}{2d} = -\frac{m_0 v_{xi}^2}{d}$$

The **average force** exerted **by the molecule** on the wall

$$\bar{F}_{i \text{ on wall}} = -\bar{F}_i = \frac{m_0 v_{xi}^2}{d}$$

The **total average force**  $\bar{F}$  exerted by the gas on the wall

$$\bar{F} = \sum_{i=1}^N \frac{m_0 v_{xi}^2}{d} = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$

For very large no. of molecules the **constant force**  $F$  on the wall is

$$F = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$

$$F = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$

The average of values of the square of the x component velocity  $\overline{v_x^2}$  is the sum of the  $v_{xi}^2$  over the number of molecules  $N$ :

$$\overline{v_x^2} = \frac{\sum_{i=1}^N v_{xi}^2}{N}$$

$$F = \frac{m_0}{d} N \overline{v_x^2}$$

- One molecule with velocity components  $v_{xi}$ ,  $v_{yi}$  and  $v_{zi}$ .

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2 \quad \text{and} \quad \overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

- Because the motion is completely random  $\overline{v^2} = 3\overline{v_x^2}$

$$F = \frac{1}{3} N \frac{m_0 \overline{v^2}}{d}$$

- The total pressure exerted on the wall of the container.

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3}N \frac{m_0 \overline{v^2}}{d^3} = \frac{1}{3} \left( \frac{N}{V} \right) m_0 \overline{v^2}$$

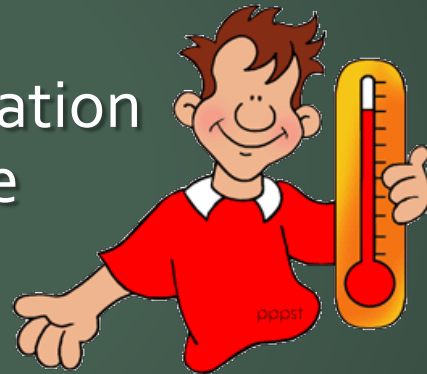
- The relationship is

$$P = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m_0 \overline{v^2} \right)$$

- This equation also relates the macroscopic quantity of pressure with a microscopic quantity of the average value of the square of the molecular speed.
- This equation tells us that **pressure is proportional to** :
  - the number of molecules per unit volume ( $N/V$ )
  - the average translational kinetic energy of the molecules



## Molecular Interpretation of Temperature



## Molecular Interpretation of Temperature

- We can take the **pressure** as it relates to the **kinetic energy** and compare it to the pressure from the **equation of state** for an ideal gas.

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right) = Nk_B T$$

- Therefore, the temperature is a direct measure of the **average molecular kinetic energy**

$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_B T$$

- Simplifying the equation relating temperature and kinetic energy gives

$$T = \frac{2}{3k_B}(\frac{1}{2}m_0\overline{v^2})$$

## Molecular Interpretation of Temperature

- This can be applied to each direction,

$$\frac{1}{2}m_0\overline{v_x^2} = \frac{1}{2}k_B T$$

$$\frac{1}{2}m_0\overline{v_y^2} = \frac{1}{2}k_B T$$

$$\frac{1}{2}m_0\overline{v_z^2} = \frac{1}{2}k_B T$$

- Each translational degree of freedom contributes an equal amount to the energy of the gas,  $\frac{1}{2} k_B T$ .
- A generalization of this result is called the **theorem of equipartition of energy**

**theorem of equipartition of energy:** Each degree of freedom contributes  $\frac{1}{2}k_B T$  to the energy of a system, where possible degrees of freedom are those associated with translation, rotation and vibration of molecules.

## Total Kinetic Energy

- The total kinetic energy is just  $N$  times the kinetic energy of each molecule.

$$K_{\text{tot trans}} = N \left( \frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

- If we have a gas with only translational energy, this is the internal energy of the gas.
- This tells us that the internal energy of an ideal gas depends only on the temperature.

## Root Mean Square Speed

- The **root mean square** (rms) speed is the square root of the average of the squares of the speeds ( $\overline{v_x^2}$ ).

$$\therefore \frac{1}{2} m_o \overline{v^2} = \frac{3}{2} k_B T \qquad \therefore \overline{v^2} = \frac{3 k_B T}{m_o}$$

- Solving for  $v_{\text{rms}}$  we find

$$v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m_o}} = \sqrt{\frac{3 R T}{M}} \qquad M \text{ is the molar mass and } M = m_o N_A$$

- At a given temperature, lighter molecules move faster than do heavier molecules.
- For example, hydrogen molecules, whose molar mass is  $2.02 \times 10^{-3}$  kg/mol, have an average speed four times that of oxygen molecules, whose molar mass is  $32.0 \times 10^{-3}$  kg/mol.

## Some Example $v_{\text{rms}}$ Values

**TABLE 21.1** *Some Root-Mean-Square (rms) Speeds*

Gas	Molar Mass (g/mol)	$v_{\text{rms}}$ at 20°C (m/s)	Gas	Molar Mass (g/mol)	$v_{\text{rms}}$ at 20°C (m/s)
H <sub>2</sub>	2.02	1902	NO	30.0	494
He	4.00	1352	O <sub>2</sub>	32.0	478
H <sub>2</sub> O	18.0	637	CO <sub>2</sub>	44.0	408
Ne	20.2	602	SO <sub>2</sub>	64.1	338
N <sub>2</sub> or CO	28.0	511			

## Example 1

- A tank used for filling helium balloons has a volume of 0.300 m<sup>3</sup> and contains 2.00 mol of helium gas at 20.0°C. Assume the helium behaves like an ideal gas.
- (A) What is the **total translational kinetic energy** of the gas molecules?

$$\begin{aligned}
 K_{\text{tot trans}} &= \frac{3}{2}nRT = \frac{3}{2}(2.00 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(293 \text{ K}) \\
 &= 7.30 \times 10^3 \text{ J}
 \end{aligned}$$

- (B) What is the **average kinetic energy per molecule**?

$$\begin{aligned}
 \frac{1}{2}m_0v^2 &= \frac{3}{2}k_{\text{B}}T = \frac{3}{2}(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) \\
 &= 6.07 \times 10^{-21} \text{ J}
 \end{aligned}$$

## Quiz

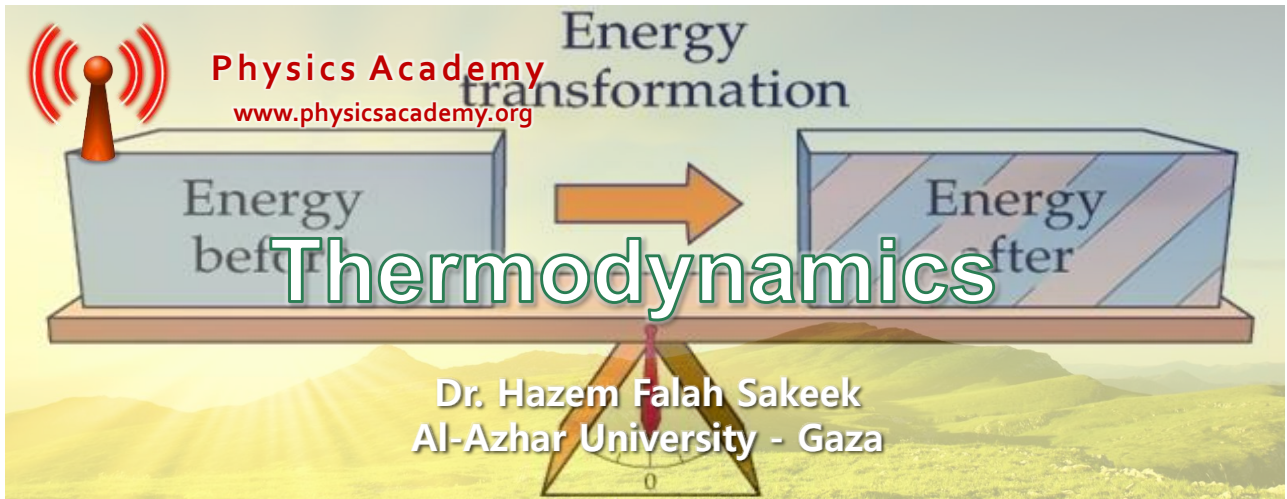
- Two containers hold an ideal gas at the same temperature and pressure. Both containers hold the same type of gas, but container B has twice the volume of container A.
- (i) What is the **average translational kinetic energy per molecule** in container B?
  - (a) twice that of container A
  - (b) the same as that of container A
  - (c) half that of container A
  - (d) impossible to determine
- (ii) From the same choices, describe **the internal energy** of the gas in container B.

## Problem to solve by yourself

1. A cylinder contains a mixture of helium and argon gas in equilibrium at 150°C. (a) What is the average kinetic energy for each type of gas molecule? (b) What is the rms speed of each type of molecule?
2. A spherical balloon of volume  $4.00 \times 10^3 \text{ cm}^3$  contains helium at a pressure of  $1.20 \times 10^5 \text{ Pa}$ . How many moles of helium are in the balloon if the average kinetic energy of the helium atoms is  $3.60 \times 10^{-22} \text{ J}$ ?
3. (a) How many atoms of helium gas fill a spherical balloon of diameter 30.0 cm at 20.0°C and 1.00 atm? (b) What is the average kinetic energy of the helium atoms? (c) What is the rms speed of the helium atoms?
4. The rms speed of an oxygen molecule ( $\text{O}_2$ ) in a container of oxygen gas is 625 m/s. What is the temperature of the gas?

إلى اللقاء مع المحاضرة (١٢)

***Equation of state of an ideal  
and real gas***

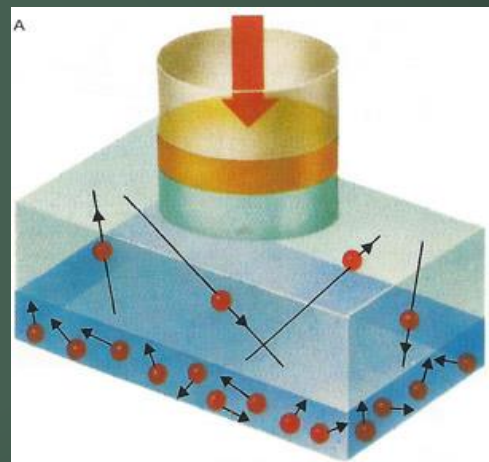


## Unit 3: The kinetic theory of gases and the Equation of state

### Lecture 12: Equation of state and Molar Specific Heat of an Ideal Gas

## Unit 3: The kinetic theory of gases and the Equation of state

- ❑ **Molecular Model of an Ideal Gas**
  - ❑ Pressure and Kinetic Energy
  - ❑ Molecular Interpretation of Temperature
- ❑ **Equation of state of an ideal and real gas**
  - ❑ Molar Specific Heat of an Ideal Gas
  - ❑ Adiabatic Processes for an Ideal Gas
- ❑ **PVT surfaces for a an ideal and real gas**
- ❑ **Phase diagrams, Triple point, critical point and Vapor pressure.**



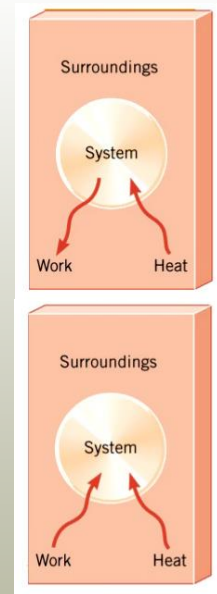
## Summary

**Heat,  $Q$**  Is an amount of energy that is supplied to or removed from a system. This will lead to a change in one or more of the thermodynamic parameters of the system e.g. the temperature,  $T$ , the volume,  $V$ , the pressure,  $P$ .

**Work,  $W$**  When a system has work done on it, or if it does work itself, then there is a flow of energy either into or out of the system. This will also lead to a change in one or more of the thermodynamics parameters of the system in the same way that gaining or losing heat,  $Q$ .

**Internal energy,  $E_{\text{int}}$**  The internal energy of a system is a measure of the total energy of the system. However, this is not possible, what we can do is to measure a change in the internal energy by recording the amount of energy either entering or leaving a system.

$$\Delta E_{\text{int}} = Q + W$$



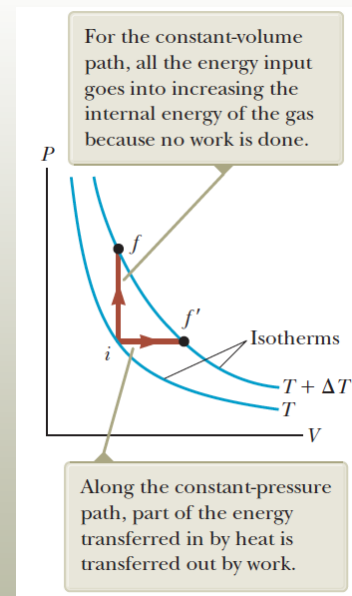
## Molar Specific Heat of an Ideal Gas

- The energy required to raise the temperature of one mole of gas from  $i$  to  $f$  depends on the path taken between the initial and final states.
- The PV diagram showing an **isovolumetric process** and an **isobaric process** that connect the same two isotherms.
- The energy transfer for the two processes can be written as

$$Q = nC_V \Delta T \text{ (constant volume)}$$

$$Q = nC_P \Delta T \text{ (constant pressure)}$$

where is  $C_V$  the molar specific heat at constant volume and  $C_P$  is the molar specific heat at constant pressure.



## Equation of state

- A thermodynamic system is one which can be described in terms of the thermodynamic co-ordinates. The co-ordinates of a thermodynamic system can be specified by **any pair** of quantities such as, **pressure (P), volume (V), temperature (f)**.

- The internal energy of a system is a single valued function of the state variable  $P, V, T$ .

$$E = f(P, V, T)$$

- We can define the state of a gas using any two of the variables  $P, V, T$ .

$$E = f(P, V) \text{ or } E = f(V, T) \text{ or } E = f(P, T)$$

في هذه المحاضرة سوف نكتفي بإيجاد معادلة الطاقة من خلال الدالة (T,V) لنحصل على بعض المفاهيم الأساسية في علم الديناميكا الحرارية، كما يمكنك عزيزي الطالب ان تدرس علاقة معادلة الطاقة مع اي متغيرين اخرين وذلك بنفس الفكرة التي سيتم شرحها. وستجد سؤال حول هذا الموضوع في نهاية المحاضرة.

## T and, V Independent (Specific Heat of a Gas)

If T and V are chosen to be independent variables then,

$$E = f(V, T) \quad (1)$$

Differentiating the equation we get

$$dE = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV \quad (2)$$

If an amount of heat  $dQ$  is supplied to a thermodynamical system, say an ideal gas and if the volume increased by  $dV$  at a constant pressure  $P$ , then according to the first law of thermodynamics  $dE = dQ + dW$

$$dQ = dE - dW \quad \text{and} \quad dW = -PdV$$

$$dQ = dE + PdV$$

$$dQ = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV + PdV \quad (3)$$

Dividing equation (3) by  $dT$

$$\frac{dQ}{dT} = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \frac{dV}{dT} + P \frac{dV}{dT}$$

$$\frac{dQ}{dT} = \left(\frac{\partial E}{\partial T}\right)_V + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \frac{dV}{dT} \quad (4)$$

From equation (4) we can conclude the following:

**Special case (1) Isochoric (isovolumetric ) process:** when the system heated at constant volume

In this case  $dV = 0$  then equation (4) become

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V = C_V \quad (5)$$

وهذا يضيف مفهوم جديد للسعة الحرارية التي عرفت سابقاً على أنها مقدار كمية الحرارة اللازمة لرفع درجة حرارة المادة درجة مئوية أو أنها التغير في كمية الحرارة بالنسبة لدرجة الحرارة عند ثبات الحجم. ومن معادلة الطاقة نجد ان السعة الحرارية عند ثبات الحجم تساوي التغير في الطاقة الداخلية للمادة بالنسبة للتغير في درجة الحرارة.

**Special case (2) Isobaric process:** when the system heated at constant pressure

In this case  $dP = 0$  then equation (4) become

$$\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \frac{dV}{dT} \quad (4)$$

$$\left(\frac{dQ}{dT}\right)_P = C_P \quad \text{And from equation (5)} \quad \left(\frac{\partial E}{\partial T}\right)_V = C_V$$

$$C_P = C_V + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \frac{dV}{dT}$$

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \frac{dV}{dT} \quad (6)$$

نلاحظ أن كل الكميات في الطرف الأيمن من المعادلة (6) تحسب من معادلة الحالة، والكميات في الطرف الأيسر يمكن إيجادها عملياً (بالتجربة)

لنطبق المعادلة (6) على غاز مثالي معزول Isolated Ideal Gas بحيث ان التغير في كمية الحرارة والشغل يساويان صفر وبالتالي التغير في الطاقة الداخلية يساوي صفر. اي ان

$$dW = 0 \text{ \& } dQ = 0, \text{ therefore } dE = 0$$

$$C_P - C_V = \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] \frac{dV}{dT} \quad (6)$$

وبالتالي فان الحد  $\left( \frac{\partial E}{\partial V} \right)_T$  في المعادلة (6) يصبح مساويا للصفر وتصبح معادلة (6) على النحو التالي:

$$C_P - C_V = P \left( \frac{dV}{dT} \right)_P \quad (7)$$

الطرف الأيمن من المعادلة هو الثابت العام للغازات  $R$  ويمكن التحقق من ذلك من خلال معادلة الحالة للغاز المثالي اذ نحصل على العلاقة الهامة التالية:

$$C_P - C_V = R$$

أي أن الفرق بين السعة الحرارية عند ثبوت الضغط والسعة الحرارية عند ثبوت الحجم يساوي مقدار ثابت وهو الثابت العام للغازات  $R$ . حيث ان  $R$  مقدار موجب فاننا نستنتج ان  $C_P$  اكبر من  $C_V$  لاي غاز مثالي.

### Special case (3) Isothermal process: when the system heated at constant temperature

علمنا سابقاً أن العملية التي تتم عند ثبوت درجة الحرارة مع وجود تسخين هي تلك العمليات التي تحدث عن تحول المادة من صورة إلى أخرى مثل تحول الصلب إلى سائل أو تحول السائل إلى بخار، وهنا تكون درجة الحرارة ثابتة بالرغم من قيامنا بتزويد حرارة للنظام. ولفهم ماذا يحدث للطاقة الداخلية سنعوض في المعادلة (3) عن  $dT = 0$  لنحصل على ما يلي:

$$dQ = \left( \frac{\partial E}{\partial T} \right)_V dT + \left( \frac{\partial E}{\partial V} \right)_T dV + P dV \quad (3)$$

$$dQ = \left[ \left( \frac{\partial E}{\partial V} \right)_T + P \right] dV \quad (8)$$

- هذا يوضح أن التغير في كمية الحرارة  $dQ$  في حالة ثبوت درجة الحرارة فإن جزء من كمية الحرارة يعمل على **زيادة الطاقة الداخلية** للمادة المتحولة بالنسبة للحجم والجزء الآخر من كمية الحرارة **يبذل شغل** وهذا الشغل بالتأكيد لزيادة المسافة بين جزيئات المادة ولهذا السبب لا يطرأ زيادة في درجة الحرارة.
- كما أن المعادلة لا نحتاج إلى تعريف السعة الحرارية عند ثبوت درجة الحرارة لأنها تساوي مالانهاية أي أن النظام في حالة ثبوت درجة الحرارة يتصرف كما لو كانت سعته الحرارية لا نهائية لان اي كمية حرارة تزود إلى النظام لن تؤدي إلى رفع درجة حرارته.

### Special case (4) Adiabatic process: when $dQ = 0$

العملية الأديباتيكية هي التي تتم عند ثبوت كمية الحرارة وتحدث لنظام معزول فلا يمكن ان تتسرب الحرارة منه او إليه وبالتالي نقول أن  $dQ = 0$  وبالتعويض عن ذلك في المعادلة (4) نحصل على

$$\frac{dQ}{dT} = \left(\frac{\partial E}{\partial T}\right)_V + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \frac{dV}{dT} \quad (4)$$

$$0 = C_V + \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \frac{dV}{dT}$$

$$C_V dT = - \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] dV$$

$$C_V \left(\frac{\partial T}{\partial V}\right) = - \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \quad (9)$$

من علاقة التمدد الحراري نعلم ان  $\Delta V = \beta V_i \Delta T$ ، وعليه فان معامل التمدد الحجمي عند ثبوت الضغط يعطى بالعلاقة التالية:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{therefore} \quad \beta V = \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P \quad \text{من المعادلة (6)}$$

$$\frac{C_P - C_V}{\beta V} = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \quad \text{نحصل على}$$

وفي حالة عملية تتم على غاز مثالي في نظام معزول يكون التغير في الطاقة الداخلية بالنسبة للحجم عند ثبوت درجة الحرارة يساوي صفر اي ان  $\left(\frac{\partial E}{\partial V}\right)_T = 0$

وبالتالي نحصل على العلاقة

$$\frac{C_P - C_V}{\beta V} = P$$

▪ بالتعويض في المعادلة (9) نحصل على

$$C_V \left( \frac{\partial T}{\partial V} \right) = - \left[ P + \left( \frac{\partial E}{\partial V} \right)_T \right] \quad (9)$$

$$C_V \left( \frac{\partial T}{\partial V} \right) = -P = - \left( \frac{C_P - C_V}{\beta V} \right)$$

$$\left( \frac{\partial T}{\partial V} \right) = \left( \frac{C_V - C_P}{C_V \beta V} \right)$$

▪ وهذه المعادلة متحققة للعملية الادياباتيكية.

## Experimental determination of **heat capacities**

### (1) For all gases

$C_V$  is a function of  $T$

$C_P$  is a function of  $T$

$C_P - C_V = \text{Constant} = R$

$\gamma = C_P/C_V$  is a function of  $T$  and  $\gamma > 1$

### (2) For mono-atomic gases (He, Ne, Ar, ....)

$C_V = 3/2 R$  for wide range of temperature

$C_P = 5/2 R$  for wide range of temperature

$\gamma = 5/3$  for wide range of temperature

### (3) For diatomic gases ( $H_2$ , $O_2$ , $N_2$ , $NO$ , $CO$ , Air, ....)

$C_V = 5/2 R$  for ordinary temperature and increase as the temperature raised

$C_P = 7/2 R$  for ordinary temperature and increase as the temperature raised

$\gamma = 7/5$  for ordinary temperature and decrease as the temperature raised

### (4) For polyatomic gases ( $NH_3$ , $CH_4$ , $Cl_2$ , $CO_2$ , ....)

$C_P$ ,  $C_V$  and  $\gamma$  vary with temperature and the variation being different for each gas

## Problem to solve by yourself

Using the same principle for  $E = f(T, V)$  find similar relation for

$$(1) E = f(P, V)$$

$$(2) E = f(P, T)$$

using partial differential equation. Hint: use the coefficient of compressibility ( $k$ ) at constant pressure

$$k = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

إلى اللقاء مع المحاضرة (١٣)

***Adiabatic Processes  
for an Ideal Gas***



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# Thermodynamics

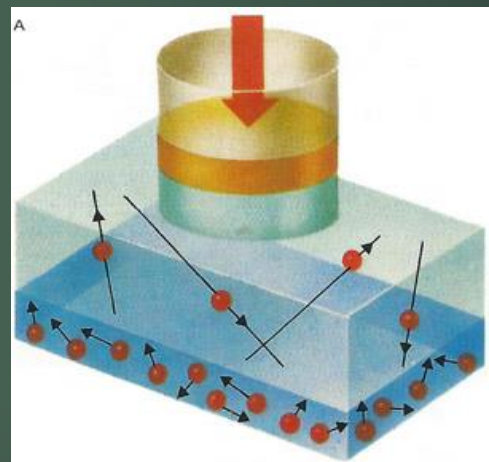
**Dr. Hazem Falah Sakeek**  
**Al-Azhar University - Gaza**

## Unit 3: The kinetic theory of gases and the Equation of state

### Lecture 13: Adiabatic Processes for an Ideal Gas

## Unit 3: The kinetic theory of gases and the Equation of state

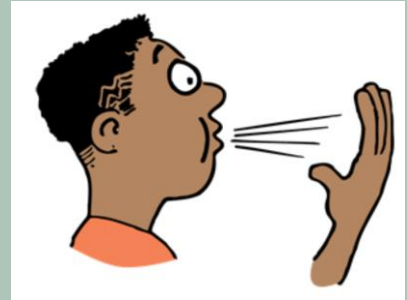
- ❑ **Molecular Model of an Ideal Gas**
  - ❑ Pressure and Kinetic Energy
  - ❑ Molecular Interpretation of Temperature
- ❑ **Equation of state of an ideal and real gas**
  - ❑ Molar Specific Heat of an Ideal Gas
  - ❑ **Adiabatic Processes for an Ideal Gas**
- ❑ PVT surfaces for an ideal and real gas
- ❑ Phase diagrams, Triple point, critical point and Vapor pressure.



## Adiabatic Processes for an Ideal Gas

- An adiabatic process is one in which **no energy** is **transferred** by heat between a **system** and its **surroundings**.
  - For example, if a gas is compressed (or expanded) rapidly, very little energy is transferred out of (or into) the system by heat, so the process is nearly adiabatic.
  - Another example of an adiabatic process is the slow expansion of a gas that is thermally insulated from its surroundings.
- All three variables in the ideal gas law ( $P$ ,  $V$ ,  $T$ ) can change during an adiabatic process.
- Assume an ideal gas is in an equilibrium state and so  $PV = nRT$  is valid.

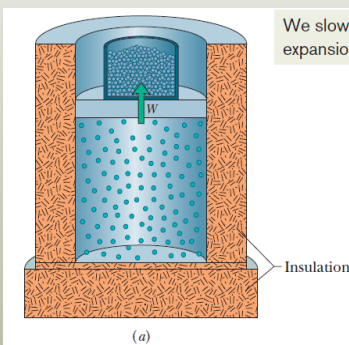
عندما يتمدد الغاز اديباتيكيًا فإنه يبذل شغلاً على المحيط ويعطي طاقة داخلية وبالتالي فإنه يبرد.



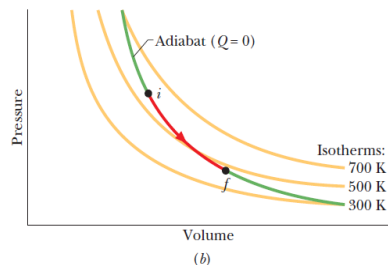
انفخ الهواء على يدك وفمك مفتوحاً وابتداً بتقليل الفتحة بشفتيك لتسمح للهواء أن يتمدد في اتجاه يدك إذا شعرت بالبرودة فهذا هو التمدد الاديباتيكي

## Gas equation during **adiabatic process**

- Let's imagine an **adiabatic gas process** involving an infinitesimal change in volume  $dV$  and an accompanying infinitesimal change in temperature  $dT$ .



We slowly remove lead shot, allowing an expansion without any heat transfer.



**Fig. 19-15** (a) The volume of an ideal gas is increased by removing mass from the piston. The process is adiabatic ( $Q = 0$ ). (b) The process proceeds from  $i$  to  $f$  along an adiabat on a  $p$ - $V$  diagram.

## Gas equation during **adiabatic process**

- From the first law of thermodynamics

$$dE = dQ + dW$$

For adiabatic process  $dQ = 0$

$$\therefore dQ = dE - dW = 0$$

Therefore

$$dE = dW$$

$$\therefore dE = C_V dT \quad \& \quad dW = -PdV$$

$$C_V dT = -PdV$$

Therefore

$$dT = \frac{-PdV}{C_V}$$

## Gas equation during **adiabatic process**

By differentiating the equation of an ideal gas  $PV = RT$  we get

$$PdV + VdP = RdT$$

$$PdV + VdP = R \frac{-PdV}{C_V}$$

$$PdV + VdP = (C_P - C_V) \frac{-PdV}{C_V}$$

$$PdV + VdP = \frac{(C_P - C_V)}{C_V} (-PdV)$$

$$PdV + VdP = -P \frac{C_P}{C_V} dV + PdV$$

$$VdP = -P \frac{C_P}{C_V} dV$$

$$\frac{dP}{P} + \frac{C_P}{C_V} \frac{dV}{V} = 0$$

$$\text{Let } \frac{C_P}{C_V} = \gamma$$

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

$$\ln P + \ln V^\gamma = \text{constant}$$

$$PV^\gamma = \text{constant}$$

وهذه معادلة الحالة للغاز المثالي في عملية اديباتيكية والتي تربط الضغط والحجم اثناء عملية اديباتيكية.

## Example 1

- Air in the cylinder of a diesel engine at 20°C is compressed **adiabatically** from an initial pressure of 1 atm and volume of 800 cm<sup>3</sup> to volume of 60 cm<sup>3</sup>. Assuming that air behaves as an ideal gas with  $\gamma=1.4$ . Find the final pressure and temperature.

$$PV^\gamma = K \quad \Rightarrow \quad P_2 V_2^\gamma = P_1 V_1^\gamma \quad \Rightarrow \quad P_2 = \frac{P_1 V_1^\gamma}{V_2^\gamma}$$

$$P_2 = 1 \text{ atm} \left( \frac{800 \text{ cm}^3}{60 \text{ cm}^3} \right)^{1.4} = 37.6 \text{ atm}$$

- From ideal gas equation  $PV = nRT$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$T_2 = \frac{P_2 V_2}{P_1 V_1} T_1 = \frac{37.6 \times 60}{1 \times 800} 293 = 826 \text{ K} = 553^\circ \text{C}$$

## The work done in adiabatic process

To find the work done during adiabatic process, we use the general equation of the work

$$W = \int P dV$$

$$PV^\gamma = K \quad \Rightarrow \quad P = \frac{K}{V^\gamma}$$

$$W = K \int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$W = K \left( \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma} \right)$$

$$PV^\gamma = K$$

$$\Rightarrow P_2 V_2^\gamma = P_1 V_1^\gamma = K$$

$$W = \frac{K V_2^{1-\gamma} - K V_1^{1-\gamma}}{1-\gamma}$$

$$W = \frac{P_2 V_2^\gamma V_2^{1-\gamma} - P_1 V_1^\gamma V_1^{1-\gamma}}{1-\gamma}$$

$$W = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

وهذه معادلة الشغل المبذول خلال عملية اديباتيكية

## Example 2

By using these relation  $PV^\gamma = K$  where  $K$  is constant, and from the ideal gas equation  $PV = nRT$  Prove that

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

### ▪ Solution

$$\text{From } P_2 V_2^\gamma = P_1 V_1^\gamma \quad \text{and} \quad P = \frac{nRT}{V}$$

$$\frac{nRT_2}{V_2} V_2^\gamma = \frac{nRT_1}{V_1} V_1^\gamma$$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

## Example 3

▪ By using these relation  $PV^\gamma = K$  where  $K$  is constant, and from the ideal gas equation  $PV = nRT$  Prove that

$$P_2^{\frac{1-\gamma}{\gamma}} T_2 = P_1^{\frac{1-\gamma}{\gamma}} T_1$$

$$P_2 V_2^\gamma = P_1 V_1^\gamma \quad V = \frac{nRT}{P}$$

$$P_2 \left( \frac{nRT_2}{P_2} \right)^\gamma = P_1 \left( \frac{nRT_1}{P_1} \right)^\gamma$$

$$P_2 \left( \frac{T_2}{P_2} \right)^\gamma = P_1 \left( \frac{T_1}{P_1} \right)^\gamma$$

$$P_2^{1-\gamma} T_2^\gamma = P_1^{1-\gamma} T_1^\gamma$$

$$\left( \frac{P_1}{P_2} \right)^{1-\gamma} = \left( \frac{T_2}{T_1} \right)^\gamma$$

$$\ln \left( \frac{P_1}{P_2} \right)^{1-\gamma} = \ln \left( \frac{T_2}{T_1} \right)^\gamma$$

$$1 - \gamma \ln \left( \frac{P_1}{P_2} \right) = \gamma \ln \left( \frac{T_2}{T_1} \right)$$

$$\frac{1-\gamma}{\gamma} \ln \left( \frac{P_1}{P_2} \right) = \ln \left( \frac{T_2}{T_1} \right)$$

$$\ln \left( \frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} = \ln \left( \frac{T_2}{T_1} \right)$$

$$\left( \frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} = \left( \frac{T_2}{T_1} \right)$$

$$P_2^{\frac{1-\gamma}{\gamma}} T_2 = P_1^{\frac{1-\gamma}{\gamma}} T_1$$

## Example 4

One gram molecule of a monoatomic ideal gas at 21°C is compressed adiabatically from an initial pressure of 1 atm to a final pressure of 50 atm. Calculate the different in temperature.

We have

$$P_1 = 1 \text{ atm}$$

$$P_2 = 50 \text{ atm}$$

$$T_1 = 273 + 27 = 300 \text{ K}$$

$$T_2 = ?$$

$$\left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}} = \left(\frac{T_2}{T_1}\right)$$

$$\gamma = \frac{5}{2} \text{ for monoatomic gas}$$

$$\left(\frac{1}{50}\right)^{\frac{1-\gamma}{\gamma}} = \left(\frac{T_2}{300}\right)$$

$$\frac{1-\gamma}{\gamma} \ln\left(\frac{1}{50}\right) = \ln\left(\frac{T_2}{300}\right)$$

$$(-0.4) \times (-3.9) = \ln T_2 - \ln 300 \quad \Rightarrow \quad 1.65 = \ln T_2 - 5.7 \quad \Rightarrow \quad \ln T_2 = 7.3 \quad \Rightarrow \quad T_2 = 1480 \text{ K}$$

## Summary

Equations for adiabatic process

$$PV^\gamma = \text{constant}$$

$$T V^{\gamma-1} = \text{constant}$$

$$P^{\frac{1-\gamma}{\gamma}} T = \text{constant}$$

$$W = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$$

Work done on isothermal process

$$W = nRT \ln \frac{V_1}{V_2}$$

## Problem to solve by yourself

- A motor car tire has a pressure of 2 atm at 27°C. If the tire suddenly bursts, find the resulting temperature.
- A quantity of air at 27°C and atmosphere pressure is suddenly compressed to half its original volume. Find the final (i) pressure and (ii) temperature.
- Air is compressed adiabatically to half of its volume. Calculate the change in its temperature.

إلى اللقاء مع المحاضرة (١٤)

***PVT surfaces for a an ideal  
and real gas***

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He Ne Ar Kr Xe Rn

# Thermodynamics

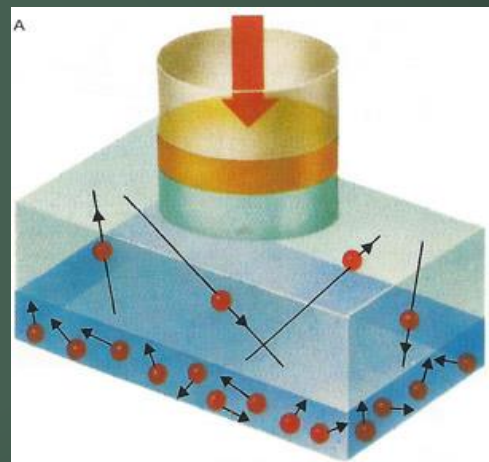
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## Unit 3: The kinetic theory of gases and the Equation of state

### Lecture 14: Real Gases Van Der Waals Equation

## Unit 3: The kinetic theory of gases and the Equation of state

- ❑ **Molecular Model of an Ideal Gas**
  - ❑ Pressure and Kinetic Energy
  - ❑ Molecular Interpretation of Temperature
- ❑ **Equation of state of an ideal and real gas**
  - ❑ Molar Specific Heat of an Ideal Gas
  - ❑ Adiabatic Processes for an Ideal Gas
- ❑ **PVT surfaces for a an ideal and real gas**
  - ❑ **Phase diagrams, Triple point, critical point and Vapor pressure.**



## Kinetic Theory – Summary

Using **Newtonian mechanics** we have established:

- the relationship between **pressure** and **K.E**;

$$P = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m_0 \overline{v^2} \right)$$

- the **universality** of the gas constant;

$$R = C_P - C_V$$

- the relationship between **temperature** and **K.E** ;

$$T = \frac{2}{3k_B} \left( \frac{1}{2} m_0 \overline{v^2} \right)$$

- the **internal energy** of an ideal gas.

$$K_{\text{tot trans}} = N \left( \frac{1}{2} m \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

## ما هي معادلة الحالة Equation of State؟

توصف حالة كتلة  $m$  من مادة معينة من خلال الاحداثيات الترموديناميكية وهي الضغط والحجم ودرجة الحرارة. وبصفة عامة هذه الكميات  $(P, V, T)$  لا يمكن ان تتغير بطريقة مستقلة عن بعضها البعض حيث ان هناك دائما علاقة تربط بين الضغط والحجم ودرجة الحرارة لتحديد حالة المادة. رياضيا نقول ان هناك معادلة تسمى معادلة الحالة لتحدد العلاقة بين تلك الكميات الفيزيائية تأخذ الصورة التالية:

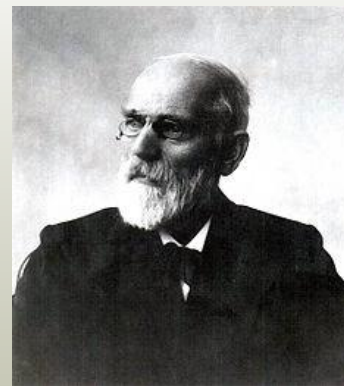
$$V = f(P, T, m)$$

وهذا يعني ان **حجم كتلة محددة من المادة** يعتمد على الضغط  $P$  ودرجة الحرارة  $T$  والكتلة  $m$  والمعادلة التي تربطهم معا تسمى معادلة الحالة Equation of State.

**ملاحظة:** من الصعب ايجاد معادلة حالة لتحديد العلاقة بين الضغط والحجم ودرجة الحرارة للمادة بدقة، لذا سنقوم بإجراء بعض التعديلات على معادلة الحالة للغاز المثالي التي قام بها العالم فاندرفال على معادلة الحالة ثم سندرس اسطح ال  $PVT$ .

## Real Gases General Observations

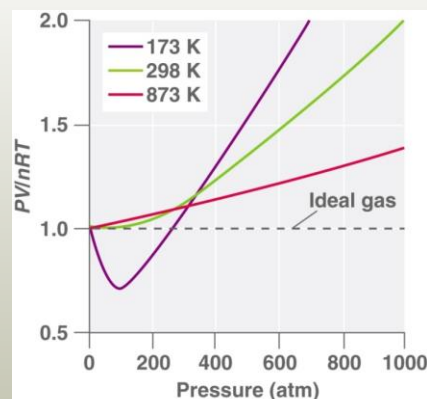
- Deviations from ideal gas law are particularly important at **high pressures** and **low temperatures**.
- **Real gases** differ from ideal gases in that there can be **interactions between molecules** in the gas state
  - **Repulsive forces** important only when molecules are nearly in contact, i.e. very high pressures.
  - **Attractive forces** operate at relatively long range (several molecular diameters).
  - At **low pressures**, neither repulsive or attractive forces dominate → **ideal behavior**



*J. van der Waals, 1837-1923,  
Professor of Physics,  
Amsterdam. Nobel Prize 1910.*

## Real Gases General Observations

- The Ideal Gas Law **ignores** both the **volume occupied by the molecules of a gas** and **all interactions between molecules**, whether attractive or repulsive.
- **In reality**, all gases have a volume and the molecules of real gases interact with one another.
- For an ideal gas, a plot of  $PV/nRT$  versus  $P$  gives a horizontal line with an intercept of **1** on the  $PV/nRT$  axis.
- **The reasons for the deviations from ideality are:**
  - **The molecules are very close to one another, thus their volume is important.**
  - **The molecular interactions also become important.**



Real gases behave ideally at ordinary temperatures and pressures. At low temperatures and high pressures real gases do not behave ideally.

## Real Gases Van Der Waals Equation

Real gases do not follow  $PV = nRT$  perfectly. The van der Waals equation corrects for the non-ideal nature of real gases.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$a$  corrects for interaction between atoms.

$b$  corrects for volume occupied by atoms.

Non-ideal Conditions when gas gets close to conditions where it will **liquefy** i.e. Lower Temperature and Higher Pressure

Gas	$a$ (L <sup>2</sup> ·atm)/mol <sup>2</sup>	$b$ (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H <sub>2</sub>	0.2420	0.0265
N <sub>2</sub>	1.352	0.0387
O <sub>2</sub>	1.364	0.0319
Cl <sub>2</sub>	6.260	0.0542
NH <sub>3</sub>	4.170	0.0371
CH <sub>4</sub>	2.273	0.0430
CO <sub>2</sub>	3.610	0.0429

### Example 1

A 4.0 L cylinder containing 500 g of chlorine. The cylinder can handle a pressure of 40 atm safely. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. The molar mass of chlorine is 70.906 g/mol. Is this cylinder likely to be safe?

**Solution:** the no. of moles we have is  $500g \left( \frac{1 \text{ mol}}{70.906 \text{ g/mole}} \right) = 7.05 \text{ mole}$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{(7.05 \cancel{\text{mol}}) [0.08206 (\cancel{\text{L}} \cdot \text{atm}) / (\cancel{\text{K}} \cdot \cancel{\text{mol}})] (298 \cancel{\text{K}})}{4.0 \cancel{\text{L}}} = 43 \text{ atm}$$

If chlorine behaves like an ideal gas, you have a real problem!

- Now let's use the van der Waals equation with the  $a$  and  $b$  values for  $\text{Cl}_2$  from table in slide 6 and from van der Waals equation

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

- Solving for  $P$  gives

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$= \frac{(7.05 \cancel{\text{mol}})(0.08206 \cancel{\text{L}} \cdot \text{atm} / \cancel{\text{K}} \cdot \cancel{\text{mol}})(298 \cancel{\text{K}})}{4.0 \cancel{\text{L}} - (7.05 \cancel{\text{mol}})(0.0542 \cancel{\text{L}} / \cancel{\text{mol}})} - \frac{(6.260^2 \cancel{\text{L}}^2 \cdot \text{atm} / \cancel{\text{mol}}^2)(7.05 \cancel{\text{mol}})^2}{(4.0 \cancel{\text{L}})^2}$$

$$= 47.7 \text{ atm} - 19.4 \text{ atm} = 28 \text{ atm}$$

- This pressure is well within the safety limits of the cylinder.
- The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

## Exercise

- A 10.0 L cylinder contains 500 g of methane (with molar mass is 16.04 g/mol). Calculate its pressure at 27°C using the
  - ideal gas law.
  - van der Waals equation.

**Answer:** a. 77 atm;

b. 67 atm

إلى اللقاء مع المحاضرة (١٥)

***PVT surfaces for a an ideal  
and real gas***



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He

Ne

Ar

Kr

Xe

Rn

# Thermodynamics

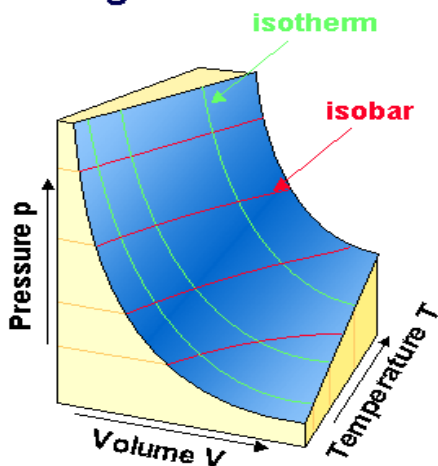
Dr. Hazem Falah Sakeek  
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## Unit 3: The kinetic theory of gases and the Equation of state

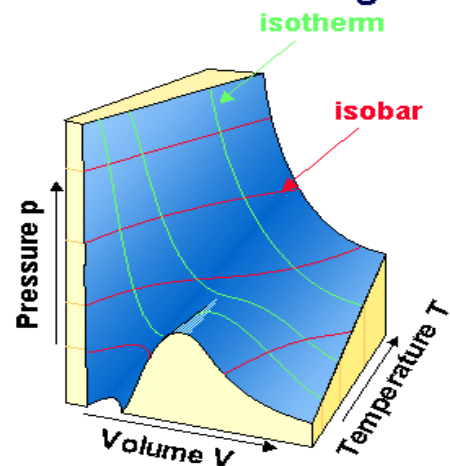
### Lecture 15: PVT surfaces for an ideal and real gas

## *P V T surfaces*

**Ideal gas**



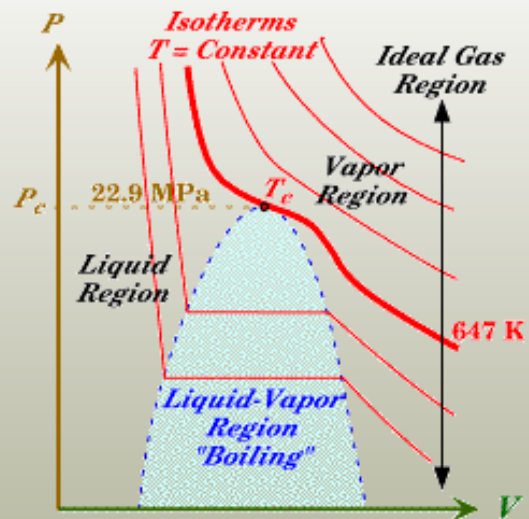
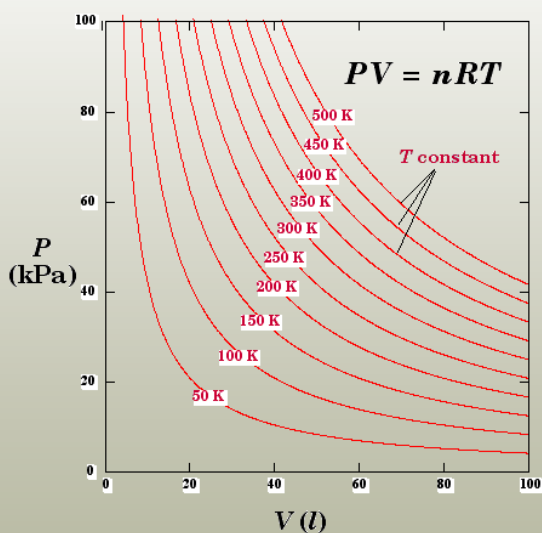
**van der Waals gas**



## PVT surfaces

- We consider a fixed amount of a real gas. The thermodynamic variables are  $P$ ,  $V$  and  $T$ .
- Equations such as that for an **ideal gas** or the **van der Waals equation**, describe the system over a **limited range of these variables**, but **no single equation is adequate for extended regions**.
- Thus,  $P$ - $V$ - $T$  data are often given in tables. However a convenient way to visualize the data is with a  $PVT$  surface.
- A cartesian coordinate system with  $P$ ,  $V$  and  $T$  as the axes is used to represent the system.

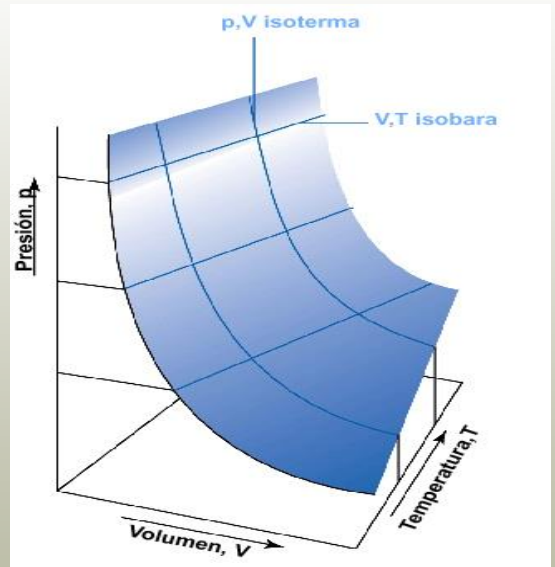
## PV diagram for Isothermal of Ideal and Real gas



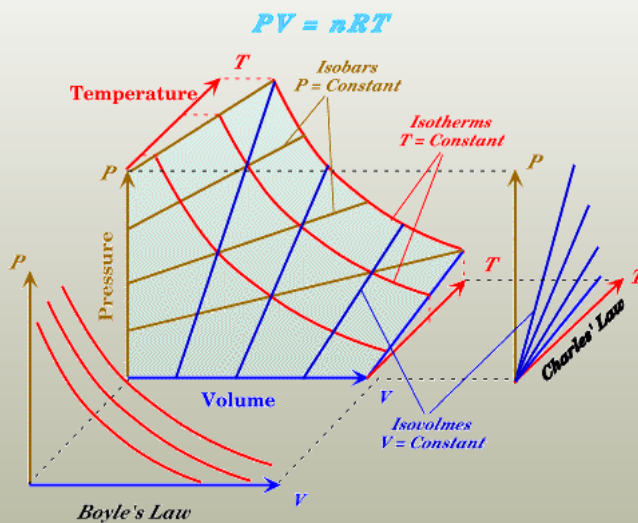
## PVT Surfaces for Ideal Gas

دعت الحاجة الى استخدام التمثيل البياني لمعادلة الحالة للمادة لعدم وجود معادلة دقيقة تربط بين الضغط ودرجة الحرارة والحجم لمختلف المواد ولمدى واسع من التغير في قيم الاحداثيات الترموديناميكية.

لذا اذا ما تم تمثيل المتغيرات الثلاثة  $P, V, T$  فإن هذا سوف يشكل اسطح ولتوضيح ذلك سوف نستعين بالشكل المبين.



## PVT Surfaces for Ideal Gas

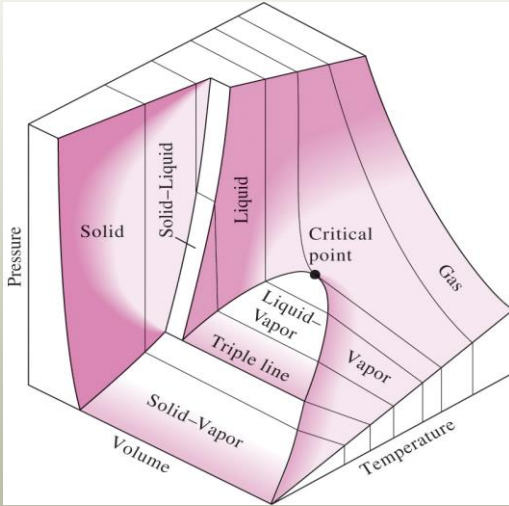


يمثل الشكل العلاقة بين الحجم (الاحداثي باللون الازرق) والضغط (الاحداثي باللون البني) ودرجة الحرارة (الاحداثي باللون الأحمر) لغاز يتصرف كغاز مثالي،

مسقط الاحداثيات على اليسار من الشكل يمثل العلاقة بين الضغط والحجم (قانون بويل).

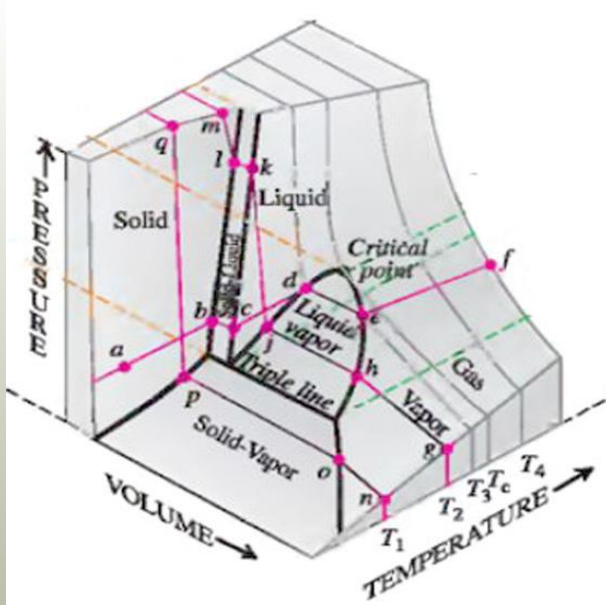
مسقط الاحداثيات على يمين الشكل يمثل العلاقة بين الضغط ودرجة الحرارة (قانون تشارلز).

## PVT Surfaces for Real Gas



■ عند زيادة الضغط وانخفاض درجات الحرارة يسلك الغاز سلوك مختلف عن الغاز المثالي حيث تتحول المادة من الحالة الغازية إلى السائلة أو الصلبة. ولكن لا تزال هناك علاقة بين الضغط والحجم ودرجة الحرارة للمادة مهما اختلفت حالتها، وهذا يعني ان للمادة معادلة حالة ولكن هنا يصبح الامر في غاية التعقيد في ايجاد معادلة رياضية لذا يتم الاستعانة بأسطح PVT لتمثيل ذلك بالرسم.

■ في الشكل اسطح PVT لمادة في حالاتها الثلاثة الغازية والسائلة والصلبة.



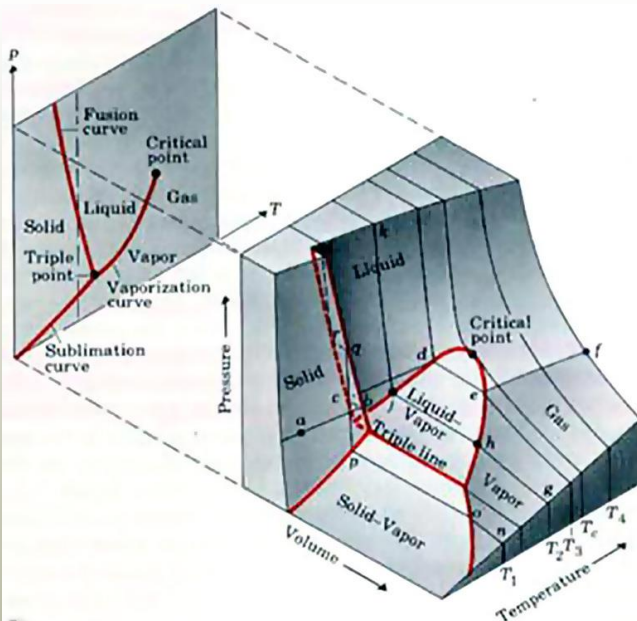
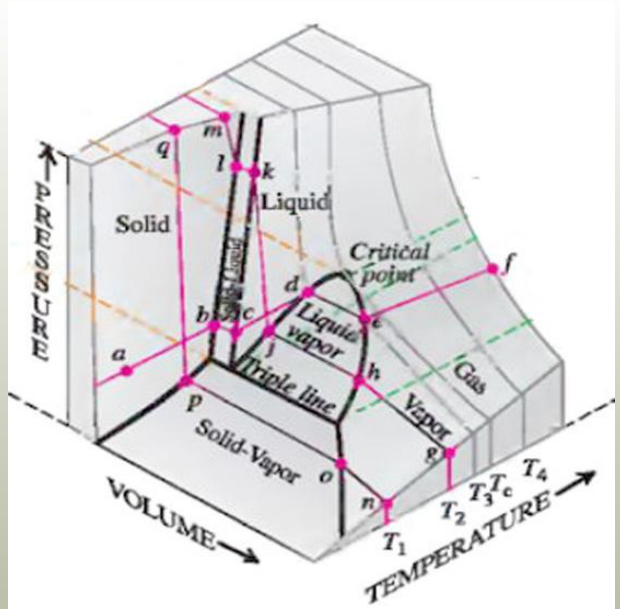
□ افترض عينة من مادة في الحالة الصلبة موضوعة في مكبس ويزداد درجة الحرارة عند ثبوت الضغط وهذا ممثل على الشكل اعلاه في المسار abcdef في البداية عند النقطة a تزداد درجة حرارة العينة نتيجة للتسخين المستمر فيزداد الحجم حتى نصل الى النقطة b التي تبدأ عندها العينة بالذوبان لتتحول من الحالة الصلبة إلى الحالة السائلة فيزداد الحجم وتثبت درجة الحرارة حتى تتحول العينة إلى الحالة السائلة (النقطة c).

□ يستمر الحجم في الزيادة وترتفع درجة الحرارة حتى نصل الى النقطة d فتتحول العينة الى الحالة الغازية وعندها يزداد الحجم بشكل اكبر وتثبت درجة الحرارة على المسار من d إلى e فتتحول العينة الى غاز ويزداد التسخين ترتفع درجة الحرارة ويزداد الحجم.

**ملاحظة:** يمكن تمثيل اية عملية على هذه المنحنيات من خلال تتبع المسار على الشكل السابق مع ملاحظة ان العمليات التي تتم عند ثبوت الضغط فإن المسار يكون متغير على الاحداثيين الحجم ودرجة الحرارة أما اذا كانت العملية عند ثبوت درجة الحرارة فإن التغير في المسار على الاحداثيين الضغط والحجم.

- أما على المسار ghjklm فيمثل عملية ضغط الغاز عند ثبوت درجة الحرارة.
- بزيادة الضغط يتحول الغاز إلى الحالة السائلة ثم إلى الحالة الصلبة مروراً بنقاط التقاطع على المنحنيات باللون الأحمر التي يحدث عندها التحول من حالة إلى أخرى مع ثبوت الضغط وعلى طول المسار يقل الحجم، وكما هو موضح في الشكل ان الحجم يقل بصورة كبيرة بزيادة الضغط عندما تكون العينة في الحالة الغازية ويقل هذا النقصان في الحجم في الحالة السائلة والحالة الصلبة.

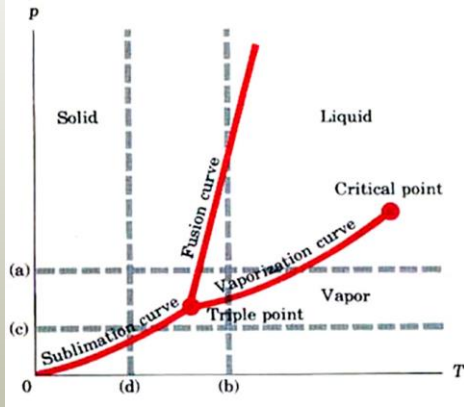
**ملاحظة:** من خلال هذه الرسومات يمكن تحديد حالة المادة عند أية ظروف من الضغط ودرجة الحرارة والمنحنيات باللون الأحمر تحدد مرحلة التحول من حالة إلى أخرى وخلال هذه المنحنيات تكون المادة متواجدة في حالتين معا اما عند الخط الذي يمثل Triple line فإن المادة تتواجد في حالاتها الثلاثة في آن واحد.



## Phase Diagram

من الملاحظ ان الاسطح PVT التحليل والقراءة، وذلك لأنها تمثل ثلاثة ابعاد ولكن لجعل الامر اكثر يسراً وواضح يمكن التعامل مع مسقط هذه الاسطح على احداثي الضغط ودرجة الحرارة، فنحصل على الشكل التالي الذي يعرف بال Phase Diagram

## Phase Diagram



□ نلاحظ أن كل نقطة على هذا المخطط تمثل حالة واحدة للمادة أما النقط على المنحنيات باللون الأحمر فتتواجد حالتين معاً للمادة. وهذه المنحنيات تسمى منحنيات التوازن Equilibrium Curves والتي تحدد قيم الضغط ودرجة الحرارة التي يمكن أن تتواجد عندها المادة في الحالة الصلبة أو الحالة السائلة أو الحالة الغازية.

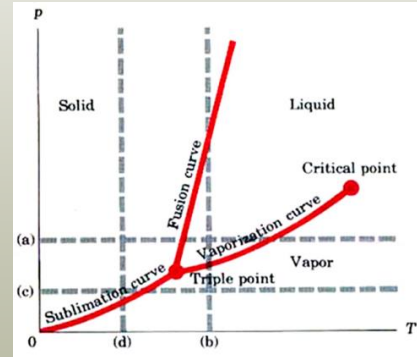
□ منحنيات التوازن هي منحني التبخر Vaporization Curve يفصل بين الحالة الغازية والسائلة ومنحني الانصهار Fusion Curve يفصل بين الحالة السائلة والصلبة ومنحني التسامي Sublimation Curve يفصل بين الحالة الغازية والصلبة.

□ تمثل الخطوط المنقطة a و c عمليات عند ثبوت الضغط بينما الخطوط b و d تمثل عمليات عند ثبوت درجة الحرارة والتقاطع بين الخطوط المنقطة والمنحنيات باللون الأحمر تحدد نقطة الانصهار ونقطة الغليان.

## النقطة الثلاثية Triple Point

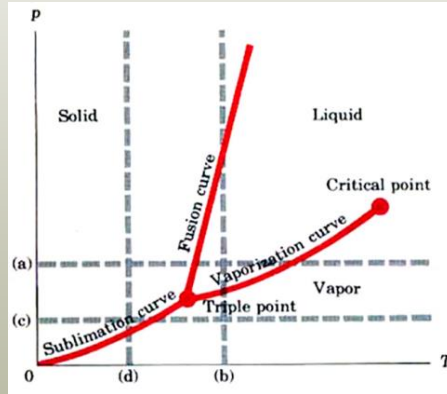
▪ كما هو موضح في الشكل السابق نقطة تقاطع منحنيات التوازن الثلاثة تعطي النقطة الثلاثية Triple Point والتي تتواجد عندها المادة في حالاتها الثلاث في نفس الوقت ولكل مادة نقطة ثلاثية وحيدة.

Triple-point data		
Substance	Temperature, K	Pressure, $10^5$ Pa
Hydrogen (normal)	13.84	0.0704
Deuterium (normal)	18.63	0.171
Neon	24.57	0.432
Nitrogen	63.18	0.125
Oxygen	54.36	0.00152
Ammonia	195.40	0.0607
Carbon dioxide	216.55	5.17
Sulfur dioxide	197.68	0.00167
<b>Water</b>	<b>273.16</b>	<b>0.00610</b>



## النقطة الحرجة Critical Point

- أما النقطة الحرجة Critical Point فهي التي تكون في نهاية منحنى التبخر والتي بعدها لا يمكن تحويل البخار إلى سائل وتسمى درجة الحرارة والضغط عندها بدرجة الحرارة الحرجة والضغط الحرج.



## تعريفات هامة

- البخار Vapor وهو الغاز عند درجة حرارة اقل من الدرجة الحرجة.
- ضغط البخار Vapor Pressure هو ضغط البخار المتواجد في حالة اتزان مع السائل أو الصلب عند اية درجة حرارة.
- نقطة الغليان Boiling Point هي درجة الحرارة التي يكون عندها ضغط البخار يساوي الضغط الجوي.
- البخار المشبع Saturated Vapor هو البخار المتواجد في حالة اتزان حراري عند درجة حرارة وضغط ما مع السائل.

إلى اللقاء مع المحاضرة (١٦)

***Problems Solving and Discussion***



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# Thermodynamics

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Lecture 16: Discussion and Problem Solving

Part One

## Question 1

If a gas is compressed isothermally, which of the following statements is true?

- (a) Energy is transferred into the gas by heat.
- (b) No work is done on the gas.
- (c) The temperature of the gas increases.
- (d) The internal energy of the gas remains constant.
- (e) None of those statements is true.

## Question 2

- When alcohol is rubbed on your body, it lowers your skin temperature. Explain this effect on the basis of kinetic theory of the gas.

- عندما يتبخر الكحول فان الجزيئات ذات السرعة العالية تتمكن من الهرب منه.
- هذا يعمل على تقليل متوسط سرعة باقي الجزيئات.
- ينعكس ذلك على انخفاض درجة الحرارة فنشعر بالبرودة.

## Exercise 1

(a) Find the number of moles in one cubic meter of an ideal gas at 20.0°C and atmospheric pressure. (b) For air, Avogadro's number of molecules has mass 28.9 g. Calculate the mass of one cubic meter of air.

(a)  $PV = nRT$

$$n = \frac{PV}{RT} = \frac{(1.013 \times 10^5 \text{ Pa})(1.00 \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(293 \text{ K})} = \boxed{41.6 \text{ mol}}$$

(b)  $m = nM = (41.6 \text{ mol})(28.9 \text{ g/mol}) = \boxed{1.20 \text{ kg}}$

## Exercise 2

An automobile tire is inflated with air originally at 10.0°C and normal atmospheric pressure. During the process, the air is compressed to 28.0% of its original volume and the temperature is increased to 40.0°C. **What is the tire pressure?**

**Note that** both temperature increase and volume decrease leads to increase the pressure.

Taking  $PV = nRT$  in the initial (i) and final (f) states, and dividing, we have

$$\frac{P_f V_f}{P_i V_i} = \frac{T_f}{T_i}$$

$$P_f = P_i \frac{V_i T_f}{V_f T_i} = (1.013 \times 10^5 \text{ Pa}) \left( \frac{V_i}{0.280 V_i} \right) \left( \frac{273 \text{ K} + 40.0 \text{ K}}{273 \text{ K} + 10.0 \text{ K}} \right) = 4.00 \times 10^5 \text{ Pa}$$

## Exercise 3

A 1.00-mol sample of hydrogen gas is warmed at **constant pressure** from 300 K to 420 K. Calculate (a) the energy transferred to the gas by heat, (b) the increase in its internal energy, and (c) the work done on the gas.

لاحظ ان الهيدروجين في هذه الحالة يتمدد، وبالتالي فان الغاز يبذل شغلا موجبا، كما ان العملية تمت عند ثبوت الضغط.

لإيجاد الطاقة التي اكتسبها الهيدروجين عن طريق الحرارة

$$Q = nC_p \Delta T$$

remember  $C_p = 7/2 R$

$$Q = (1.00 \text{ mol})(28.8 \text{ J/mol} \cdot \text{K})(120 \text{ K}) = 3.46 \text{ kJ}$$

## Exercise 3, continue

▪ لإيجاد التغير في الطاقة الداخلية نستخدم العلاقة العامة لكل الغازات وهي

$$\Delta E_{int} = nC_V\Delta T \quad \text{remember } C_V = 5/2 R$$

$$\Delta E_{int} = (1.00\text{mol})(20.4\text{J/mol}\cdot\text{K})(120\text{K}) = 2.45\text{kJ}$$

▪ لإيجاد الشغل المبذول على الغاز نستخدم القانون الاول للديناميكا الحرارية

$$\Delta E_{int} = Q + W$$

$$W = \Delta E_{int} - Q = 2.45\text{ kJ} - 3.46\text{ kJ} = -1.01\text{ kJ}$$

## Exercise 4

(a) How many atoms of helium gas fill a spherical balloon of diameter 30.0 cm at 20.0°C and 1.00 atm? (b) What is the average kinetic energy of the helium atoms? (c) What is the rms speed of the helium atoms? (the molar mass of helium is 4.0026 g/mol).

**Solution (a)** The volume of the balloon is  $V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(0.150\text{ m})^3 = 1.41 \times 10^{-2}\text{ m}^3$

From the equation  $PV = nRT$  we can get the quantity of gas

$$n = \frac{PV}{RT} = \frac{(1.013 \times 10^5 \text{ N/m}^2)(1.41 \times 10^{-2} \text{ m}^3)}{(8.314 \text{ N}\cdot\text{m/mol}\cdot\text{K})(293 \text{ K})} = 0.588 \text{ mol}$$

▪ The number of molecules is

$$N = nN_A = (0.588\text{mol})(6.02 \times 10^{23} \text{ molecules/mol})$$

$$N = 3.54 \times 10^{23} \text{ helium atoms}$$

## Exercise 3, continue

(b) The kinetic energy is  $\bar{K} = \frac{1}{2} m_o \overline{v^2} = \frac{3}{2} k_B T$

$$\bar{K} = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) = 6.07 \times 10^{-21} \text{ J}$$

(c) the root-mean-square speed is given by

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{2\bar{K}}{m_o}}$$

$$m_o = \frac{M}{N_A} = \frac{4.002 \text{ g/mol}}{6.02 \times 10^{23} \text{ molecules/mol}} = 6.65 \times 10^{-24} \text{ g} = 6.65 \times 10^{-27} \text{ kg}$$

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{2\bar{K}}{m_o}} = \sqrt{\frac{2 \times 6.07 \times 10^{-21} \text{ J}}{6.65 \times 10^{-27} \text{ kg}}} = 1.35 \text{ km/s}$$

## Exercise 4

- A 3.00-g lead bullet at 30.0°C is fired at a speed of 240 m/s into a large block of ice at 0°C, in which it becomes embedded. **What quantity of ice melts?**

**Solution:** the energy lost by the bullet equals the energy gained by the ice

$$\Delta K_b + Q_b = Q_{ice}$$

$$\frac{1}{2} m_b v_b^2 + m_b c_{Pb} |\Delta T| = L_f \Delta m_{\text{melted}} \quad \Rightarrow \quad \Delta m_{\text{melt}} = m_b \left( \frac{\frac{1}{2} v_b^2 + c_{Pb} |\Delta T|}{L_f} \right)$$

$$\Delta m_{\text{melt}} = (3.00 \times 10^{-3} \text{ kg}) \left( \frac{\frac{1}{2} (240 \text{ m/s})^2 + (128 \text{ J/kg} \cdot ^\circ\text{C})(30.0^\circ\text{C})}{3.33 \times 10^5 \text{ J/kg}} \right)$$

$$\Delta m_{\text{melt}} = \frac{86.4 \text{ J} + 11.5 \text{ J}}{3.33 \times 10^5 \text{ J/kg}} = 2.94 \times 10^{-4} \text{ kg} = 0.294 \text{ g}$$

## Exercise 5

In an insulated vessel, 250 g of ice at 0°C is added to 600 g of water at 18.0°C. (a) What is the final temperature of the system? (b) How much ice remains when the system reaches equilibrium?

الحل: يفقد الماء حرارة بمقدار  $mc\Delta T$  في حين ان الثلج يكتسب حرارة بمقدار  $L\Delta m$  علينا ان نقارن الكميتين لنرى ان كان الثلج سيذوب بالكامل ام لا.

(a) If all 250 g of ice is melted it must absorb energy

$$Q_f = L_f \Delta m = (0.250 \text{ kg})(3.33 \times 10^5 \text{ J/kg}) = 83.3 \text{ kJ}$$

(b) The energy released when 600 g of water cools from 18.0°C to 0°C

$$|Q| = |mc\Delta T| = (0.600 \text{ kg})(4186 \text{ J/kg} \cdot ^\circ\text{C})(18.0^\circ\text{C}) = 45.2 \text{ kJ}$$

حيث ان الطاقة اللازمة لإذابة 250 جرام من الثلج عند صفر مئوية اكثر من الحرارة الناتجة عن تبريد 600 جرام من الماء من 18°C إلى درجة الصفر المئوية فان الثلج لا يذوب بالكامل، وتكون درجة الحرارة النهائية للنظام عند 0°C.

## Exercise 5, continue

▪ (b) How much ice remains when the system reaches equilibrium?

▪ يزود الماء عندما يبرد من درجة حرارة 18°C إلى درجة حرارة 0°C مقدار من الطاقة يساوي 45.2 kJ وهي تلك التي يكتسبها الثلج ليذوب حسب العلاقة  $Q = L_f \Delta m$

$$\Delta m = \frac{Q}{L_f} = \frac{45.2 \times 10^3 \text{ J}}{3.33 \times 10^5 \text{ J/kg}} = 0.136 \text{ kg}$$

▪ وتكون كمية الثلج المتبقية هي

$$m' = 0.250 \text{ kg} - 0.136 \text{ kg} = 0.114 \text{ kg}$$

## Exercise 6

An ideal gas is enclosed in a cylinder with a movable piston on top of it. The piston has a mass of 8,000 g and an area of 5.00 cm<sup>2</sup> and is free to slide up and down, **keeping the pressure of the gas constant.**

How much work is done on the gas as the temperature of 0.200 mol of the gas is raised from 20.0°C to 300°C?

Solution: For constant pressure  $W = -\int_i^f P dV = -P\Delta V = -P(V_f - V_i)$

$$W = -P \left( \frac{nRT_h}{P} - \frac{nRT_c}{P} \right) = -nR(T_h - T_c)$$

$$= -(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(280 \text{ K}) = -466 \text{ J}$$

يمكن الحل بطريقة أخرى وهي إيجاد مقدار الضغط والذي يساوي الضغط الجوي مضافاً له ضغط وزن المكبس.

## Exercise 7

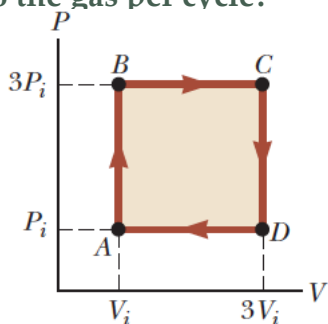
An ideal gas initially at  $P_i$ ,  $V_i$ , and  $T_i$  is taken through a cycle as shown in the Figure. (a) Find the net work done on the gas per cycle for 1.00 mol of gas initially at 0°C. (b) What is the net energy added by heat to the gas per cycle?

The work done during each step of the cycle equals the negative of the area under that segment of the PV curve.

$$(a) W = W_{DA} + W_{AB} + W_{BC} + W_{CD}$$

$$W = -P_i(V_i - 3V_i) + 0 - 3P_i(3V_i - V_i) + 0 = \boxed{-4P_iV_i}$$

$$W = -4P_iV_i = -4nRT_i = -4(1.00)(8.314)(273) = \boxed{-9.08 \text{ kJ}}$$



(b) The initial and final values of  $T$  for the system are equal. Therefore,  $\Delta E_{\text{int}} = 0$

$$Q = -W = \boxed{4P_iV_i}$$

## إلى اللقاء مع المحاضرة (١٧)

### ***More Problems Solving and Discussion***



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# Thermodynamics

Dr. Hazem Falah Sakeek  
Al-Azhar University - Gaza

Lecture 17: Discussion and Problem Solving

Part Two

## Exercise 1

A glass window has an area of  $3.00 \text{ m}^2$  and a thickness of  $0.600 \text{ cm}$ . If the temperature difference between its faces is  $25.0^\circ\text{C}$ , **what is the rate of energy transfer by conduction through the window?** (thermal conductivity of glass  $0.800 \text{ W/m}^\circ\text{C}$ )

$$\begin{aligned}
 H &= \frac{Q}{t} = kA \left( \frac{\Delta T}{L} \right) \\
 &= \frac{(0.800 \text{ W/m}^\circ\text{C})(3.00 \text{ m}^2)(25.0^\circ\text{C})}{6.00 \times 10^{-3} \text{ m}} \\
 &= 1.00 \times 10^4 \text{ W}
 \end{aligned}$$

## Exercise 2

A cylinder contains a mixture of helium and argon gas in **equilibrium** at 150°C. (a) What is the average kinetic energy for each type of gas molecule? (b) What is the **rms speed** of each type of molecule? (molar mass of He is 4.00 g/mol, molar mass of Ar is 39.9 g/mol)

من النظرية الحركية للغازات يمكن ان نحصل على المطلوب، علما بان كلا النوعين من الجزيئات لهما نفس متوسط الطاقة الحركية لان الطاقة الحركية تعتمد بشكل كبير على درجة الحرارة.

$$\begin{aligned}\therefore \bar{K} &= \frac{1}{2} m_o \overline{v^2} = \frac{3}{2} k_B T \\ &= \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K}) (273 + 150) \text{ K}\end{aligned}$$

$$\bar{K} = 8.76 \times 10^{-21} \text{ J}$$

## Exercise 2, continue

(b) The root-mean square velocity can be calculated from the kinetic energy:

$$\begin{aligned}v_{rms} &= \sqrt{\overline{v^2}} \\ \therefore \bar{K} &= \frac{1}{2} m_o \overline{v^2} \\ \frac{2\bar{K}}{m_o} &= \overline{v^2}\end{aligned}$$

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{2\bar{K}}{m_o}}$$

The masses of the molecules are

$$m_{\text{He}} = \frac{(4.00 \text{ g/mol})(10^{-3} \text{ kg/g})}{6.02 \times 10^{23} \text{ atoms/mol}} = 6.64 \times 10^{-27} \text{ kg}$$

$$m_{\text{Ar}} = \frac{(39.9 \text{ g/mol})(10^{-3} \text{ kg/g})}{6.02 \times 10^{23} \text{ atoms/mol}} = 6.63 \times 10^{-26} \text{ kg}$$

$$v_{\text{rms, He}} = \sqrt{\frac{2(8.76 \times 10^{-21} \text{ J})}{6.64 \times 10^{-27} \text{ kg}}} = 1.62 \times 10^3 \text{ m/s}$$

$$v_{\text{rms, Ar}} = \sqrt{\frac{2(8.76 \times 10^{-21} \text{ J})}{6.63 \times 10^{-26} \text{ kg}}} = 514 \text{ m/s}$$

## Exercise 3

A spherical balloon of volume  $4.00 \times 10^3 \text{ cm}^3$  contains helium at a pressure of  $1.20 \times 10^5 \text{ Pa}$ . **How many moles** of helium are in the balloon if the average kinetic energy of each helium atom is  $3.60 \times 10^{-22} \text{ J}$ ?

لاستخدام معادلة الغاز المثالي لإيجاد عدد المولات نحتاج ان نعرف درجة الحرارة، ويمكن ان نستفيد من متوسط طاقة حركة ذرات الهليوم لحساب درجة الحرارة على النحو التالي:

$$\frac{1}{2} m_o \overline{v^2} = \frac{3}{2} k_B T$$

$$T = \frac{2}{3} \left( \frac{\frac{1}{2} m_o \overline{v^2}}{k_B} \right) = \frac{2}{3} \left( \frac{3.60 \times 10^{-22} \text{ J}}{1.38 \times 10^{-23} \text{ J/K}} \right) = 17.4 \text{ K}$$

From  $PV = nRT$  gives

$$n = \frac{PV}{RT} = \frac{(1.20 \times 10^5 \text{ N/m}^2)(4.00 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J/mol} \cdot \text{K})(17.4 \text{ K})} = 3.32 \text{ mol}$$

## Exercise 4

A 2.00-mol sample of a diatomic ideal gas expands slowly and **adiabatically** from a pressure of 5.00 atm and a volume of 12.0 L to a final volume of 30.0 L. (a) **What is the final pressure of the gas?** (b) **What are the initial and final temperatures?** Find (c)  $Q$ , (d)  $\Delta E_{\text{int}}$ , and (e)  $W$  for the gas during this process.

نتوقع من هذه العملية الادياباتيكية ان كمية الحرارة  $Q$  تساوي صفر اي لا يكتسب النظام حرارة وتكون الشغل المبذول على حساب درجة الحرارة فتتخفض وايضا يقل الضغط عن 2 atm.

(a) In an adiabatic process  $P_i V_i^\gamma = P_f V_f^\gamma$

remember  $\gamma = \frac{7}{5} = 1.40$  for diatomic ideal gas,

$$P_f = P_i \left( \frac{V_i}{V_f} \right)^\gamma = (5.00 \text{ atm}) \left( \frac{12.0 \text{ L}}{30.0 \text{ L}} \right)^{1.40} = 1.39 \text{ atm}$$

## Exercise 4, continue

(b) The initial temperature is

$$T_i = \frac{P_i V_i}{nR} = \frac{(5.00 \text{ atm})(1.013 \times 10^5 \text{ Pa/atm})(12.0 \times 10^{-3} \text{ m}^3)}{(2.00 \text{ mol})(8.314 \text{ N} \cdot \text{m/mol K})} = 366 \text{ K}$$

the final temperature is  $T_f = \frac{P_f V_f}{nR} = 253 \text{ K}$

(c) This is an adiabatic process, so  $Q = 0$

## Exercise 4, continue

(d) For any process,

$$\Delta E_{\text{int}} = nC_V \Delta T \quad \text{remember } C_V = 5/2 R \text{ for diatomic ideal gas,}$$

$$\Delta E_{\text{int}} = \frac{5}{2} (2.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(253 \text{ K} - 366 \text{ K}) = -4\,660 \text{ J}$$

(e) The work

$$W = \Delta E_{\text{int}} - Q = -4\,660 \text{ J} - 0 = -4\,660 \text{ J}$$

- The work done on the gas is negative, so positive work is done by the gas on its environment as the gas expands.

## Exercise 5

Helium gas at atmospheric pressure and temperature of 273K is expanded **adiabatically** from a 12-liter volume to a 33-liter volume. Find the final **temperature** and **pressure** of the gas and the **work** done on the gas. (For helium,  $\gamma = 1.67$ )

To find the final pressure, we use the relation

$$pV^\gamma = \text{constant} = p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$p_2 = \frac{p_1 V_1^\gamma}{V_2^\gamma} = \frac{(1.01 \times 10^5 \text{ Pa})(12 \ell)^{1.67}}{(33 \ell)^{1.67}} = 1.86 \times 10^4 \text{ Pa}.$$

To find the final temperature, we use the relation

$$TV^{\gamma-1} = \text{constant} = T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = \frac{T_1 V_1^{\gamma-1}}{V_2^{\gamma-1}} = \frac{(273 \text{ K})(12 \ell)^{0.67}}{(33 \ell)^{0.67}} = 139 \text{ K}$$

The work done by an ideal gas in an adiabatic process is

$$W = \frac{P_2 V_2 - P_1 V_1}{1 - \gamma}$$

$$W = \frac{(1.86 \times 10^4)(33 \times 10^{-3}) - (1.03 \times 10^5)(12 \times 10^{-3})}{1 - 1.67}$$

$$W = 895 \text{ J}$$

إلى اللقاء مع المحاضرة (١٨)

***More Problems Solving and  
Discussion***



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# Thermodynamics

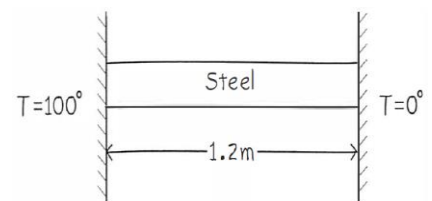
Dr. Hazem Falah Sakeek  
Al-Azhar University - Gaza

## Lecture 17: Discussion and Problem Solving

### Part Three

### Exercise 1

A long steel rod that is insulated to prevent heat loss along its sides is in perfect thermal contact with a large container of boiling water at one end and a 3.0-kg block of ice at the other. The steel rod is 1.2 m long with cross-sectional area  $3.50 \text{ cm}^2$ . How long does it take for the block of ice to melt? The ice block is initially at  $0^\circ\text{C}$  and the thermal conductivity of steel is  $50.2 \text{ W/m.K}$



لحساب الزمن اللازم لإذابة الثلج علينا ان نحسب كمية الحرارة اللازمة لإذابته، ومن ثم نستخدم معادلة التوصيل الحراري لحساب الزمن اللازم.

The heat required to melt the ice is the heat of fusion for ice:

$$Q_{\text{melt}} = m_{\text{ice}} L_f = (3.0 \text{ kg})(3.34 \times 10^5 \text{ J/kg}) = 1.0 \times 10^6 \text{ J}$$

## Exercise 1, continue

- The rate of heat flow is given by

$$H = \frac{\Delta Q}{\Delta t} = kA \frac{T_H - T_C}{L}$$

$$= (50.2 \text{ W}/(\text{m} \cdot \text{K})) (6.5 \times 10^{-4} \text{ m}^2) \frac{(100^\circ\text{C}) - (0^\circ\text{C})}{(1.2 \text{ m})} = 2.7 \text{ W}$$

- The time required to melt the ice is

$$\Delta t = \frac{Q_{\text{melt}}}{H} = \frac{(10^6 \text{ J})}{(2.7 \text{ W})} = 370,000 \text{ s}$$

## Exercise 2

The surface of the Sun has a temperature of about 5800 K. The radius of the Sun is  $6.96 \times 10^8 \text{ m}$ . Calculate the total energy radiated by the Sun each second. Assume that the emissivity of the Sun is 0.965.

$$\rho = \sigma A e T^4$$

$$= (5.6696 \times 10^{-8} \text{ W}/\text{m}^2 \cdot \text{K}^4) \left[ 4\pi (6.96 \times 10^8 \text{ m})^2 \right] (0.965) (5800 \text{ K})^4$$

$$\rho = 3.77 \times 10^{26} \text{ W}$$

## Exercise 3

An **ideal gas** initially at 300 K undergoes an **isobaric expansion** at 2.50 kPa. If the volume increases from 1.00 m<sup>3</sup> to 3.00 m<sup>3</sup> and 12.5 kJ is transferred to the gas by heat, what are (a) the change in its internal energy and (b) its final temperature?

$$\Delta E_{int} = Q + W$$

$$W = -P\Delta V = -2.50 \times 10^3 \text{ Pa} (3.00 - 1.00) \text{ m}^3 = -5000 \text{ J}$$

$$\Delta E_{int} = Q + W = 12500 - 5000 = 7500 \text{ J}$$

(b) The final temperature  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$T_2 = \frac{V_2}{V_1} T_1 = \frac{3.00}{1.00} (300 \text{ K}) = 900 \text{ K}$$

## Exercise 4

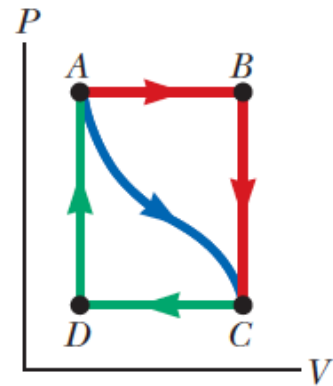
One mole of an ideal gas does 3000 J of work on its surroundings as it expands **isothermally** to a final pressure of 1.00 atm and final volume of 25.0 L. **Determine the initial volume.**

سوف نستخدم الشغل حتى نحصل على الحجم الابتدائي. لاحظ هنا ان العملية تمت عند ثبوت درجة الحرارة وعليه فان الشغل يعطى بالعلاقة

$$\begin{aligned}
 W &= -nRT \ln\left(\frac{V_f}{V_i}\right) \\
 &= -P_f V_f \ln\left(\frac{V_f}{V_i}\right) \\
 W &= P_f V_f \ln\left(\frac{V_i}{V_f}\right)
 \end{aligned}
 \quad
 \begin{aligned}
 \frac{W}{P_f V_f} &= \ln\left(\frac{V_i}{V_f}\right) \\
 \exp\left(\frac{W}{P_f V_f}\right) &= \frac{V_i}{V_f}
 \end{aligned}
 \quad
 \begin{aligned}
 V_i &= V_f \exp\left(+\frac{W}{P_f V_f}\right) \\
 &= (0.0250) \exp\left[\frac{-3000}{0.0250(1.013 \times 10^5)}\right] \\
 &= \boxed{0.00765 \text{ m}^3}
 \end{aligned}$$

## Exercise 5

In the Figure, the **change in internal energy** of a gas that is taken from **A** to **C** along the **blue path** is **+800 J**. **The work done on the gas along the red path ABC is -500 J**. (a) How much energy must be added to the system by heat as it goes from **A** through **B** to **C**? (b) If the pressure at point **A** is five times that of point **C**, what is the work done on the system in going from **C** to **D**? (c) What is the energy exchanged with the surroundings by heat as the gas goes from **C** to **A** along the **green path**? (d) If the change in internal energy in going from point **D** to point **A** is **+500 J**, how much energy must be added to the system by heat as it goes from point **C** to point **D**?



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**(a) How much energy must be added to the system by heat as it goes from A through B to C?**

$$\Delta E_{\text{int}, ABC} = \Delta E_{\text{int}, AC} \quad \text{نقطة البداية هي نفس نقطة النهاية على المسارين}$$

$$\Delta E_{\text{int}, ABC} = Q_{ABC} + W_{ABC}$$

$$Q_{ABC} = 800\text{J} - (-500\text{J}) = 1300\text{J}$$

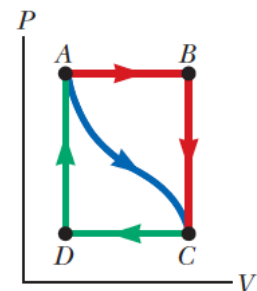
**(b) If the pressure at point A is five times that of point C, what is the work done on the system in going from C to D?**

$$\text{We have} \quad P_A = 5P_C \quad W_{CD} = \text{??????}$$

$$W_{CD} = -P_C \Delta V_{CD} \quad \text{But,} \quad \Delta V_{AB} = -\Delta V_{CD}$$

$$W_{CD} = \frac{1}{5} P_A \Delta V_{AB} = \frac{1}{5} W_{AB}$$

$$W_{CD} = 100\text{J} \quad (+ \text{ means that work is done on the system})$$



$$\Delta E_{\text{int}, AC} = 800\text{J}$$

$$W_{ABC} = -500\text{J}$$

$$\text{Note: } W_{ABC} = W_{AB} + W_{BC} = W_{AB}$$

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(c) What is the energy exchanged with the surroundings by heat as the gas goes from C to A along the green path?

(c)  $W_{CDA} = W_{CD}$  لان العملية على المسار DA تمت عند ثبوت الحجم

so that

$$Q_{CA} = \Delta E_{int, CA} - W_{CDA} = -800 \text{ J} - 100 \text{ J} = -900 \text{ J}$$

(– means that energy must be removed from the system by heat)

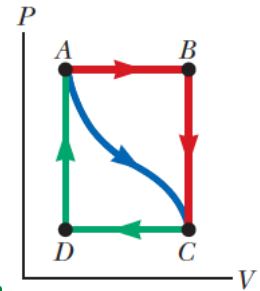
(d) If the change in internal energy in going from point D to p is +500 J, how much energy must be added to the system by heat as it goes from point C to point D?

$$Q_{CD} = \Delta E_{int, CD} - W_{CD}$$

$$\Delta E_{int, CD} = \Delta E_{int, CDA} - \Delta E_{int, DA} = -800 \text{ J} - 500 \text{ J} = -1300 \text{ J}$$

and

$$Q_{CD} = \Delta E_{int, CD} - W_{CD} = -1300 \text{ J} - 100 \text{ J} = -1400 \text{ J}$$



$$\Delta E_{int, AC} = 800 \text{ J}$$

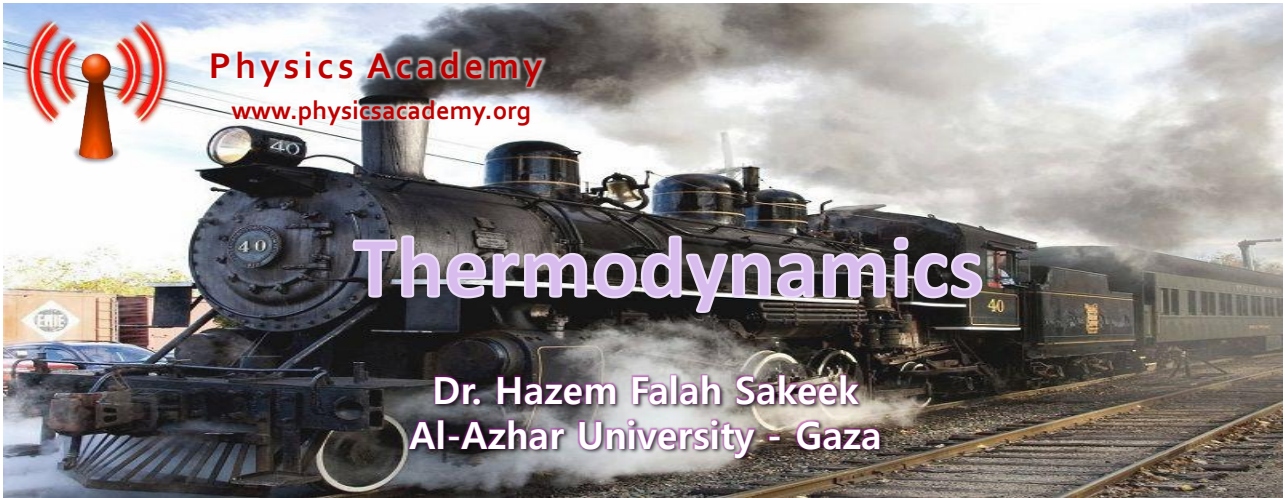
$$W_{ABC} = -500 \text{ J}$$

$$W_{CD} = 100 \text{ J}$$

$$\Delta E_{int, DA} = 500 \text{ J}$$

إلى اللقاء مع المحاضرة (١٩)

***Engines, Refrigerators and the second law of thermodynamics***



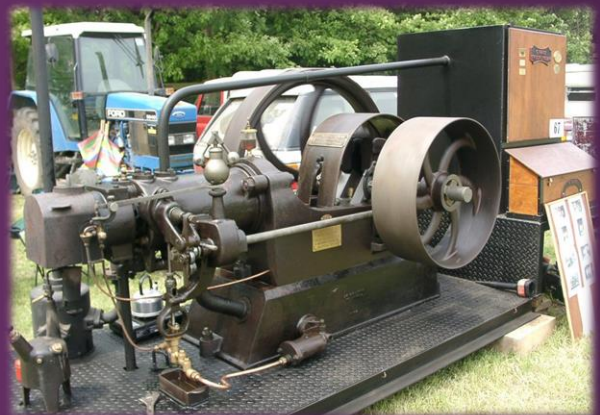
## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 19: Heat Engines and the Second Law of Thermodynamics

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### ❑ Heat Engines and the Second Law of Thermodynamics

- ❑ Stirling engine
- ❑ Gasoline engine
- ❑ Heat Pumps and Refrigerators
- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



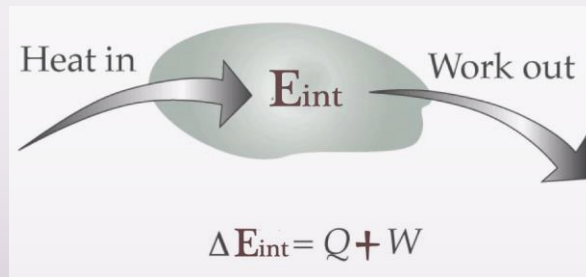
## Goals for Unit 4

- To learn what makes a process **reversible** or **irreversible**
- To understand **heat engines** and their **efficiency**
- To learn how **internal combustion engines** operate
- To learn the operation of **refrigerators** and heat engines
- To see how the **second law** of thermodynamics limits the operations of heat engines and refrigerators
- To do calculations with **Carnot engines** and **refrigerators**
- To understand **entropy** and to use it to analyze thermodynamic processes



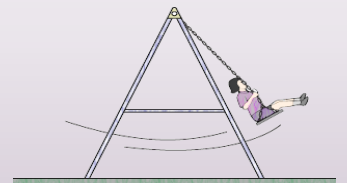
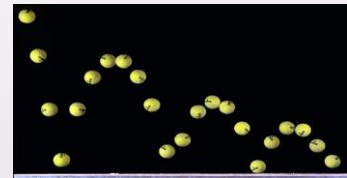
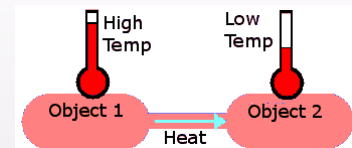
## First Law of Thermodynamics – Review

- The first law is a statement of **Conservation of Energy**.
- The first law states that a **change in internal energy in a system** can occur as a result of energy transfer **by heat, by work, or by both**.
- Only certain types of energy-conversion and energy-transfer processes actually take place in nature.



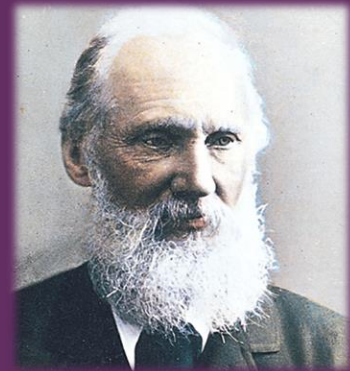
## Processes do not violate the first law, but never happened

- ❑ When two objects at different temperatures are placed in thermal contact with each other, the net transfer of energy by heat is always from the warmer object to the cooler object, **never from the cooler to the warmer**.
- ❑ A rubber ball dropped to the ground bounces several times and eventually comes to rest, **but a ball lying on the ground never gathers internal energy from the ground and begins bouncing on its own**.
- ❑ An oscillating pendulum eventually comes to rest. The mechanical energy of the system is converted to internal energy in the air, the pendulum, and the suspension; **the reverse conversion of energy never occurs**.



## The Second Law of Thermodynamic

- Establishes which processes do occur and which do not occur.
- This directionality is governed by the second law.
- These types of processes are **irreversible**.
  - An irreversible process is one that occurs naturally in one direction only.
  - No irreversible process has been observed to run backwards.
  - An important engineering implication is the **limited efficiency of heat engines**.



**William Thomson, Lord Kelvin**  
1824 – 1907  
British physicist and mathematician

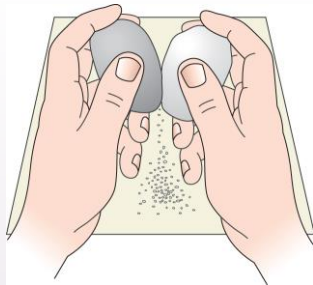
His work in thermodynamics led to the idea that energy cannot pass spontaneously from a colder object to a hotter object.



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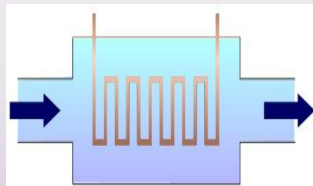
## تحويل الشغل إلى حرارة



مثال (١) عندما نقوم بحك حجرين تحت الماء، فإن الشغل المبذول ضد قوة الاحتكاك يتحول إلى طاقة داخلية تؤدي إلى زيادة درجة حرارة الحجرين.

من ثم تنتقل الحرارة إلى الماء (الوسط المحيط)، ولكن إذا افترضنا أن كتلة الماء كبيرة جداً فلن يكون هناك أي ارتفاع لدرجة حرارة الماء. ويعتبر الماء في هذه الحالة بمستودع حراري heat reservoir.

نلاحظ هنا أن حالة الحجر في بداية العملية مثل حالته في نهاية العملية وأن نتيجة العملية هو تحول الشغل الميكانيكي إلى حرارة.



مثال (٢) عندما يمر تيار كهربائي في مقاومة مغمورة في ماء بكمية كبيرة، فترتفع درجة حرارة المقاومة وتنتقل الحرارة منها إلى الماء، ولكن لا ترتفع درجة حرارة الماء لأنه يعتبر في هذه الحالة كمستودع حراري.

نلاحظ تحول الشغل الكهربائي إلى حرارة بدون حدوث أي تغير في الأحداثات التيرموديناميكية للمقاومة الكهربائية.

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## تحويل الشغل إلى حرارة

▪ نستنتج ان اي نوع من الشغل  $W$  يبذل على نظام في حالة اتصال حراري مع مستودع حراري، فان الحرارة  $Q$  تنساب عبر النظام بدون ان تحدث اي تغير في حالة النظام. ويقوم النظام هنا بدور الوسيط بين الشغل والحرارة.

▪ نستنتج من القانون الاول للديناميكا الحرارية فان الشغل يساوي الحرارة اي ان  $W = Q$ .

▪ اي ان تحول الشغل إلى حرارة يحدث بكفاءة 100%.

▪ تستمر عملية التحول هذه إلى مالا نهاية.

ماذا الان لو اردنا ان نفكر في العملية العكسية .... اي تحويل الحرارة إلى شغل؟ (فكرة عمل المحركات الحرارية).

## مبدأ تحويل الحرارة إلى شغل

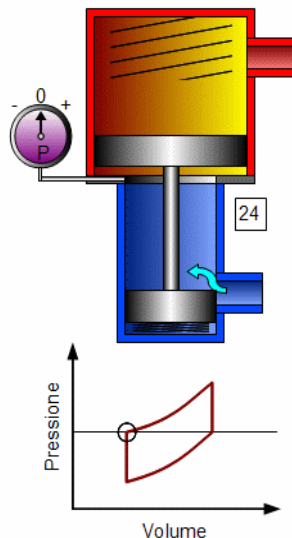
يجب ان يكون هناك عملية او سلسلة من العمليات بحيث تستمر عملية التحويل من الحرارة إلى شغل بشكل مستمر، وبدون توقف الى مالا نهاية، وبدون حدوث تغير في حالة النظام.

هل عملية تمدد غاز مثالي عند ثبوت درجة الحرارة isothermal process تعتبر مثالا جيدا لتحويل الحرارة إلى شغل.

▪ ان التغير في الطاقة الداخلية عند ثبوت درجة الحرارة يساوي صفر، وتكون  $Q = W$ ، وهنا نقول ان الحرارة تحولت بالكامل إلى شغل. لكن انتظر!!!

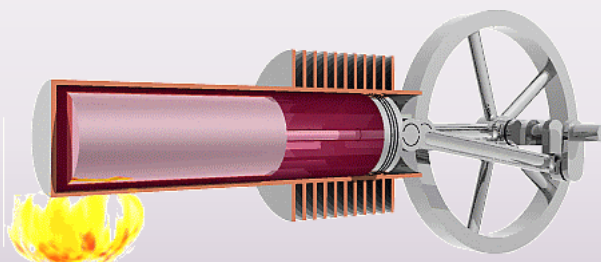
▪ في عملية تمدد الغاز المثالي عند ثبوت درجة الحرارة يحدث تغير في حالة الغاز اي يزداد حجمه ويقل ضغطه حتى يصل إلى الضغط الجوي. وتتوقف عملية التمدد عندما يصبح ضغط الغاز مساوي للضغط الجوي.

إذا لا يمكن اعتبار ان عملية تمدد الغاز المثالي عند ثبوت درجة الحرارة عملية تحول الحرارة إلى شغل عملية مستمرة!



## متطلبات تحويل الحرارة إلى شغل

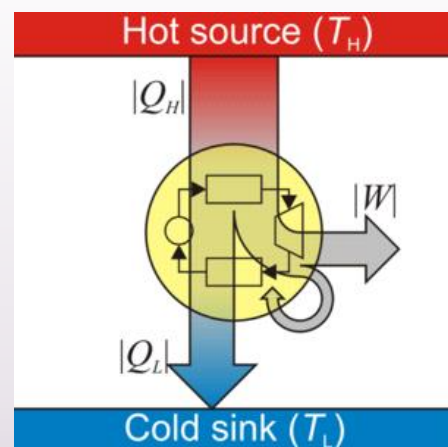
- نحتاج إلى سلسلة من العمليات الترموديناميكية التي تعيد النظام إلى حالته الابتدائية. أي مرور النظام في دورة متصلة cycle.
- كل عملية من عمليات الدورة الترموديناميكية تشتمل على إنجاز شغل أو تدفق حرارة بين النظام والمحيط.
- الوسط المحيط بالنظام عبارة عن مستودعين أحدهما ساخن hot reservoir (درجة حرارته أعلى من درجة حرارة النظام) والآخر بارد cold reservoir (درجة حرارته أقل من درجة حرارة النظام).



## Definitions

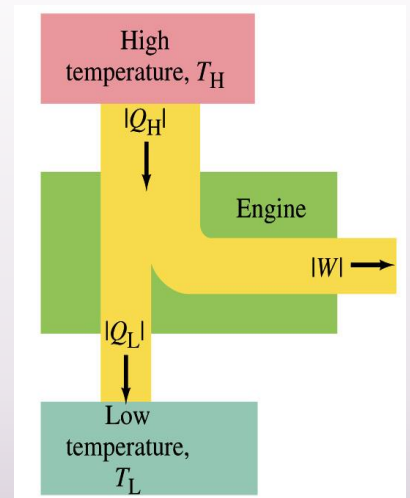
- The **heat** exchange between the system and the hot reservoir (High temperature) is  $|Q_H|$
- The **heat** exchange between the system and the cold reservoir (Low temperature) is  $|Q_L|$
- The **work** exchange between the system and surroundings is  $|W|$

جميع الكميات السابقة لها نفس الوحدة وهي الجول وسوف نتعامل مع القيمة المطلقة لها على أن نهتم بتحديد اتجاهها على المخطط.



# Heat Engine

- If  $|Q_H|$  is larger than  $|Q_L|$  and If  $|W|$  done by the system, then the machine that cause the system to undergo the cycle called a **heat engine**.
- A **heat engine** is a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work.
- Since it is a cyclical process,  $\Delta E_{int} = 0$
- Therefore,  $|W| = |Q_H| - |Q_L|$
- The net work  $|W|$  done by a heat engine equals the net energy transferred to it.



## Thermal Efficiency of a Heat Engine

- Thermal efficiency is defined as the ratio of the net work done by the engine during one cycle to the energy input at the higher temperature.

$$\text{Thermal Efficiency} = \frac{\text{work output}}{\text{heat input}}$$

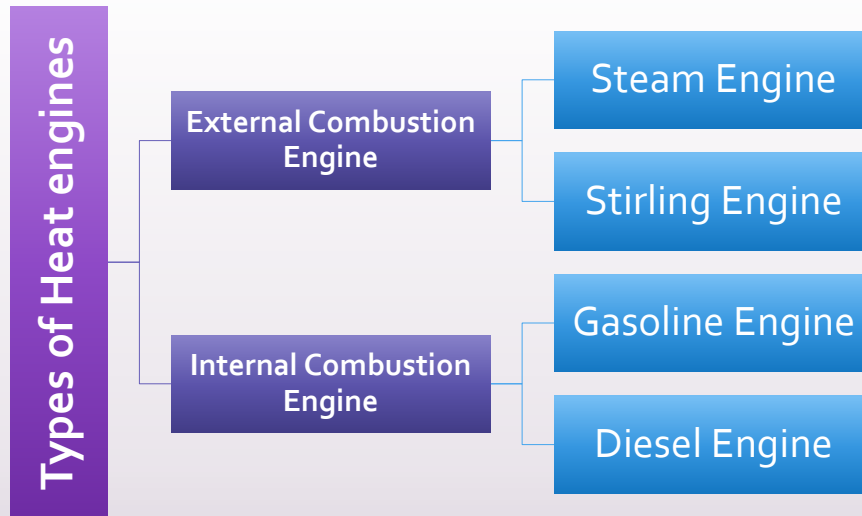
$$\eta = \frac{|W|}{|Q_H|}$$

$$\eta = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

- In practice, all heat engines expel only a fraction of the input energy by mechanical work.
- Therefore, their efficiency is always less than 100%. To have  $\eta = 100\%$ ,  $Q_L$  must be 0

**Perfect Heat Engine (never exist)**

It is impossible to construct such an engine.



## Example 1

An engine transfers  $2.00 \times 10^3 \text{ J}$  of energy from a hot reservoir during a cycle and transfers  $1.50 \times 10^3 \text{ J}$  as exhaust to a cold reservoir.

- **(A)** Find the efficiency of the engine.

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{1.50 \times 10^3 \text{ J}}{2.00 \times 10^3 \text{ J}} = 0.250, \text{ or } 25.0\%$$

- **(B)** How much work does this engine do in one cycle?

$$|W| = |Q_H| - |Q_L| = 2.00 \times 10^3 \text{ J} - 1.50 \times 10^3 \text{ J} = 5.0 \times 10^2 \text{ J}$$

## Problem to solve by yourself

- An engine absorbs 1.70 kJ from a hot reservoir at 277°C and expels 1.20 kJ to a cold reservoir at 27°C in each cycle. (a) What is the engine's efficiency? (b) How much work is done by the engine in each cycle? (c) What is the power output of the engine if each cycle lasts 0.300 s?
- A heat engine takes in 360 J of energy from a hot reservoir and performs 25.0 J of work in each cycle. Find (a) the efficiency of the engine and (b) the energy expelled to the cold reservoir in each cycle.
- A particular heat engine has a mechanical power output of 5.00 kW and an efficiency of 25.0%. The engine expels  $8.00 \times 10^3$  J of exhaust energy in each cycle. Find (a) the energy taken in during each cycle and (b) the time interval for each cycle.

إلى اللقاء مع المحاضرة (٢٠)

***Stirling engine***  
***Gasoline engine***



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# Thermodynamics

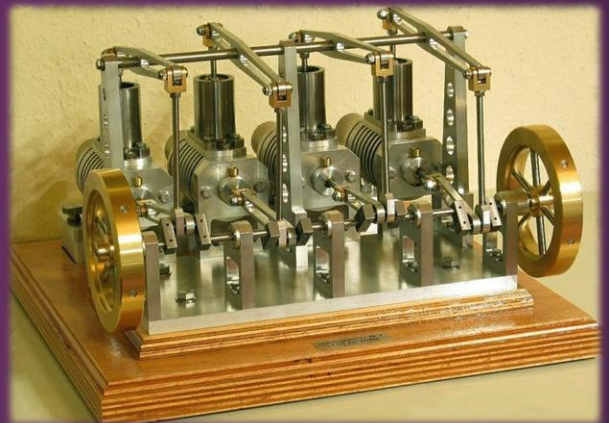
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## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 20: Stirling engine

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

- ❑ Heat Engines and the Second Law of Thermodynamics
  - ❑ Stirling engine
  - ❑ Gasoline engine
- ❑ Heat Pumps and Refrigerators
- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



## Types of Heat engines

External Combustion Engine

Steam Engine

Stirling Engine

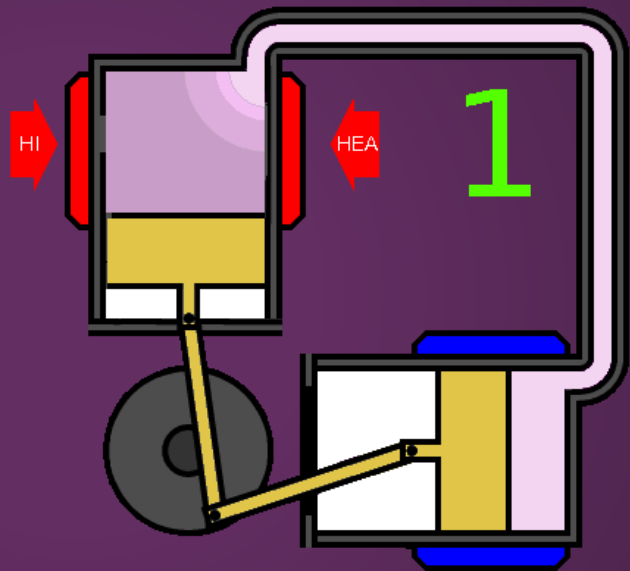
Internal Combustion Engine

Gasoline Engine

Diesel Engine

## Stirling Engine

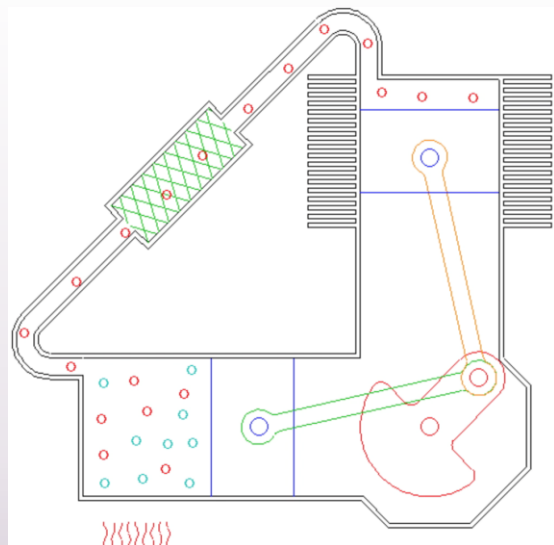
External Combustion Engine



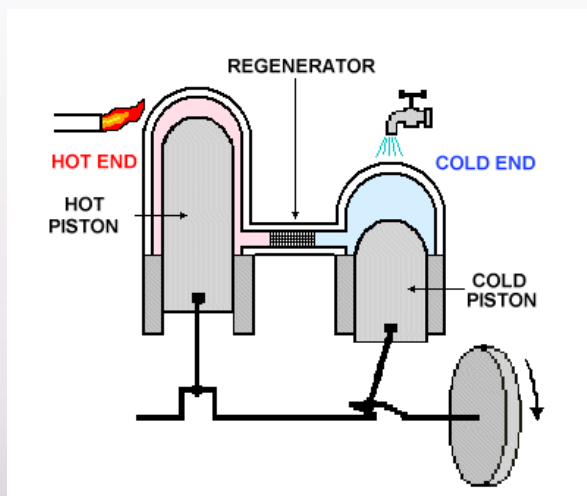
## Stirling engine

- ❑ The Stirling engine was invented and patented by Robert Stirling in 1816.
- ❑ A **Stirling engine** is a heat engine that operates by **cyclic compression and expansion** of air *at different temperatures, such that there is a net conversion of heat energy to mechanical work.*

استخدم هذا المحرك في القطارات والسيارات قبل اكتشاف المحركات ذات الاحتراق الداخلي. ويمتاز محرك ستيرلينج بكفاءته العالية وقلة التلوث الذي يخرج من العادم ولكن تكلفه تصنيعه باهظة.

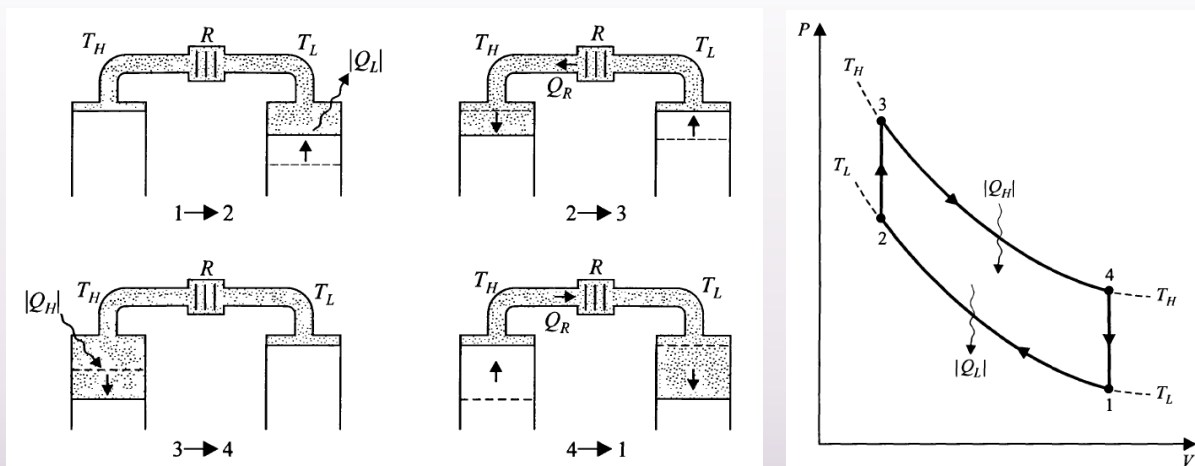


## Principle of Stirling Engine Operation



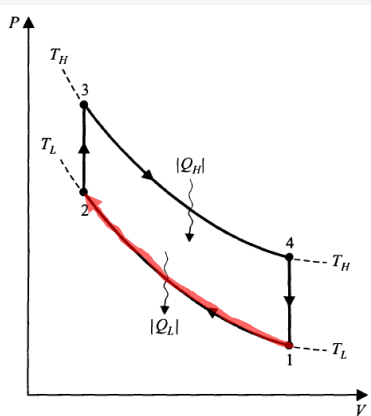
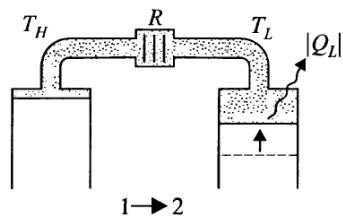
- يتركب هذا المحرك من اسطوانتين cylinder تحتوي كل اسطوانة على مكبس piston متصل بعمود نقل الحركة.
- توجد الاسطوانة الأولى على اليسار كما في الشكل عند المستودع الحراري الساخن والثانية على اليمين عند المستودع الحراري البارد.
- تتصل الاسطوانتين من خلال أنبوب يوجد في وسطه مادة عازلة لتفصل بين المنطقة الباردة والحرارة تسمى regenerator.
- يوجد غاز الهيدروجين او الهيليوم (النظام) بين الاسطوانتين ومحصور من خلال المكبسين.

تتكون دورة عمل محرك ستيرلينج من خلال اربع مراحل موضحة في الشكل أعلاه وممثلة على منحنى الضغط والحجم PV Diagram.



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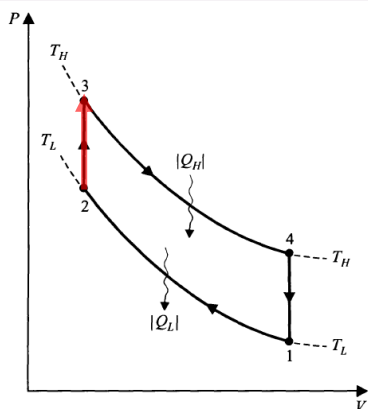
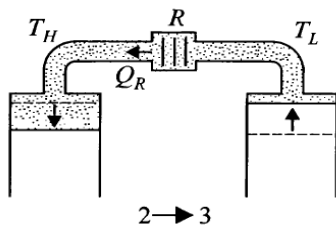
## المرحلة الأولى

□ عندما يكون المكبس الأيسر ثابت في أعلى مستوى له يتحرك المكبس الأيمن إلى الأعلى إلى منتصف الاسطوانة ضاغطاً الغاز الذي يفقد كمية حرارة  $Q_L$  إلى المستودع البارد، وتكون عملية ضغط الغاز في هذه المرحلة تحت درجة حرارة ثابتة عند  $T_L$ . ويقل الحجم ويزداد الضغط.

□ تمثل هذه المرحلة على منحنى PV بالمسار 1 إلى 2

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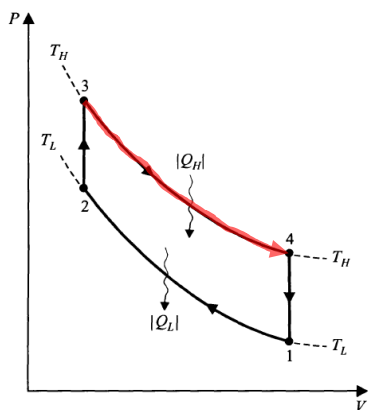
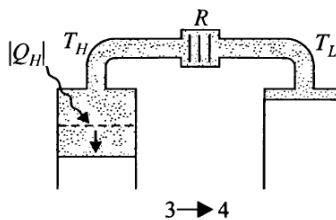


### المرحلة الثانية

□ يتحرك المكبس الأيسر للأسفل بينما يستمر المكبس الأيمن في الحركة للأعلى وهذا يعني أن حجم الغاز يبقى ثابتاً.

□ ينتقل الغاز من الجانب البارد إلى الجانب الحار عبر ال regenerator، ترتفع درجة حرارة الغاز إلى  $T_H$  ويزداد ضغطه مع ثبوت الحجم.

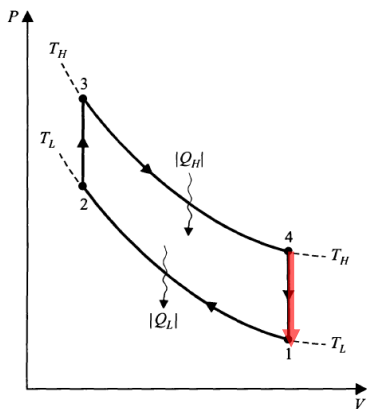
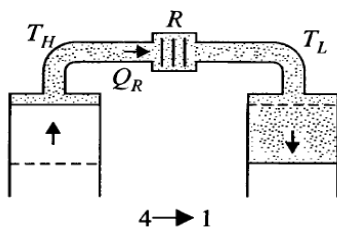
□ تمثل هذه المرحلة على منحنى PV بالمسار 2 إلى 3



### المرحلة الثالثة

□ يتحرك المكبس الأيسر للأسفل بينما يثبت المكبس الأيمن عند أعلى مستوى له ويمتص الغاز حرارة من المستودع الحار  $Q_H$  ويزداد حجمه ويقل ضغطه عند ثبوت درجة الحرارة عند  $T_H$ .

□ تمثل هذه المرحلة على منحنى PV بالمسار 3 إلى 4



### المرحلة الرابعة

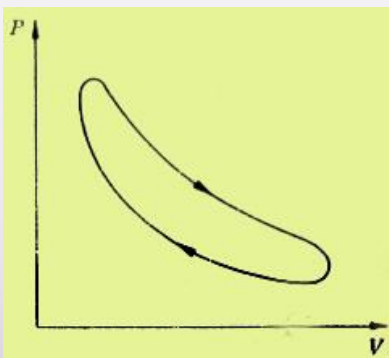
□ يتحرك المكبس الأيسر للأعلى ويتحرك المكبس الأيمن إلى الأسفل وعندها يكون حجم الغاز ثابتاً.

□ ينتقل الغاز إلى الاسطوانة على اليمين عند المستودع البارد وتقل درجة حرارته إلى  $T_L$  وضغطه ينخفض ويعود الغاز إلى وضعه الابتدائي لتكرار الدورة من جديد.

□ تمثل هذه المرحلة على منحنى PV بالمسار 4 إلى 1

▪ يمكن تلخيص الدورة السابقة لمحرك ستيرلينج على أن امتصاص الحرارة  $Q_H$  عند درجة حرارة  $T_H$  وفقدان حرارة  $Q_L$  عند درجة حرارة  $T_L$  والفرق هو مقدار الشغل الذي بذله الغاز على المحيط الخارجي (المكبس المتصل بعمود نقل الحركة).

$$|W| = |Q_H| - |Q_L|$$

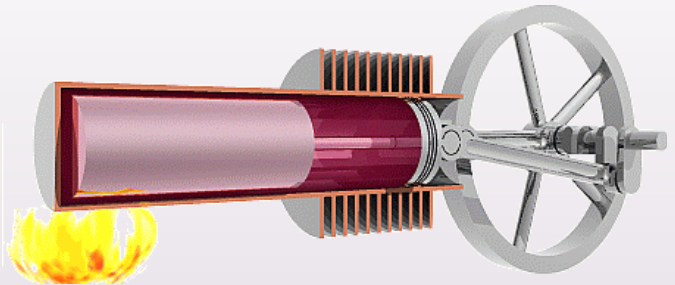


▪ تجدر الإشارة هنا إلى أن العديد من الافتراضات تم اعتبارها أثناء شرح فكرة عمل دورة ستيرلينج وتمثيلها على منحنى الضغط والحجم ومن هذه الافتراضات ما يلي:

▪ (1) أن الغاز مثالي (2) لا يوجد تسرب للغاز من المكبس (3) لا يوجد فقد حراري من الاسطوانة إلى الخارج (4) لا يوجد احتكاك

▪ وعليه فإن الشكل الأقرب للواقع لدورة ستيرلينج إذا أخذنا في الاعتبار العوامل السابقة فإنها كما في الشكل الموضح.

## Stirling Engine in Action



إلى اللقاء مع المحاضرة (٢١)

***Gasoline engine***



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# Thermodynamics

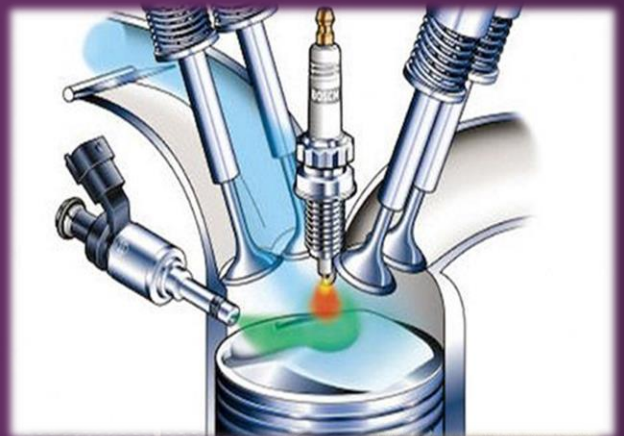
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## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 21: Gasoline engine

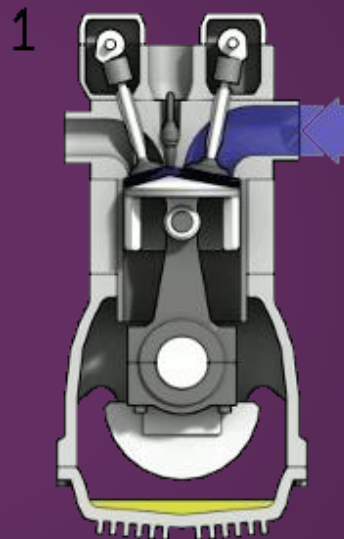
## Unit 4: Engines, Refrigerators and the second law of thermodynamics

- ❑ Heat Engines and the Second Law of Thermodynamics
  - ❑ Stirling engine
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- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



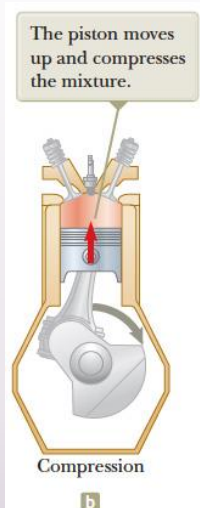
# Gasoline Engine

## Internal Combustion Engine



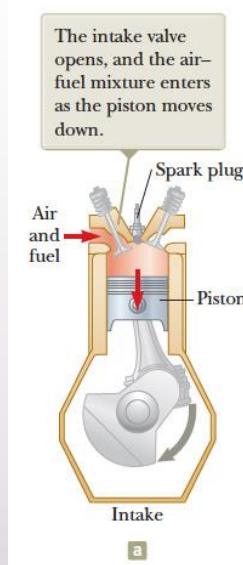
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### (2) مرحلة الانضغاط Compression Stroke

يغلق صمام الأخذ عندما يبدأ المكبس في الحركة للأعلى ليضغط خليط الوقود والهواء وترتفع درجة حرارته تدريجياً ليساعد على رفع كفاءة الاحتراق.

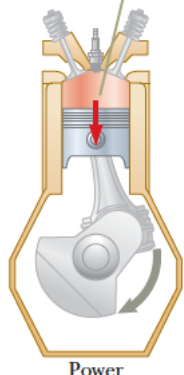


### (1) مرحلة الأخذ Intake Stroke

يبدأ المكبس عمله في الحركة من أعلى موضع له ليتحرك إلى الأسفل حيث يكون صمام الإدخال Intake valve مفتوحاً ليدخل خليط من الوقود والهواء إلى داخل اسطوانة الاحتراق.

تكون نسبة الوقود صغيرة بالنسبة للهواء ولكن كافية لإحداث الاحتراق.

The hot gas pushes the piston downward.



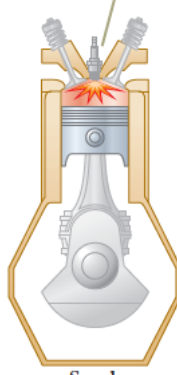
Power

d

#### Power (4) مرحلة القوة Stroke

يدفع الغاز المكبس بقوة للأسفل. مما ينتج عنه انخفاض الضغط ودرجة الحرارة.

The spark plug fires and ignites the mixture.



Spark

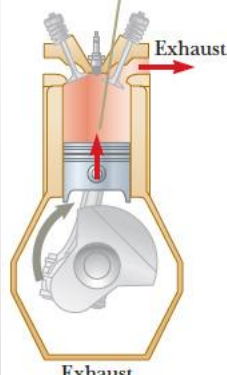
c

#### Ignition (3) مرحلة الاحتراق Stroke

في اللحظة التي يصل فيها المكبس إلى أعلى ارتفاع له يصبح الخليط عند ضغط عالي تنطلق شرارة كهربائية لينتج عنها احتراق (انفجار) للوقود المكون للخليط.

ترتفع كلا من درجة الحرارة والضغط ارتفاعاً هائلاً وتكون هذه المرحلة تحت حجم ثابت لان العملية تتم بسرعة.

The piston moves up and pushes the remaining gas out.



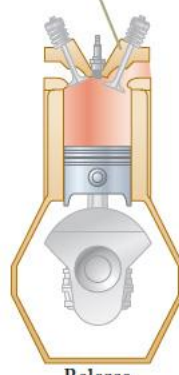
Exhaust

f

#### Exhaust (6) مرحلة العادم Stroke

يتحرك المكبس إلى الأعلى نتيجة لدوران ناقل الحركة طاردا ما تبقى من نواتج الاحتراق ليبدأ دورة جديدة بسحب كمية جديدة من الهواء والوقود.

The exhaust valve opens, and the residual gas escapes.



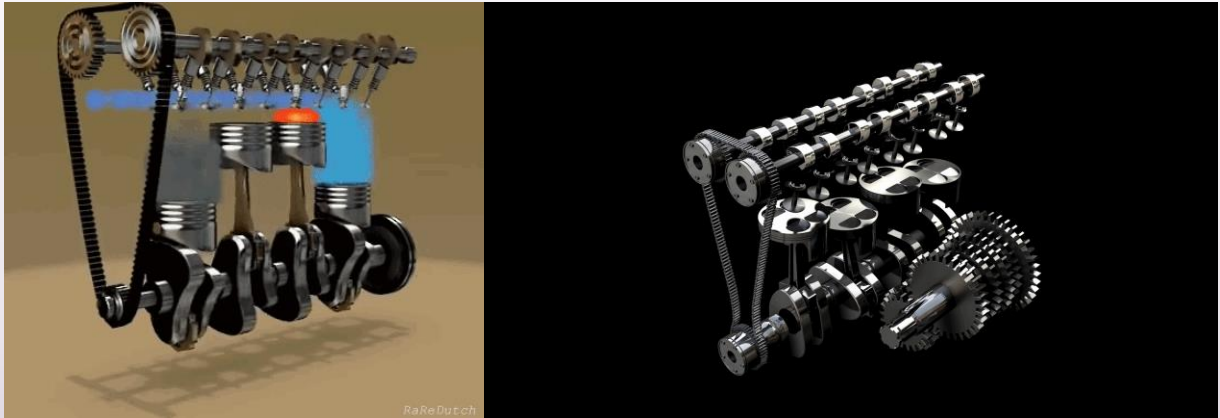
Release

e

#### (5) مرحلة صمام العادم Exhaust

عندما يصل المكبس في حركته للأسفل إلى أدنى قيمة له يفتح صمام العادم لتخرج نواتج الاحتراق من المكبس ومنه إلى العادم.

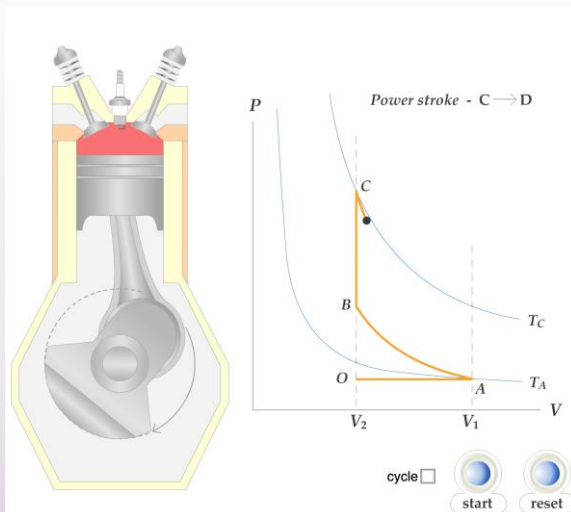
# Gasoline Engine in Action



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## Otto Cycle



The behavior of a gasoline engine can be approximated by assuming a set of ideal conditions

- (1) The system is at all times air.
- (2) All processes are quasi-static.
- (3) There is no friction.
- (4) There is no loss of heat through the walls of the piston.
- (5) The processes are reversible.

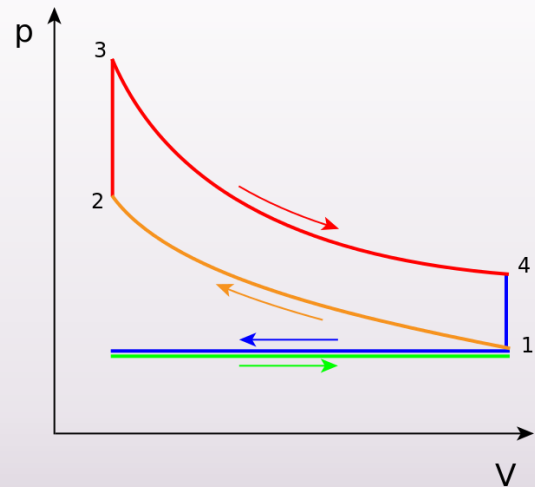
These assumptions lead to idealized Otto cycle plotted on a PV diagram.

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# Otto Cycle

- Process 0–1 intake stroke
- Process 1–2 compression stroke
- Process 2–3 ignition phase
- Process 3–4 expansion stroke
- Process 4–1 idealized heat rejection
- Process 1–0 exhaust stroke

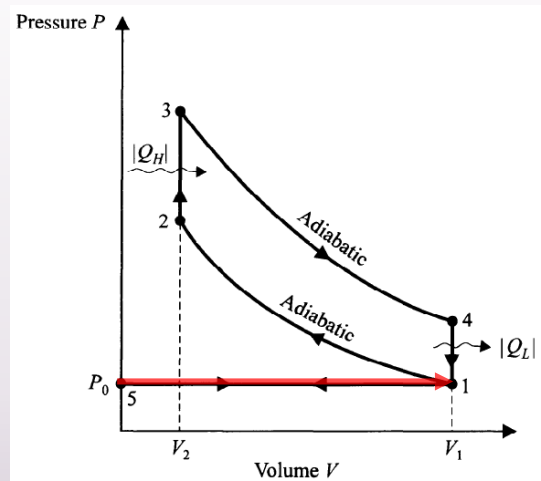


## The Efficiency of Otto Cycle

- Process 5 → 1 represents intake stroke, the volume of the piston varies from zero to  $V_1$  as the number of moles varies from zero to  $n$ , according to the equation

$$P_0 V = nRT_1$$

- $P_0$  is the atmospheric pressure and  $T_1$  is the temperature of the air outside.

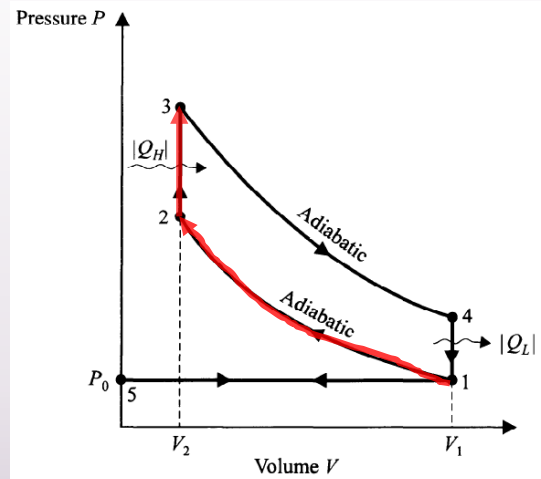


## The Efficiency of Otto Cycle

- Process 1 → 2 represents adiabatic compression stroke. Temperature rise from  $T_1$  to  $T_2$  according to the equation

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

- Process 2 → 3 isochoric increase of temperature and pressure of  $n$  moles of air. The system absorbed heat  $|Q_H|$  and the temperature increased from  $T_2$  to  $T_3$ .

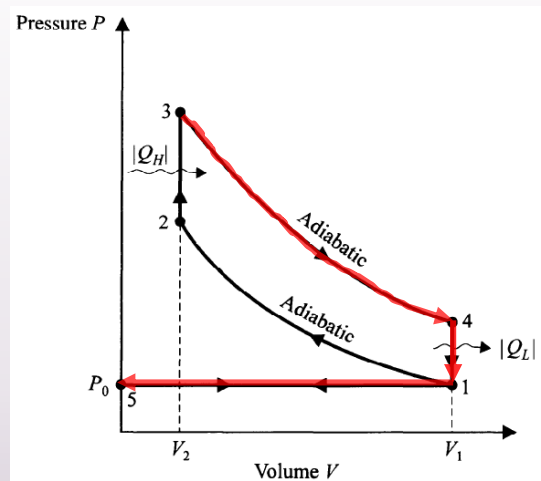


## The Efficiency of Otto Cycle

- Process 3 → 4 represents adiabatic Power stroke. Temperature rise from  $T_3$  to  $T_4$  according to the equation

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

- Process 4 → 1 isochoric decrease of temperature and pressure of  $n$  moles of air. The system reject heat  $|Q_L|$  and the temperature decrease from  $T_4$  to  $T_1$ .
- Process 1 → 5 represents the exhaust stroke, isobaric at atmospheric pressure. Both  $V_1$  and  $n$  varies to zero.



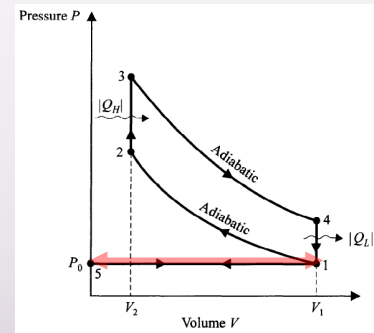
# The Efficiency of Otto Cycle

- The isobaric processes  $5 \rightarrow 1$  and  $1 \rightarrow 5$  cancel each other.
- The remaining 4 processes only two involve a flow of heat. Absorption of  $|Q_H|$  in the process  $2 \rightarrow 3$ , and rejection of  $|Q_L|$  in the process  $4 \rightarrow 1$

$$|Q_H| = \int_{T_2}^{T_3} C_V dT = C_V(T_3 - T_2)$$

$$|Q_L| = - \int_{T_4}^{T_1} C_V dT = C_V(T_4 - T_1)$$

□ Thermal Efficiency  $\eta = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$



From the equation during the adiabatic processes

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

By division both equation

$$\frac{T_1}{T_4} = \frac{T_2}{T_3}$$

Multiply by -1 both side and add  $\frac{T_4}{T_4}$  to the right side and add  $\frac{T_3}{T_3}$  to the left side

$$\frac{T_4 - T_1}{T_4} = \frac{T_3 - T_2}{T_3}$$

$$\frac{T_4 - T_1}{T_3 - T_2} = \frac{T_4}{T_3} = \frac{T_1}{T_2}$$

$$\eta = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

$$\eta = 1 - \frac{T_1}{T_2}$$

- $T_1$  and  $T_2$  are the temperatures at the beginning and end of the compression stroke.
- Thermal efficiency of gasoline engine working in Otto cycle depends on the temperature before and after compression.
- If  $T_1 = 300\text{K}$  and  $T_2 = 580\text{ K}$  the efficiency is 48%.
- This is the optimum efficiency for ideal gasoline engine. The actual efficiency is in the range of 20% to 30%.

## Problem to solve by yourself

- Show that the thermal efficiency of an engine operating in an idealized Otto cycle is given by Equation

$$\eta = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

- An engine absorbs 1.70 kJ from a hot reservoir at 277°C and expels 1.20 kJ to a cold reservoir at 27°C in each cycle. (a) What is the engine's efficiency? (b) How much work is done by the engine in each cycle? (c) What is the power output of the engine if each cycle lasts 0.300 s?
- A heat engine takes in 360 J of energy from a hot reservoir and performs 25.0 J of work in each cycle. Find (a) the efficiency of the engine and (b) the energy expelled to the cold reservoir in each cycle.

إلى اللقاء مع المحاضرة (٢٢)

***Heat Pumps and Refrigerators***

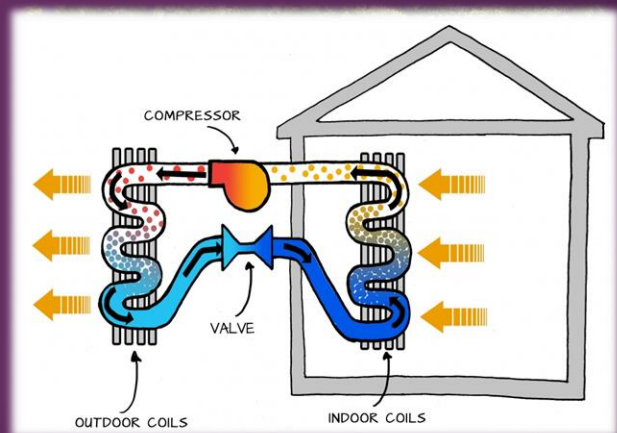


## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 22: Heat Pumps and Refrigerators

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

- ❑ Heat Engines and the Second Law of Thermodynamics
  - ❑ Stirling engine
  - ❑ Gasoline engine
- ❑ **Heat Pumps and Refrigerators**
- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



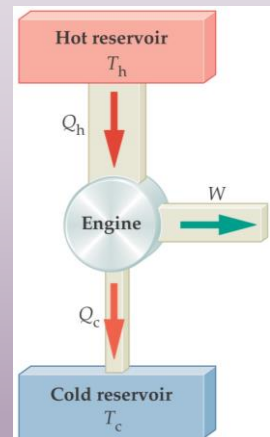
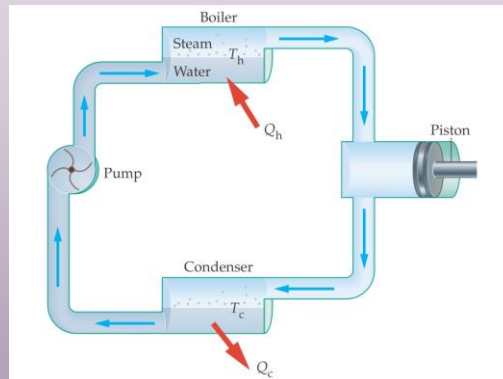
## Heat Engine, review

The **heat engine** is a machine that takes a working substance through a **cycle** in such a sequence of processes that some **heat is absorbed by the system from a high-temperature heat reservoir**, a **smaller amount of heat is rejected to a low-temperature heat reservoir**, and the a **net amount of work is done by the system on the surrounding**.

All heat engines have:

- Working substance
- High-temperature reservoir
- Low-temperature reservoir
- Cyclical engine

What if we wanted to transfer energy from the cold reservoir to the hot reservoir?



## Heat Pump or Refrigerator

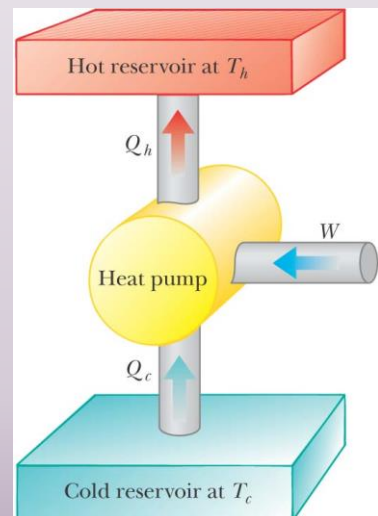
Refrigerator is a machine perform a cycle of sequence of processes **opposite** to the heat engine, i.e. some **heat is absorbed by the system from a heat reservoir at a low temperature**, a larger amount of heat is rejected to a heat reservoir at a **high temperature** and a **net amount of work is done on the system**.

ويسمى النظام الذي يقوم بدورة التبريد في الثلاجة باسم Refrigerant

$|Q_H|$  represents the amount of **heat rejected** by the refrigerant to the high-temperature reservoir

$|Q_L|$  represents the amount of **heat absorbed** by the refrigerant from the low-temperature reservoir

$|W|$  represents the net **work done on** the refrigerant by the surrounding

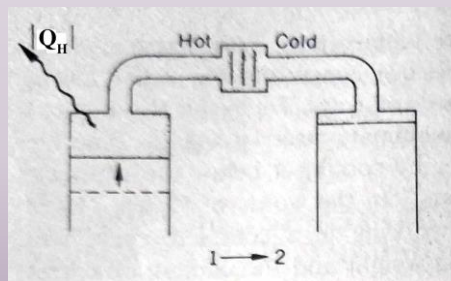
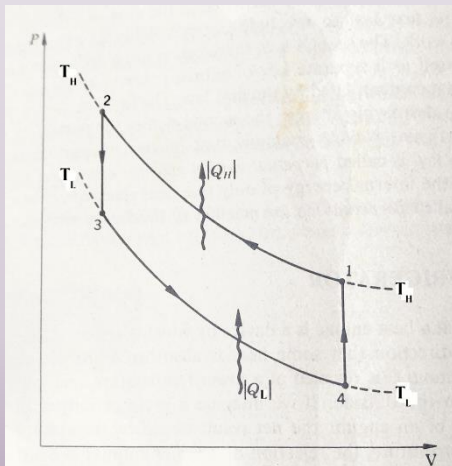


## Refrigerator Cycle (Sterling Refrigerator)

□ لتوضيح فكرة عمل الثلاجة سنقوم باستخدام محرك ستيرلنج ولكن من خلال عكس دورة عمله التي سبق وأن شرحناها في المحاضرة (٢٠).

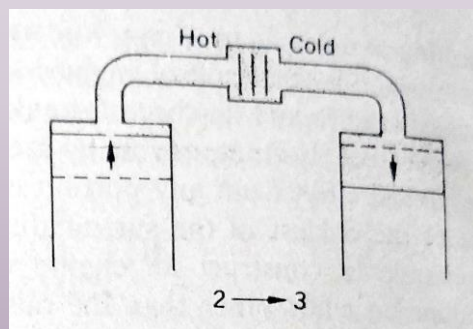
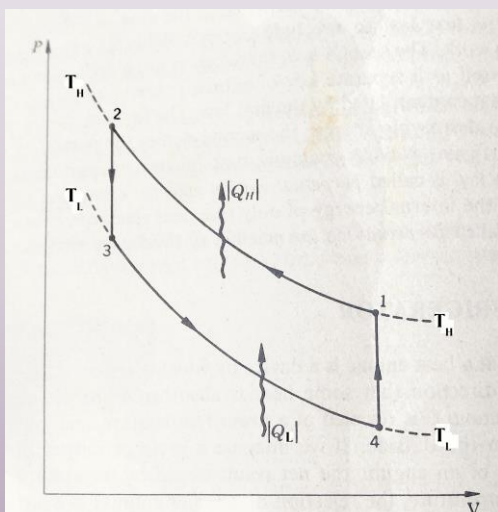
### □ المرحلة من 1 إلى 2

بينما يكون المكبس الأيمن ثابتاً يتحرك المكبس الأيسر إلى الأعلى ضاغطاً الغاز في عملية عند درجة حرارة ثابتة، ويفقد النظام كمية حرارة  $Q_H$  إلى المستودع الحار.



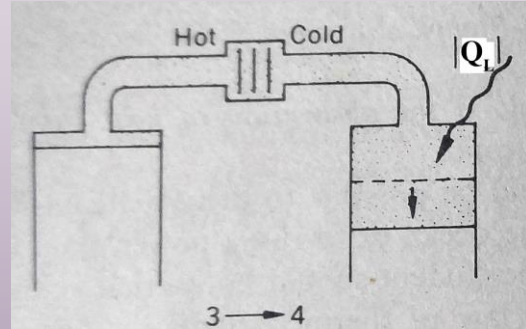
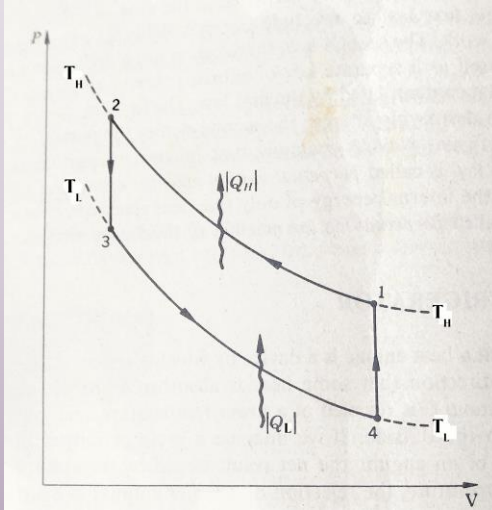
### □ المرحلة من 2 إلى 3

كلًا من المكسبين يتحركان في اتجاهين متعاكسين حيث يستمر المكبس الأيسر في الحركة إلى الأعلى ويتحرك المكبس الأيمن إلى الأسفل، وهنا يكون التغير في الحجم ثابتاً، وينتقل الغاز من الأسطوانة على اليسار إلى الأسطوانة على اليمين حيث المستودع البارد وتنخفض درجة الحرارة من  $T_H$  إلى  $T_L$  ويقل الضغط.



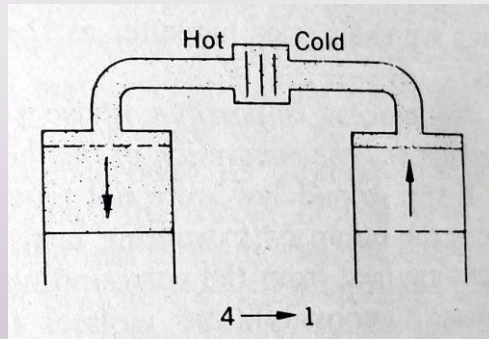
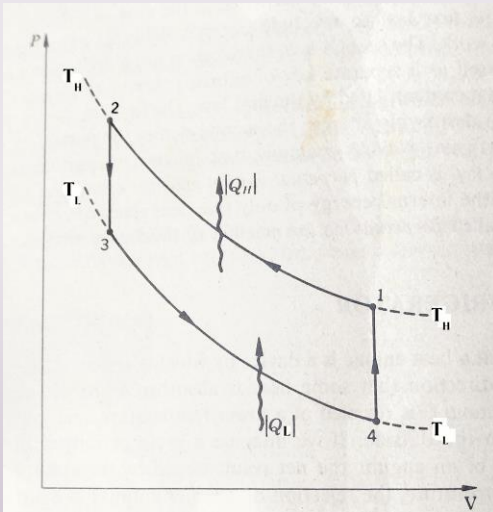
### □ المرحلة من 3 إلى 4

يُثبت المكبس الأيسر في أعلى مستوى له بينما يستمر المكبس الأيمن في الحركة نحو الأسفل نتيجة لتمدد الغاز في المكبس، ويمتص الغاز حرارة من المستودع البارد وتكون العملية تحت درجة حرارة ثابتة، وفي هذه العملية ينخفض الضغط ويزداد الحجم.



### □ المرحلة من 4 إلى 1

يتحرك المكبس في اتجاهين متعاكسين وتكون العملية في هذه المرحلة تحت حجم ثابت بحيث ينتقل الغاز من الأسطوانة اليمنى إلى الأسطوانة اليسرى، ويزداد الضغط وترتفع درجة الحرارة من  $T_L$  إلى  $T_H$ .



## معامل الإنجاز للتلاجة Coefficient of Performance

- The effectiveness of a heat pump is described in terms of a number called the **coefficient of performance (COP)**. In the heating mode, the COP is defined as the ratio of the energy transferred to the hot reservoir to the work required to transfer that energy:

$$COP = \frac{\text{energy transferred at high temperature}}{\text{work done by the heat pump}}$$

$$COP (\text{heating mode}) = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}$$

Because  $Q_H$  is generally greater than  $W$ , typical values for the COP are greater than unity.

- For a heat pump operating in the cooling mode, we define the COP in terms of  $Q_L$ :

$$COP = \frac{\text{heat absorbed from cold reservoir}}{\text{work done on refrigerant}}$$

$$COP (\text{cooling mode}) = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

A good refrigerator should have a high COP, typically 5 or 6

### Example 1

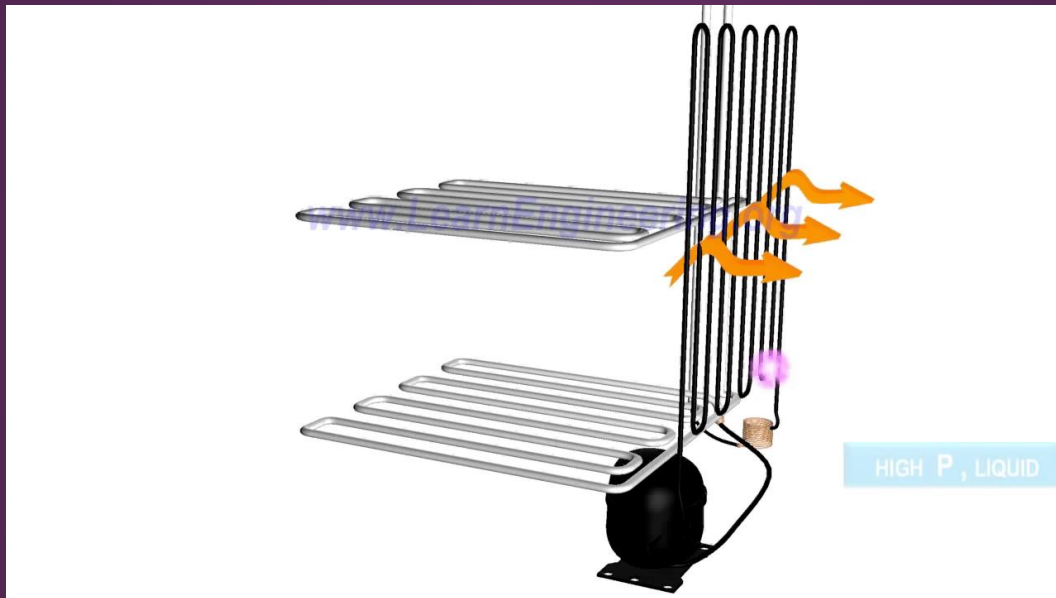
If the coefficient of performance of a refrigerator is 5 find the ratio of the heat rejected to the work done on the refrigerant.

$$COP = \frac{Q_L}{W} = 5 \quad \text{and} \quad Q_L = Q_H - W$$

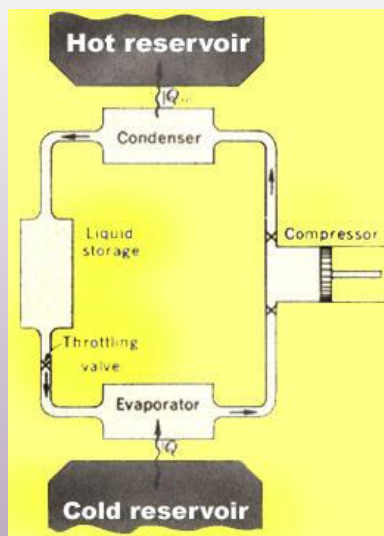
$$\frac{Q_H - W}{W} = 5$$

$$\frac{Q_H}{W} = 6 \quad \rightarrow \quad Q_H = 6W$$

إذا كانت المضخة الحرارية تعمل من خلال مولد كهربائي، فهذا يعني أنه مقابل كل 1 جول شغل يبذله المولد يحرر 6 جول من الطاقة الحرارية. وهذه الفكرة طرحها العالم كلفن في 1852 لتدفئة منزله في سكتلندا.



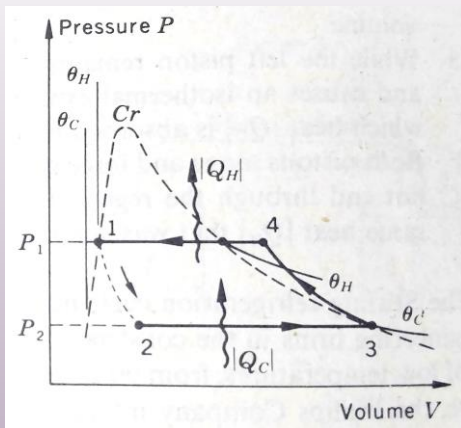
## الثلاجة المنزلية Home Refrigerator



تعمل الثلاجة المنزلية بالحفاظ على درجة حرارة منخفضة للمواد داخل الثلاجة حيث يكون داخل الثلاجة هو المستودع البارد

تقوم فكرة عمل الثلاجة المنزلية من خلال دورة غاز الفريون والذي تم اختياره لمواصفاته المناسبة للتبريد حيث أن غاز الفريون النقطة الحرجة له عند درجة حرارة الغرفة والضغط الجوي.

يكون غاز الفريون في البداية في الحالة السائلة ومتواجد في Liquid storage وعند تشغيل الثلاجة فإن ال Compressor يقوم ببذل شغل على الغاز لدفعه من خلال صمام ال Throttling الذي يحول السائل ذو الضغط المرتفع إلى رزاز عند ضغط اقل وتنخفض درجة حرارته، وعندما يصل إلى ال Evaporator يكتسب الفريون حرارة  $Q_L$  من المستودع البارد (داخل الثلاجة) وتحت تأثير المضخة Compressor ينتقل الغاز إلى المكثف Condenser حيث يتكثف غاز الفريون على سطح المكثف ويتردد حرارة  $Q_H$  إلى المستودع الحار ويتحول الغاز إلى سائل ويعود السائل إلى Liquid storage لتتكرر الدورة السابقة.



يوضح الشكل المقابل غاز الفريون في الثلاجة المنزلية على منحنى الضغط والحجم والتي تتكون من المراحل التالية:

- **المرحلة من 1 إلى 2** عملية تحويل السائل إلى رزاز throttling process والتي ينخفض فيها الضغط ودرجة الحرارة.
- **المرحلة من 2 إلى 3** تبخر السائل عند درجة حرارة ثابتة وضغط ثابت حيث يمتص الغاز كمية حرارة  $Q_L$  من المستودع البارد يؤدي إلى تبريد المواد داخل الثلاجة.
- **المرحلة من 3 إلى 4** ضغط الغاز في عملية اديباتيكية ترتفع درجة حرارة الغاز إلى درجة أعلى من  $T_H$ .
- **المرحلة من 4 إلى 1** عند ضغط ثابت تنخفض درجة حرارة الغاز نتيجة تكثفه إلى  $T_H$ .

## Example 2

- A certain refrigerator has a COP of 5.00. When the refrigerator is running, its power input is 500W. A sample of water of mass 500g and temperature 20.0°C is placed in the freezer. How long does it take to freeze the water to ice at 0°C? Assume that all other parts of the refrigerator stay at the same temperature and there is no leakage of energy from the exterior, so that the operation of the refrigerator results only in energy being extracted from the water.
- تقوم فكرة ايجاد الزمن اللازم لإتمام هذه العملية على معدل سحب الطاقة الحرارية من الماء والذي يعتمد بدوره على قدرة الثلاجة. سنقوم في البداية بحساب الحرارة اللازمة سحبها من 500 جرام من الماء عند 20 درجة مئوية إلى ثلج عند درجة صفر.

$$Q_L = mc\Delta T + mL_f = m(c\Delta T + L_f)$$

$$Q_L = (0.500 \text{ kg})[(4186 \text{ J/kg C})(20.0 \text{ C}) + 3.33 \times 10^5 \text{ J/kg}] = 2.08 \times 10^5 \text{ J}$$

## Example 2, continue

- الآن نحتاج ان نقوم بحساب الشغل اللازم (الطاقة) التي يجب ان نزودها للثلاجة لتقوم بسحب مقدرا  $Q_L$  من الطاقة الحرارية وسوف نستخدم معادلة معامل انجاز الثلاجة

$$COP = \frac{Q_L}{W} \quad \rightarrow \quad W = \frac{Q_L}{COP} = \frac{2.08 \times 10^5 \text{ J}}{5}$$

$$W = 4.17 \times 10^4 \text{ J}$$

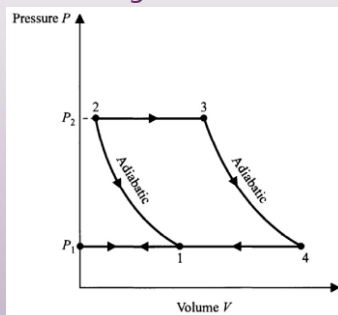
- والآن من قدرة الثلاجة 500W نستطيع ان نقدر الزمن اللازم لتلك العملية

$$P = \frac{W}{\Delta t} \quad \rightarrow \quad \Delta t = \frac{4.17 \times 10^4 \text{ J}}{500} = 83.3 \text{ s}$$

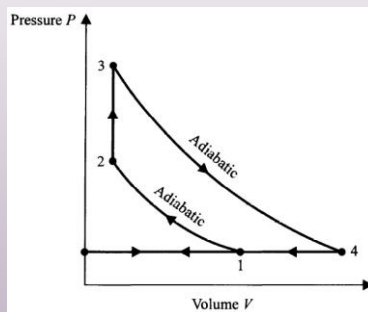
- هل من تفسير للزمن القصير الذي يختلف تماما عن ما نلاحظه عمليا!

## Problem to solve by yourself

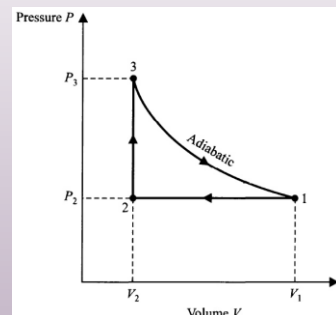
Prove that the efficiency of the following PV diagrams which represents cycles of different engines.



$$\eta = 1 - \left( \frac{P_1}{P_2} \right)^{(\gamma-1)/\gamma}$$



$$\eta = 1 - \gamma \frac{T_4 - T_1}{T_3 - T_2}$$



$$\eta = 1 - \gamma \left( \frac{(V_1/V_2) - 1}{(P_3/P_2) - 1} \right)$$

إلى اللقاء مع المحاضرة (٢٣)

***Reversible and Irreversible Processes***  
***The Carnot Engine***

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# Carnot Cycle

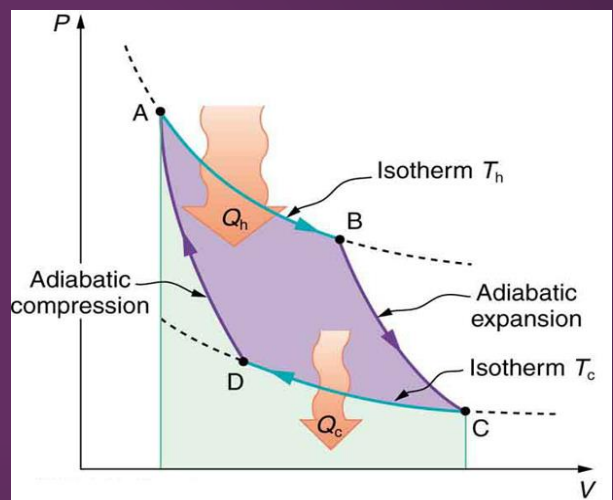
Dr. Hazem Falah Sakeek  
Al-Azhar University - Gaza

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 23: Reversible and Irreversible Processes and The Carnot Engine

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

- ❑ Heat Engines and the Second Law of Thermodynamics
  - ❑ Stirling engine
  - ❑ Gasoline engine
- ❑ Heat Pumps and Refrigerators
- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



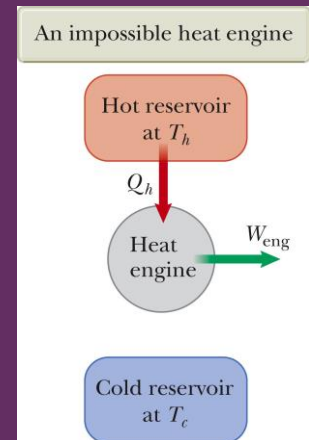
# Second Law of Thermodynamics

## Kelvin-Planck Form

- ✓ It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work.

## Clausius Form

- ✓ It is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from one object to another object at a higher temperature without the input of energy by work.
- ✓ Or – energy does not transfer spontaneously by heat from a cold object to a hot object.



## Perfect Heat Engine (never exist)

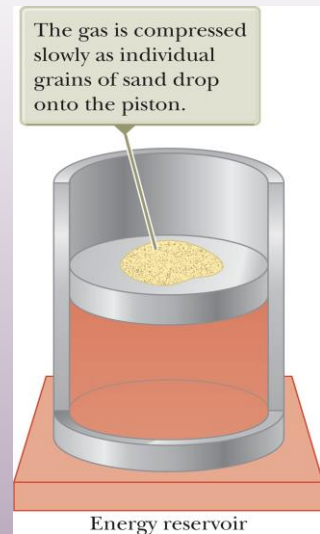
It is impossible to construct such an engine.

# Reversible and Irreversible Processes

- A **reversible process** the system undergoing the process can be returned to its initial conditions along the same path on a  $PV$  diagram, and every point along this path is an equilibrium state.
- An **irreversible process** does not meet these requirements.
  - All natural processes are known to be irreversible.
  - Reversible processes are an idealization, but some real processes are good approximations.
- A **real process** that is a good approximation of a reversible one will occur very slowly.
  - The system is always very nearly in an equilibrium state.
- A general characteristic of a reversible process is that there are **no dissipative** effects (friction or turbulence) that convert mechanical energy to internal energy present.

# Reversible and Irreversible Processes, Summary

- ❑ The reversible process is an idealization.
- ❑ All real processes on Earth are irreversible.
- ❑ Example of an approximate reversible process:
  - ❑ The gas is compressed isothermally
  - ❑ The gas is in contact with an energy reservoir
  - ❑ Continually transfer just enough energy to keep the temperature constant



Given that, an interesting question to ask is: If we put all engineering and practical issues aside, **what is the most efficient engine that you can make as far as physics is concerned?**



## Carnot Engine

- In 1824, a French engineer named Sadi Carnot became interested in this question.
- The result was a theoretical engine called the **Carnot engine** that operates in a cycle consisting of two **isothermal processes** and two **adiabatic processes**
- A heat engine operating in an **ideal, reversible** cycle (now called a Carnot cycle) between two reservoirs is the most efficient engine possible.
- This sets an upper limit on the efficiencies of all other engines **because it is a perfectly reversible cycle**.



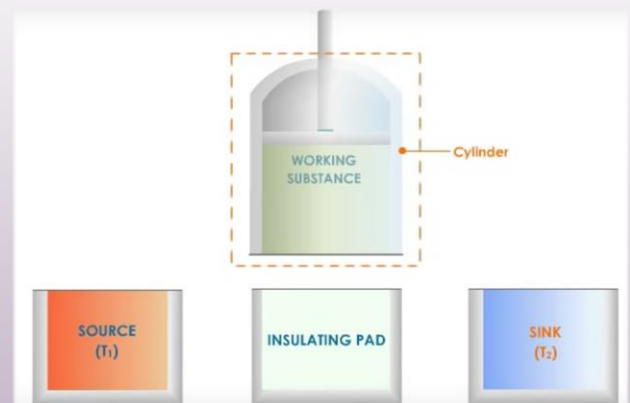
**Sadi Carnot**  
1796 – 1832  
French engineer

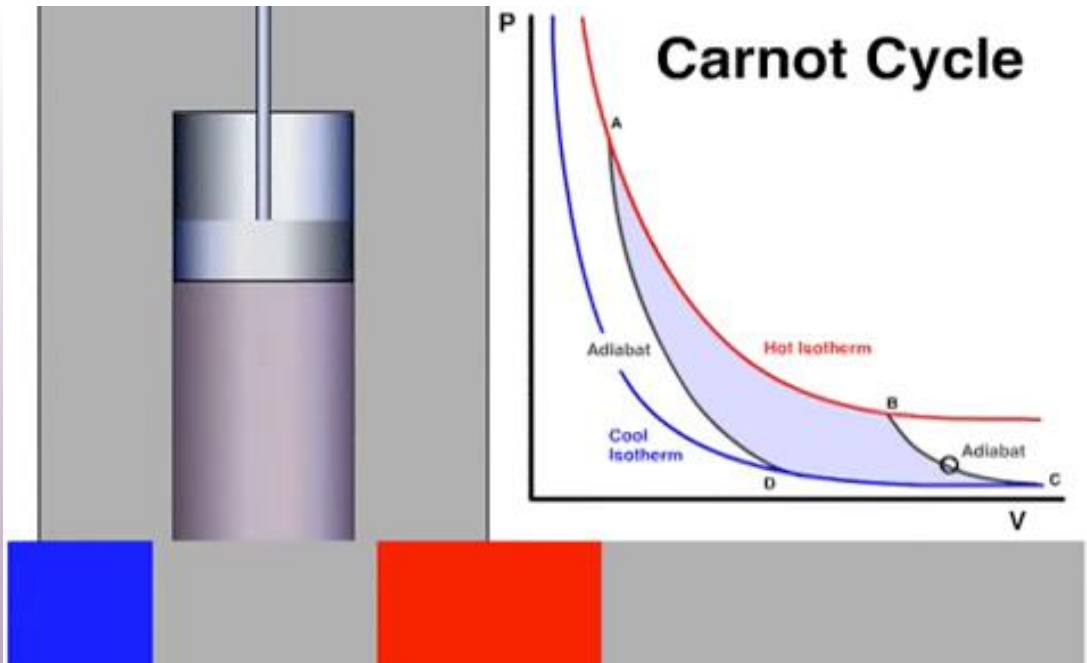
First to show quantitative relationship between work and heat.

## Carnot's Theorem

Unfortunately, as a practical engine, the Carnot engine rather useless. Actually it's impossible to get it to work at all because any real process is not perfectly reversible. Still, on paper at least, this is the most efficient engine you can possibly make, which makes it very useful.

*No real (irreversible) heat engine operating between two energy reservoirs can be more efficient than a Carnot (reversible) engine operating between the same two reservoirs.*





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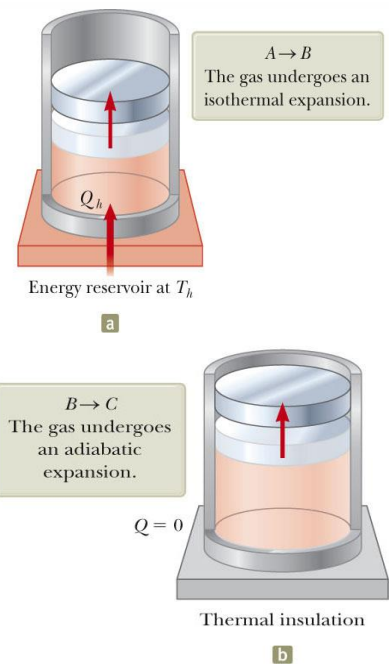
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## Carnot Cycle, A to B

- $A \rightarrow B$  is an isothermal expansion.
- The gas is placed in contact with the high temperature reservoir,  $T_H$ .
- The gas absorbs heat  $|Q_H|$ .
- The gas does work  $W_{AB}$  in raising the piston.

## Carnot Cycle, B to C

- $B \rightarrow C$  is an adiabatic expansion.
- The base of the cylinder is replaced by a thermally nonconducting wall.
- No energy enters or leaves the system by heat.
- The temperature falls from  $T_H$  to  $T_L$ .
- The gas does work  $W_{BC}$ .

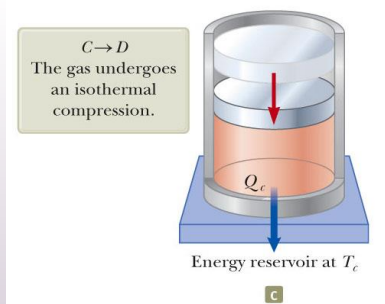


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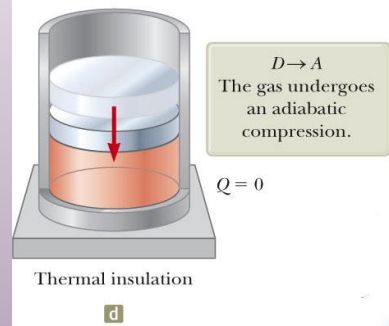
## Carnot Cycle, C to D

- $C \rightarrow D$  is an isothermal compression.
- The gas is placed in thermal contact with the cold temperature reservoir.
- The gas expels energy  $|Q_c|$ .
- Work  $W_{CD}$  is done on the gas.



## Carnot Cycle, D to A

- $D \rightarrow A$  is an adiabatic compression.
- The base is replaced by a thermally nonconducting wall.
  - So no heat is exchanged with the surroundings.
- The temperature of the gas increases from  $T_L$  to  $T_H$ .
- The work done on the gas is  $W_{DA}$ .



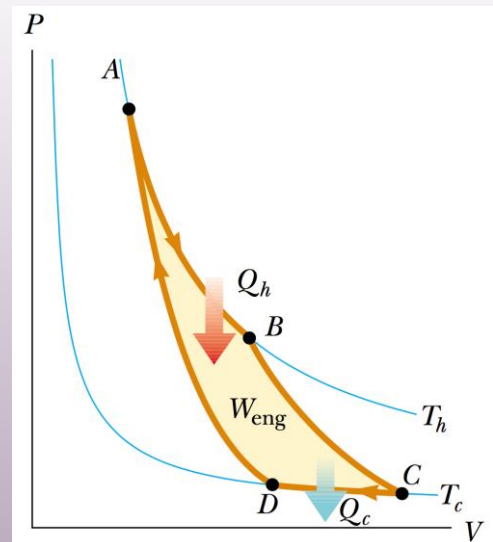
## The four steps of the Carnot cycle

process  $A \rightarrow B$  is an isothermal expansion at  $T_H$

Process  $B \rightarrow C$  is an adiabatic expansion

Process  $C \rightarrow D$  is an isothermal compression at  $T_L$

Process  $D \rightarrow A$  is an adiabatic compression

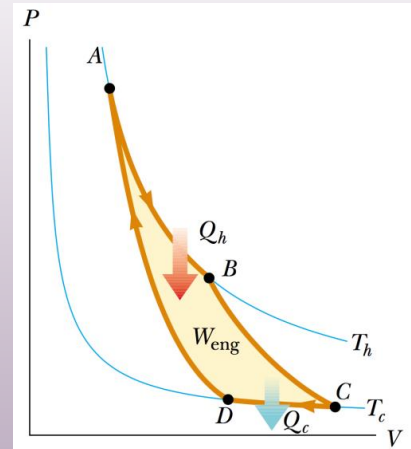


## The efficiency of the Carnot cycle

- Because it's a closed cycle, the total change in internal energy  $\Delta U$  is zero, the work done is the area enclosed in the PV-cycle, and is equal to  $W = Q_H - Q_L$ .
- The efficiency is given by

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

- But for the Carnot cycle we can take this further. Firstly, we need to work out  $Q_H$  and  $Q_L$  and these come from the two isothermal processes in the cycle A-B and C-D.
- Given an isothermal process has  $\Delta U = 0$ , this means  $Q = -W$  and so we can write:



$$Q_H = -W_{AB} = nRT_H \ln \frac{V_B}{V_A}$$

$$Q_L = -W_{CD} = nRT_C \ln \frac{V_C}{V_D}$$

Dividing the second expression by the first, we find that

$$\frac{Q_L}{Q_H} = \frac{T_C \ln \frac{V_C}{V_D}}{T_H \ln \frac{V_B}{V_A}}$$

For any adiabatic process, the temperature and volume are related by

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

Applying this result to the adiabatic processes  $B \rightarrow C$  and  $D \rightarrow A$ , we obtain

$$T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1}$$

$$T_H V_A^{\gamma-1} = T_L V_D^{\gamma-1}$$

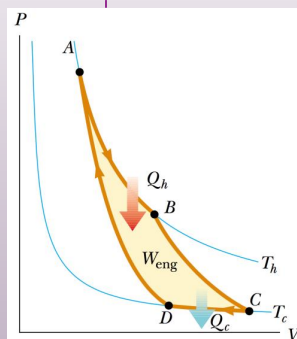
Dividing the first equation by the second, we obtain

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1}$$

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

$$\frac{Q_L}{Q_H} = \frac{T_C}{T_H}$$

$$\eta = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_C}{T_H}$$



## Efficiency of a Carnot Engine

- ❑ Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_C}{T_H}$$

- ❑ Temperatures must be in Kelvins
- ❑ All Carnot engines operating between the same two temperatures will have the same efficiency.

## Notes About Carnot Efficiency

- ❑ Efficiency is 0 if  $T_h = T_c$
- ❑ Efficiency is 100% only if  $T_c = 0$  K
  - ❑ Such reservoirs are not available
  - ❑ Efficiency is always less than 100%
- ❑ The efficiency increases as  $T_c$  is lowered and as  $T_h$  is raised.
- ❑ In most practical cases,  $T_c$  is near room temperature, 300 K
  - ❑ So generally  $T_h$  is raised to increase efficiency.

## Carnot Cycle in Reverse

- ❑ Theoretically, a Carnot-cycle heat engine can run in reverse.
- ❑ This would constitute the most effective heat pump available.
- ❑ This would determine the maximum possible COPs for a given combination of hot and cold reservoirs.

❑ **In heating mode:** 
$$COP = \frac{Q_H}{W} = \frac{T_H}{T_H - T_L}$$

❑ **In cooling mode:** 
$$COP = \frac{Q_L}{W} = \frac{T_L}{T_H - T_L}$$

- ❑ In practice, the COP is limited to values below 10.

## Example

An ideal gas is taken through a Carnot cycle. The isothermal expansion occurs at 250°C, and the isothermal compression takes place at 50.0°C. The gas takes in 1200 J of energy from the hot reservoir during the isothermal expansion. Find (a) the energy expelled to the cold reservoir in each cycle and (b) the net work done by the gas in each cycle.

- Isothermal expansion at  $T_H = 523 \text{ K}$
- Isothermal compression at  $T_L = 323 \text{ K}$

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_C}{T_H}$$

$$(a) \quad \frac{Q_L}{Q_H} = \frac{T_C}{T_H} \quad \longrightarrow \quad Q_L = Q_H \frac{T_C}{T_H} \quad \longrightarrow \quad Q_L = 1200 \frac{323}{523} = 741 \text{ J}$$

$$(b) \quad W = Q_H - Q_L \quad \longrightarrow \quad W = 1200 - 741 = 459 \text{ J}$$

## Problem to solve by yourself

- A Carnot engine has a power output of 150 kW. The engine operates between two reservoirs at  $20.0^{\circ}\text{C}$  and  $500^{\circ}\text{C}$ . (a) How much energy does it take in per hour? (b) How much energy is lost per hour in its exhaust?
- The exhaust temperature of a Carnot heat engine is  $300^{\circ}\text{C}$ . What is the intake temperature if the efficiency of the engine is 30.0%?
- A Carnot heat engine uses a steam boiler at  $100^{\circ}\text{C}$  as the high-temperature reservoir. The low-temperature reservoir is the outside environment at  $20.0^{\circ}\text{C}$ . Energy is exhausted to the low-temperature reservoir at the rate of 15.4 W. (a) Determine the useful power output of the heat engine. (b) How much steam will it cause to condense in the high- temperature reservoir in 1.00 h?

إلى اللقاء مع المحاضرة (٢٤)

## *Entropy and the Second Law of Thermodynamics*



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# Thermodynamics

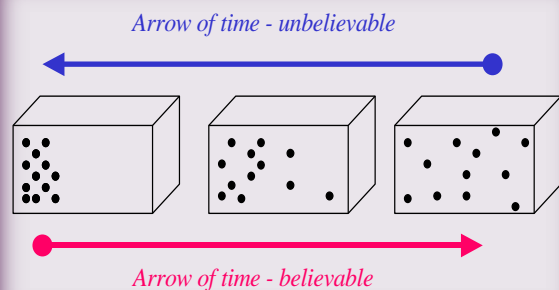
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## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 24: Entropy and the Second Law of Thermodynamics

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

- ❑ Heat Engines and the Second Law of Thermodynamics
  - ❑ Stirling engine
  - ❑ Gasoline engine
- ❑ Heat Pumps and Refrigerators
- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



The **zeroth law of thermodynamics** involves the concept of **temperature**.

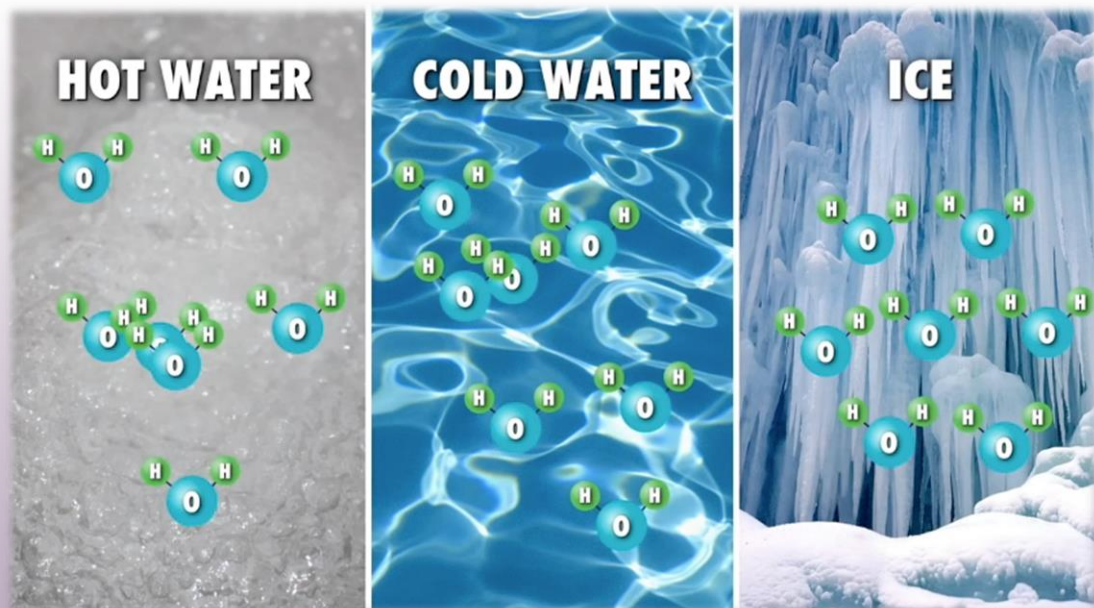
يصف القانون الصفري للديناميكا الحرارية الاتزان الحراري بين الأجسام المتلامسة أو في نظام حراري. ونشأ عنه تعريف درجة الحرارة

The **first law of thermodynamics** involves the concept of **internal energy**.

ينص القانون الاول للديناميكا الحرارية ان الطاقة لا يمكن ان تستحدث او تتلاشى وان مقدار الطاقة الكلي في الكون ثابت لا يتغير.

The **second law of thermodynamics** involves the concept of **entropy**.

الانتروبي (العشوائية) هو مقدار يصف ويحدد الطاقة الغير متوفرة لبذل شغل في عملية حرارية اي ان مع تحول الطاقة او انتقالها من مكان لآخر فان المزيد منها يفقد. وينص القانون الثاني للديناميكا الحرارية ايضا على ان هناك ميل طبيعي للأنظمة المعزولة إلى التغير والتحول تلقائيا نحو حالة توزيع تلقائيا إلى حالة اكثر عشوائية.



## مفهوم الانتروبي Entropy

- أصل كلمة **انتروبي** أو **العشوائية** أو **الفوضى** أو **الانظام** مأخوذ عن اليونانية ومعناها **تحول**، وهي من ابتكار العالم كلوزيوس في 1865 ليصف انسياب الحرارة من الجسم الساخن إلى الجسم البارد.
- ينص القانون الثاني للديناميكا الحرارية على مبدأ أساسي يقول: أي تغير يحدث تلقائياً في نظام فيزيائي لا بد وأن يصحبه ازدياد في مقدار "الانتروبي".**
- يميل أي نظام مغلق إلى التغير أو التحول تلقائياً نحو زيادة الانتروبي له حتى يصل إلى حالة توزيع متساو في جميع أجزائه، مثال على ذلك سقوط قطرة من الحبر في كوب ماء.

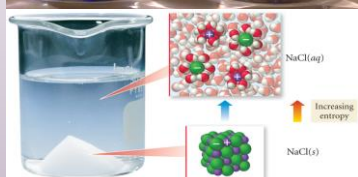


- نلاحظ أن قطرة الحبر تنتشر تدريجياً في الماء حتى يصبح كل جزء من الماء متجانساً، فنقول أن انتروبي النظام ازدادت. أي أن مجموع إنتروبي نقطة الحبر النقية + إنتروبي الماء النقية تكون أقل من إنتروبي النظام "حبر ذائب في ماء".

## أمثلة مختلفة لتوضيح الزيادة في الانتروبي للنظام



- اختلاط نقطة الحبر بالماء سهل ويتم طبيعياً، أما إذا أردنا فصل نقطة الحبر ثانياً عن الماء ليصبح لدينا ماء نقي وحبر نقي فذلك عملية صعبة ولا تتم إلا ببذل شغل. فنقول أن حالة المخلوط له إنتروبي كبيرة، بينما حالة الماء النقي والحبر النقي فهي حالة يكون الانتروبي لها منخفضة.



- من السهل إذابة الملح في الماء اما إعادة فصل الملح عن طريق التبخير، أي بذل طاقة، وهنا نقول أن انتروبي المحلول الملحي أعلى من انتروبي الملح النقي والماء النقي.



- البلورات التي تتشكل من محلول ملحي عندما يتبخر الماء. تعد البلورات أكثر ترتيباً من جزيئات الملح في المحلول، لكن تبخر الماء أكثر عشوائية من المحلول المائي. وعندما نتحدث عن العملية بالكامل فإن الانتروبي أو العشوائية للنظام تزداد.

## Microstates vs. Macrostates



Dice Sum (Macrostate)	Dice Combinations (Microstates)
2	1+1
3	1+2, 2+1
4	1+3, 2+2, 3+1
5	1+4, 2+3, 3+2, 4+1
6	1+5, 2+4, 3+3, 4+2, 5+1
7	1+6, 2+5, 3+4, 4+3, 5+2, 6+1
8	2+6, 3+5, 4+4, 5+3, 6+2
9	3+6, 4+5, 5+4, 6+3
10	4+6, 5+5, 6+4
11	5+6, 6+5
12	6+6

A **macrostate** is a description of the system's conditions from a macroscopic point of view.

A **microstate** is a particular configuration of the individual constituents of the **macrostate** of the system.

For a given **macrostate**, a number of **microstates** are possible.

*The more microstates that belong to a particular macrostate, the higher the probability that macrostate will occur.*

## Microstates vs. Macrostates in Physical systems

▪ يتغير أي نظام فيزيائي من لحظة إلى أخرى من حالة مجهرية microstate إلى أخرى.

▪ بالاعتماد على العلاقة بين احتمالية الحالات الجاهرية وعدد الحالات المجهرية لها نجد أن احتمالية النظام تتحول مع الزمن من حالة جاهرية منتظمة إلى حالة جاهرية عشوائية وذلك لوجود حالات مجهرية أكثر في الحالة الجاهرية الأكثر عشوائية.



## Spontaneous vs Nonspontaneous

Spontaneous	Nonspontaneous
Ice melting at room temperature	Water freezing at room temperature
A ball rolling downhill	A ball rolling uphill
The rusting of iron bar at room temperature	The conversion of rust back to iron metal at room temperature
Water freezing at $-10^{\circ}\text{C}$	Ice melting at $-10^{\circ}\text{C}$
two gases mixing	Separate two gases

Spontaneous processes can **release energy** (a ball rolling downhill), **require energy** (ice melting at temperatures above  $0^{\circ}\text{C}$ ), or involve **no energy change** at all (two gases mixing).

Why this direction of is favorable?

In thermodynamics spontaneous processes will occur without any out side intervention given enough time

## Entropy

*A measure of randomness or disorder*

- ☐ The natural tendency of things is to tend toward greater disorder.
- ☐ This is because there are many ways (or positions) that lead to disorder, but very few that lead to an ordered state.



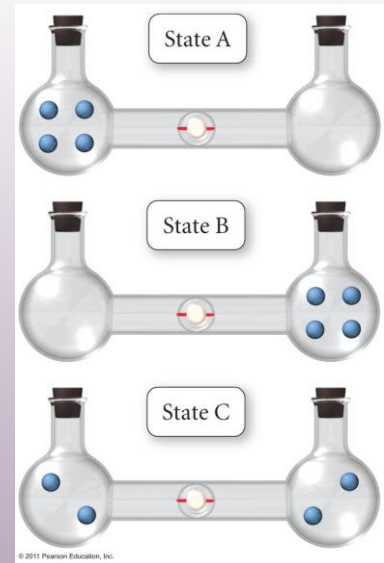
# Entropy

Gases will spontaneously and uniformly mix because the mixed state has more possible arrangements (a larger value of macrostate and higher entropy) than the unmixed state.

## The 2<sup>nd</sup> Law of Thermodynamics

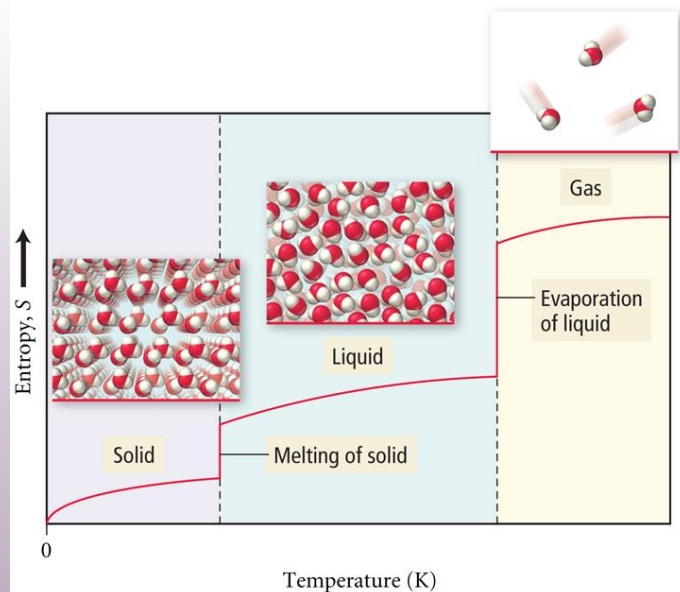
*In any spontaneous process there is always an increase in the entropy of the universe.*

إذا سمح لنظام ديناميكي حراري معزول مكون من أجزاء كثيرة بتغيير حالته تلقائياً، فإن هذه التغيرات تتم في اتجاه زيادة الفوضى (الانتروبي).



Gases have more entropy than liquids or solids.

Why?

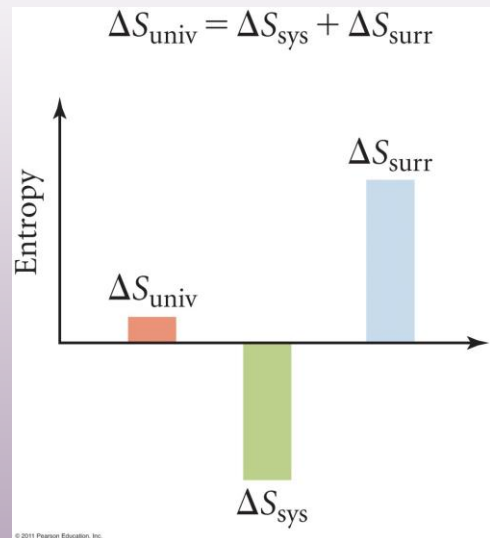


# Change in Entropy of the universe

Water spontaneously freezes at a temperature below 0°C. Therefore, the process increases the entropy of the universe!!!

- The water molecules become much more ordered as they freeze, and experience a decrease in entropy. **The process also releases heat**, and this **heat warms** gaseous molecules in air, and increases the entropy of the surroundings.
- Since the process is spontaneous below 0°C,  $\Delta S_{\text{surr}}$  **must be greater** in magnitude than  $\Delta S$  of the water molecules.

Entropy can be viewed as the *dispersal or randomization of energy*.



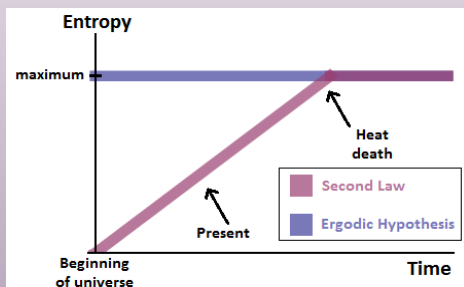
## ملاحظة وتوضيح

- من احد الاشياء التي يشرحها القانون الثاني للديناميكا الحرارية هو انه من المستحيل ان نقوم بتحويل الطاقة الحرارية إلى طاقة ميكانيكية بكفاءة تصل إلى 100%!!!
- بعد عملية تسخين الغاز لزيادة ضغطه لتحريك المكبس، هناك دائما حرارة تبقى في الغاز ولا يمكن الاستفادة منها لبذل المزيد من الشغل.
- هذا الفقد في الحرارة يجب التخلص منه بتحويله إلى البيئة المحيطة وعادة ما يكون الغلاف الجوي.
- علاوة على ان اي جهاز او محرك يحتوي على اجزاء متحركة يكون هناك احتكاك بينها، وهذا يحول الطاقة الميكانيكية إلى حرارة مفقودة لا يمكن الاستفادة منها ويجب التخلص منها عن طريق المبددات الحرارية.
- لهذا السبب ترفض مؤسسات براءة الاختراع استقبال الاختراعات التي تدعي الحركة الابدية.



# Heat Death of the Universe

- Ultimately, the entropy of the Universe should reach a maximum value.
- At this value, the Universe will be in a state of uniform temperature and density.
- All physical, chemical, and biological processes will cease.
  - The state of perfect disorder implies that no energy is available for doing work. This state is called the **heat death of the Universe**.



يتوقع القانون الثاني للديناميكا الحرارية أيضا نهاية العالم. ذلك يعني ان الكون سوف ينتهي بموت حراري heat death بحيث ان كل شيء يكون عند نفس درجة الحرارة. عندها يكون هذا هو الحد الأقصى لمستوى العشوائية، اذا كان كل شيء في الكون عند نفس درجة الحرارة فانه لا يكون هناك بذلك شغل وكل الطاقة سوف تكون كحركة عشوائية للذرات والجزيئات.

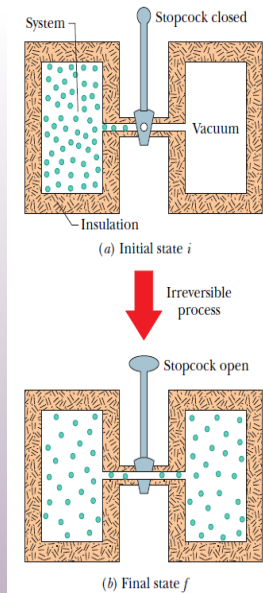
## Clausius definition of Entropy

- The original formulation of entropy dealt with the transfer of energy by heat in a **reversible process**.
- Let  $dQ_r$  be the amount of energy transferred by heat when a system follows a reversible path. **The change in entropy,**

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

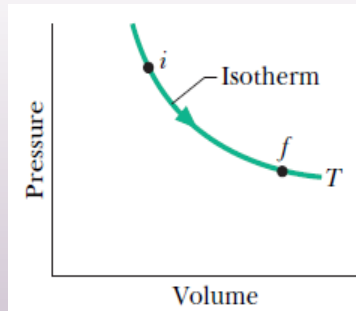
Change in entropy

- **If an irreversible process occurs in a closed system, the change in entropy  $\Delta S$  of the system always increases; it never decreases.**
- Unit of  $\Delta S$  is J/K, The change in entropy depends only on the endpoints and is independent of the actual path followed.



free expansion

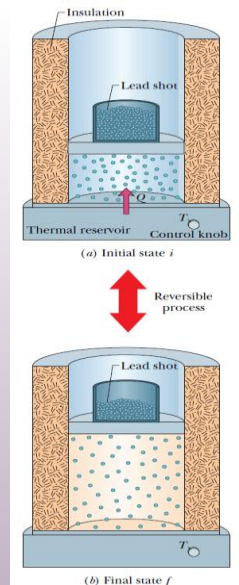
Entropy change of an **irreversible process** can be found with a **reversible one** connecting the initial and final states.



$$\Delta S = S_f - S_i = \frac{1}{T} \int_i^f dQ.$$

$$\int dQ = Q,$$

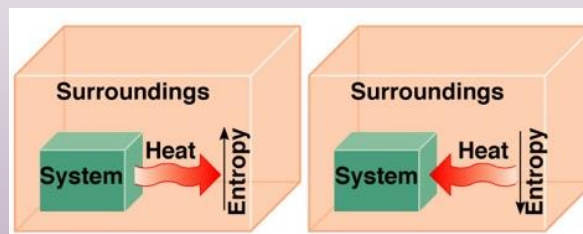
$$\Delta S = S_f - S_i = \frac{Q}{T} \quad (\text{change in entropy, isothermal process}).$$



an isothermal process

## Note

- When energy is absorbed by the system,  $dQ_r$  is positive and the entropy of the system increases.
- When energy is expelled by the system,  $dQ_r$  is negative and the entropy of the system decreases.



- The meaningful quantity is the **change in entropy** and not the entropy itself.

## Example 1

A solid that has a latent heat of fusion  $L_f$  melts at a temperature  $T_m$ . Calculate the change in entropy of this substance when a mass  $m$  of the substance melts.

$$\Delta S = \int_i^f \frac{dQ}{T}$$

$$\Delta S = \frac{1}{T_m} \int_i^f dQ = \frac{Q}{T_m} \quad \Delta S = \frac{mL_f}{T_m}$$

- When a solid melts, its entropy increases because the molecules are much more disordered in the liquid state than they are in the solid state.
- The positive value for  $\Delta S$  means that the substance in its liquid state does not spontaneously transfer energy from itself to the warm surroundings and freeze because to do so would involve a spontaneous increase in order and a decrease in entropy.

## Example 2

A Styrofoam cup holding 125 g of hot water at 100°C cools to room temperature, 20.0°C. What is the change in entropy of the room? Neglect the specific heat of the cup and any change in temperature of the room.

▪ الماء الساخن يفقد حرارة بمقدار  $Q = mc\Delta T$  والغرفة المحيطة تكتسب حرارة بنفس المقدار.

$$Q_{\text{room}} = (mc|\Delta T|)_{\text{water}}$$

$$\Delta S = \frac{Q_{\text{room}}}{T} = \frac{(mc|\Delta T|)_{\text{water}}}{T} = \frac{0.125 \text{ kg}(4186 \text{ J/kg} \cdot ^\circ\text{C})(100 - 20)^\circ\text{C}}{293 \text{ K}} = 143 \text{ J/K}$$

▪ عندما يبرد الماء تقل الانتروبي له ولكن هذا النقصان اقل من 143 J/K ، وذلك لان درجة حرارة الماء كبيرة وتساوي 393 وهذا يجعل الانتروبي لها صغيرا بالمقارنة مع انتروبي الغرفة عند درجة حرارة 293 ولاحظ انه كلما كبر المقام (درجة الحرارة قل الانتروبي) بالتالي فان التغير الكلي في انتروبي الـ universe والمكون من الماء والغرفة يكون موجبا.

إلى اللقاء مع المحاضرة (٢٥)

***More about Entropy***



## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 25: Entropy and the Second Law of Thermodynamics

## Unit 4: Engines, Refrigerators and the second law of thermodynamics

- ❑ Heat Engines and the Second Law of Thermodynamics
  - ❑ Stirling engine
  - ❑ Gasoline engine
- ❑ Heat Pumps and Refrigerators
- ❑ Reversible and Irreversible Processes
- ❑ The Carnot Engine
- ❑ Entropy and the Second Law
- ❑ Entropy on a Microscopic Scale



## Entropy Changes in Non-isolated Systems

- The increase in entropy described in the second law is that of the **system and its surroundings**.
- When a system and its surroundings interact in an irreversible process, **the increase in entropy of one is greater than the decrease in entropy of the other**.
- The change in entropy of the **Universe** must be **greater than zero for an irreversible process** and **equal to zero for a reversible process**.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

## Change in entropy in Carnot engine (reversible)

- In one cycle, the engine takes in energy  $Q_h$  from the hot reservoir and expels energy  $Q_c$  to the cold reservoir.
- These energy transfers occur only during the isothermal portions of the Carnot cycle;
- Therefore, the total change in entropy for one cycle is

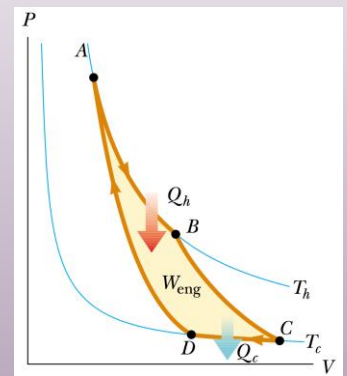
$$\Delta S = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}$$

But  $\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$

from the evaluation of the efficiency of Carnot engine

$$\therefore \Delta S = 0 \quad \text{for reversible cycle}$$

$$\oint \frac{dQ}{T} = 0 \quad \text{for reversible cycle}$$



## The entropy of the **ideal gas**

Suppose that an ideal gas undergoes a quasistatic, reversible process from an initial state having temperature  $T_i$  and volume  $V_i$  to a final state described by  $T_f$  and  $V_f$ . Let us calculate the change in entropy of the gas for this process.

From first law of thermodynamics  $dQ_r = dE_{int} - dW$

We Know that  $dW = -PdV$   $dE_{int} = nC_V dT$   $P = \frac{nRT}{V}$

$$\therefore dQ_r = dE_{int} + PdV$$

$$dQ_r = nC_V dT + nRT \frac{dV}{V}$$

Divide all terms by T

## The entropy of the **ideal gas**

$$\frac{dQ_r}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$\Delta S = \int_i^f \frac{dQ_r}{T}$$

$$\therefore \Delta S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

- $\Delta S$  depends only on the initial and final states and is independent of the path between the states.
- For a cyclic process ( $T_i = T_f$  and  $V_i = V_f$ ), So  $\Delta S = 0$ .

## Change in entropy in real engine (Irreversible)

- In an irreversible process like conduction or radiation, heat is lost ( $Q$ ) by a body at a higher temperature  $T_h$  and is the heat ( $Q$ ) gained by the body at a lower temperature  $T_c$ .
- Consider the hot and the cold bodies as one system
- Loss in entropy of the hot body =  $\frac{Q}{T_h}$
- Gain in entropy of the cold body =  $\frac{Q}{T_c}$
- Therefore, the total increase in entropy of the system

$$\Delta S = \frac{Q}{T_c} - \frac{Q}{T_h}$$

It is a positive quantity because  $T_c$  is less than  $T_h$

$$\therefore \Delta S > 0 \quad \text{for all irreversible cycle}$$

## Example 1

An irreversible engine operating between the temperatures of 550 K and 300 K extracts 1200 J of heat from the hot reservoir and produces 450 J of work. How much is the change in entropy in the process?

$$\Delta S = \frac{Q_c}{T_c} - \frac{Q_h}{T_h}$$

$$Q_h = 1200J \quad T_h = 550J \quad T_c = 300J \quad W = 450J$$

$$\therefore Q_c = 1200 - 450J = 750J$$

$$\Delta S = \frac{750}{300} - \frac{1200}{550} = +0.318J/K$$

## Entropy Change in Thermal Conduction

- Consider a system consisting of a hot reservoir and a cold reservoir that are in thermal contact with each other and isolated from the rest of the Universe.
- Because the cold reservoir absorbs energy  $Q$ , its entropy increases by  $Q/T_c$ .
- At the same time, the hot reservoir loses energy  $Q$ , so its entropy change is  $-Q/T_h$ .
- Because  $T_h > T_c$  the increase in entropy of the cold reservoir is greater than the decrease in entropy of the hot reservoir.
- Therefore, the change in entropy of the system (and of the Universe) is greater than zero:

$$\Delta S_U = \frac{Q}{T_c} + \frac{-Q}{T_h} > 0$$

## Example 2

- A large, cold object is at 273 K, and a second large, hot object is at 373 K. Show that it is impossible for a small amount of energy—for example, 8.00 J—to be transferred spontaneously by heat from the cold object to the hot one without a decrease in the entropy of the Universe and therefore a violation of the second law.

■ لتبسيط المعالجة الرياضية عند اجراء التكامل سنفترض ان درجتي الحرارة لا تتغير.

■  $\Delta S_h = \frac{Q_r}{T_h} = \frac{8.00 \text{ J}}{373 \text{ K}} = 0.0214 \text{ J/K}$  is

■ The entropy change of the cold object is  $\Delta S_c = \frac{Q_r}{T_c} = \frac{-8.00 \text{ J}}{273 \text{ K}} = -0.0293 \text{ J/K}$

$$\Delta S_U = \Delta S_c + \Delta S_h = -0.0079 \text{ J/K}$$

This decrease in entropy of the Universe is in violation of the second law. That is, **the spontaneous transfer of energy by heat from a cold to a hot object cannot occur.**

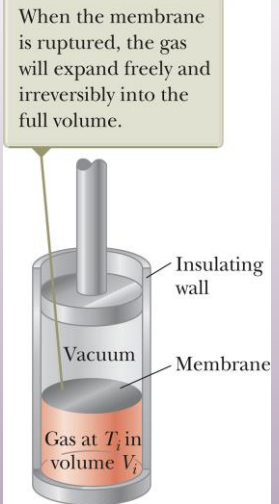
## Entropy Change in a Free Expansion

- Consider an adiabatic free expansion. This process is irreversible since the gas would not spontaneously crowd into half the volume after filling the entire volume .
- $Q = 0$  but we need to find  $Q_r$
- Choose an isothermal, reversible expansion in which the gas pushes slowly against the piston while energy enters from a reservoir to keep  $T$  constant

$$\Delta S = \int_i^f \frac{dQ_r}{T} = \frac{1}{T} \int_i^f dQ_r$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Since  $V_f > V_i$ ,  $\Delta S$  is positive  
This indicates that both the entropy and the disorder of the gas increase as a result of the irreversible adiabatic expansion.



## Example 3

One kilogram of water at 0°C is heated to 100°C. Compute its change in entropy.

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T}$$

$$dQ = mc dT$$

$$\Delta S = mc \int_{T_1}^{T_2} \frac{dT}{T} = mc \ln \frac{T_2}{T_1}$$

$$\Delta S = 1000 \times 4.168 \ln \frac{373}{273} = 1308 \text{ J/K}$$

## Entropy Change during special process

- For Adiabatic Process  $dQ = 0$

$$\Delta S = 0 \quad \text{for adiabatic process}$$

- For Isothermal Process  $T$  is constant

$$\Delta S = \frac{1}{T} \int dQ = \frac{L_f}{T} \quad \text{or} \quad \frac{L_v}{T}$$

- For Isochoric Process  $V$  is constant

$$\Delta S = \int \frac{dQ}{T} = nc_v \int_{T_1}^{T_2} \frac{dT}{T} = nc_v \ln \frac{T_2}{T_1}$$

- For Isobaric Process  $P$  is constant

$$\Delta S = \int \frac{dQ}{T} = nc_p \int_{T_1}^{T_2} \frac{dT}{T} = nc_p \ln \frac{T_2}{T_1}$$

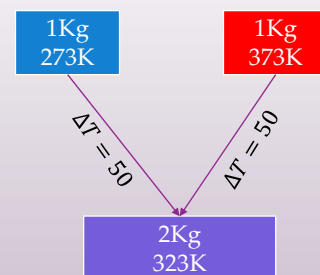
## Example 4 Entropy Change in Calorimetric Processes

Suppose 1Kg of water at 373 K is mixed with 1kg of water at 273 K. What is the total change in entropy?

$$\Delta S_1 = mc \ln \frac{T_f}{T_1} = 1 \times 4186 \times \ln \frac{323}{273} = 704 \text{ J/K}$$

$$\Delta S_2 = mc \ln \frac{T_f}{T_2} = 1 \times 4186 \times \ln \frac{323}{373} = -503 \text{ J/K}$$

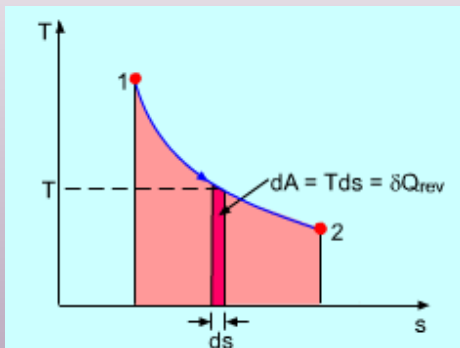
$$\Delta S = \Delta S_1 + \Delta S_2 = 101 \text{ J/K}$$



نلاحظ من هذا المثال عند خلط ماء ساخن مع ماء بارد في علمية غير عكوسة ان التغير الكلي في الانتروبي مقدارا موجبا. معنى ان الانتروبي يزداد عند خلط الماء الساخن مع البارد انهما بعد فترة سوف يصبحان عند نفس درجة الحرارة وعندها نخسر تحويل الحرارة إلى شغل ميكانيكي. بالتأكيد لا يكون هناك نقصان في الطاقة إنما النقصان يكون فقط في فرصة تحول الحرارة المتدفقة من الحار إلى البارد إلى شغل. ولهذا عند ازدياد الانتروبي فان طاقة أكثر تصبح غير متوفرة وعندها يكون الكون في حالة عشوائية أكثر.

## TS diagram

- إذا قمنا برسم العلاقة بين درجة الحرارة  $T$  والانتروبي  $S$  فان العملية بين القطين 1 و 2 تكون على النحو الموضح في الشكل.
- تمثل المساحة  $dA$  حاصل ضرب التغير في الانتروبي في درجة الحرارة والتي تساوي التغير في كمية الحرارة  $dQ$

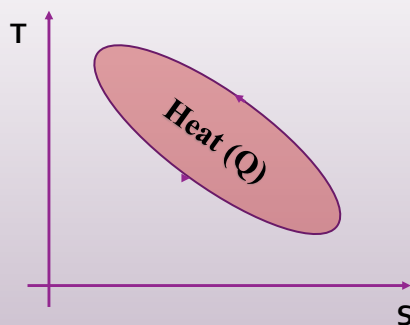


$$dA = TdS$$

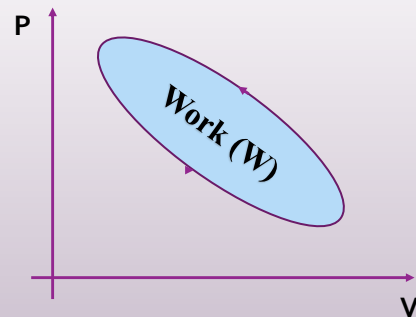
$$\therefore A = \int TdS \quad \therefore Q = \int TdS$$

إذا المساحة تحت منحنى TS تمثل كمية الحرارة.

## TS diagram vs PV diagram



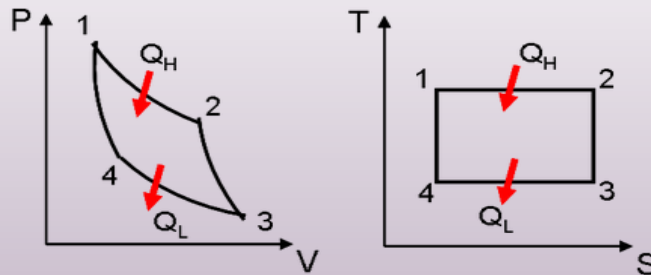
المساحة تحت منحنى الانتروبي ودرجة الحرارة تمثل كمية الحرارة.



المساحة تحت منحنى الضغط والحجم تمثل الشغل

## Efficiency of Carnot engine

يمكن إيجاد كفاءة دروة محرك كارنو بسهولة عندما نمثل الدورة على منحنى TS



$$\eta = \frac{Q_H - Q_L}{Q_H} = \frac{T_H \Delta S - T_L \Delta S}{T_H \Delta S} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}$$

## Problem to solve by yourself

- An ice tray contains 500 g of liquid water at 0°C. Calculate the change in entropy of the water as it freezes slowly and completely at 0°C.
- The temperature at the surface of the Sun is approximately 5 700 K , and the temperature at the surface of the Earth is approximately 290 K. What entropy change occurs when 1 000 J of energy is transferred by radiation from the Sun to the Earth?
- At a pressure of 1 atm, liquid helium boils at 4.20 K . The latent heat of vaporization is 20.5 kJ/kg. Determine the entropy change (per kilogram) of the helium resulting from vaporization.
- Calculate the change in entropy of 250 g of water heated slowly from 20.0°C to 80.0°C.
- A rigid tank of small mass contains 40.0 g of argon, initially at 200°C and 100 kPa. The tank is placed into a reservoir at 0°C and allowed to cool to thermal equilibrium. (a) Calculate the volume of the tank. (b) Calculate the change in internal energy of the argon. (c) Calculate the energy transferred by heat. (d) Calculate the change in entropy of the argon. (e) Calculate the change in entropy of the constant-temperature bath.

إلى اللقاء مع المحاضرة (٢٦)

***Problems Solving and Discussion***



## Unit 4: Engines, Refrigerators and the second law of thermodynamics

### Lecture 26: Discussion and Problem Solving

#### Exercise 1

A particular heat engine has a mechanical power output of 5000 W and an efficiency of 25.0%. The engine expels 8000 J of exhaust energy in each cycle. Find (a) the energy taken in during each cycle and (b) the time interval for each cycle.

(a) the energy taken in during each cycle      (b) the time interval for each cycle.

$$\because Q_H = W + Q_C \quad Q_C = 8000J$$

$$\gamma = 1 - \frac{Q_C}{Q_H} = 0.25$$

$$Q_H = \frac{Q_C}{1 - \gamma} = \frac{8000J}{1 - 0.25} = 10700J$$

$$W = Q_H - Q_C = 2667J$$

$$\because P = \frac{W}{\Delta t}$$

$$\because \Delta t = \frac{W}{P} = \frac{2667J}{5000J/sec} = 0.533 sec$$

## Exercise 2

Suppose a heat engine is connected to two energy reservoirs, one a pool of molten aluminum ( $660^{\circ}\text{C}$ ) and the other a block of solid mercury ( $-38.9^{\circ}\text{C}$ ). The engine runs by freezing 1.00 g of aluminum and melting 15.0 g of mercury during each cycle. ( $L_{f(\text{Al})} = 3.97 \times 10^5 \text{ J/kg}$ ; and  $L_{f(\text{Hg})} = 1.18 \times 10^4 \text{ J/kg}$ . **What is the efficiency of this engine?**

The heat  $Q_c$  to melt 15.0 g of Hg is  $|Q_c| = mL_f = (15 \times 10^{-3} \text{ kg})(1.18 \times 10^4 \text{ J/kg}) = 177 \text{ J}$

The heat  $Q_h$  to freeze 1.00 g of aluminum is  $|Q_h| = mL_f = (10^{-3} \text{ kg})(3.97 \times 10^5 \text{ J/kg}) = 397 \text{ J}$

The work output is  $W_{\text{eng}} = |Q_h| - |Q_c| = 220 \text{ J}$

The efficiency is  $e = \frac{W_{\text{eng}}}{|Q_h|} = \frac{220 \text{ J}}{397 \text{ J}} = 0.554$ , or 55.4%

The theoretical (Carnot) efficiency  $\frac{T_h - T_c}{T_h} = \frac{933 \text{ K} - 243.1 \text{ K}}{933 \text{ K}} = 0.749 = 74.9\%$

## Exercise 3

One of the most efficient heat engines ever built is a coal-fired steam turbine in the Ohio River, operating between  $1870^{\circ}\text{C}$  and  $430^{\circ}\text{C}$ . (a) What is its maximum theoretical efficiency? (b) The actual efficiency of the engine is 42.0%. How much mechanical power does the engine deliver if it absorbs  $1.40 \times 10^5 \text{ J}$  of energy each second from its hot reservoir?

$T_c = 430^{\circ}\text{C} = 703 \text{ K}$   $T_h = 1870^{\circ}\text{C} = 2143 \text{ K}$

- (a) What is its maximum theoretical efficiency?

$$\gamma = \frac{T_h - T_c}{T_h} = \frac{2143 - 703}{2143} = 0.672 \text{ or } 67.2\%$$

- (b) How much mechanical power does the engine deliver .....

$$\gamma = \frac{W}{Q_H} = 0.42 \text{ and } Q_H = 1.4 \times 10^5 \text{ J} \quad W = \gamma Q_H = 0.42 \times 1.4 \times 10^5 \text{ J} = 5.88 \times 10^4 \text{ J}$$

the power is  $P = \frac{W}{\Delta t}$   $P = \frac{5.88 \times 10^4 \text{ J}}{1 \text{ sec}} = 5.88 \times 10^4 \text{ watt}$

## Exercise 4

How much work does an ideal Carnot refrigerator require to remove 1.00 J of energy from liquid helium at 4.00 K and expel this energy to a room-temperature (293 K) environment?

$$COP = \frac{Q_L}{W} = \frac{T_L}{T_H - T_L}$$

$$(COP)_{carnot\ refrig} = \frac{T_C}{\Delta T} = \frac{4K}{293K - 4K} = 0.0138$$

$$(COP)_{carnot\ refrig} = \frac{Q_C}{W}$$

$$W = \frac{Q_C}{COP} = \frac{1J}{0.0138} = 72.2J$$

## Exercise 5

An ideal gas is taken through a Carnot cycle. The isothermal expansion occurs at 250°C, and the isothermal compression takes place at 50.0°C. The gas takes in 1200 J of energy from the hot reservoir during the isothermal expansion. Find (a) the energy expelled to the cold reservoir in each cycle and (b) the net work done by the gas in each cycle.

(a) the energy expelled to the cold reservoir (b) the net work done by the gas in each cycle

$$\gamma_{carnot\ engine} = 1 - \frac{T_C}{T_H} = 1 - \frac{Q_C}{Q_H}$$

$$\frac{T_C}{T_H} = \frac{Q_C}{Q_H}$$

$$Q_C = Q_H \frac{T_C}{T_H} = 1200J \left( \frac{323K}{523K} \right) = 741 J$$

$$W = Q_H - Q_C = 1200J - 741J = 459 J$$

## Exercise 6

In a cylinder of an automobile engine, immediately after combustion the gas is confined to a volume of  $50.0 \text{ cm}^3$  and has an initial pressure of  $3 \times 10^6 \text{ Pa}$ . The piston moves outward to a final volume of  $300 \text{ cm}^3$ , and the gas expands without energy transfer by heat. (a) What is the final pressure of the gas? (b) How much work is done by the gas in expanding?

(a) The gas expands adiabatically so we will use  $P_i V_i^\gamma = \text{constant}$  to find the final pressure

$$P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_f = P_i \left( \frac{V_i}{V_f} \right)^\gamma = (3.00 \times 10^6 \text{ Pa}) \left( \frac{50.0 \text{ cm}^3}{300 \text{ cm}^3} \right)^{1.40} = 2.44 \times 10^5 \text{ Pa}$$

▪ (b) With  $Q = 0$ , the amount of work can be found from the change in internal energy.

$$W_{\text{eng}} = Q - \Delta E = -\Delta E = -nC_V \Delta T = -nC_V (T_f - T_i)$$

نحتاج ان نحسب  $C_V$

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} \quad \text{therefore} \quad (\gamma - 1)C_V = R$$

$$C_V = \frac{R}{1.40 - 1} = 2.50 R$$

$$W_{\text{eng}} = n(2.50 R)(T_i - T_f) = 2.50 P_i V_i - 2.50 P_f V_f$$

$$W_{\text{eng}} = 2.50 [(3.00 \times 10^6 \text{ Pa})(50.0 \times 10^{-6} \text{ m}^3) - (2.44 \times 10^5 \text{ Pa})(300 \times 10^{-6} \text{ m}^3)]$$

$$W_{\text{eng}} = 192 \text{ J}$$

## Exercise 7

An engine operates in a cycle shown in the Figure. Fuel is sprayed into the cylinder at the point of maximum compression,  $B$ . Combustion occurs during the expansion  $B \rightarrow C$ , which is modeled as an isobaric process. Show that the efficiency of an engine operating in this idealized diesel cycle is

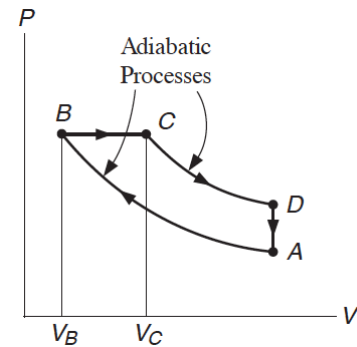
$$e = 1 - \frac{1}{\gamma} \left( \frac{T_D - T_A}{T_C - T_B} \right)$$

The energy transfers by heat over the paths  $CD$  and  $BA$  are zero since they are adiabatic:

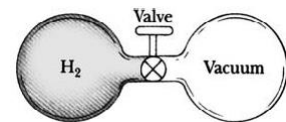
$$Q_{BC} = nC_P(T_C - T_B) > 0 \quad |Q_h| = Q_{BC}$$

$$Q_{DA} = nC_V(T_A - T_D) < 0 \quad |Q_c| = |Q_{DA}|$$

$$e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \left( \frac{T_D - T_A}{T_C - T_B} \right) \frac{C_V}{C_P} \quad e = 1 - \frac{1}{\gamma} \left( \frac{T_D - T_A}{T_C - T_B} \right)$$



## Exercise 8



A 1.00-mol sample of  $H_2$  gas is contained in the left side of the container shown in the Figure, which has equal volumes left and right. The right side is evacuated. When the valve is opened, the gas streams into the right side. (a) What is the entropy change of the gas? (b) Does the temperature of the gas change? Assume the container is so large that the hydrogen behaves as an ideal gas.

(a) What is the entropy change of the gas? (b) Does the temperature of the gas change?

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) \quad \text{For free expansion;}$$

$$\Delta S = (1.00 \text{ mole})(8.314 \text{ J/mole} \cdot \text{K}) \ln \left( \frac{2}{1} \right)$$

$$\Delta S = 5.76 \text{ J/K}$$

يتمدد الغاز في وعاء مفرغ ولهذا فان الشغل المبذول يساوي صفر. وتتم عملية التمدد في زمن قصير اي عملية اديباتيكية. ومن القانون الاول في الديناميكا الحرارية فان التغير في الطاقة الداخلية يساوي صفر. وحيث ان الغاز يتصرف كغاز مثالي، فانه لا يكون هناك اي تغير في درجة الحرارة لان الطاقة الداخلية لم تتغير.

## Exercise 9

A 1.00-mol sample of an ideal monatomic gas, initially at a pressure of 1.00 atm and a volume of 0.025 m<sup>3</sup>, is heated to a final state with a pressure of 2.00 atm and a volume of 0.040 m<sup>3</sup>. **Determine the change in entropy of the gas in this process.**

$$\therefore \Delta S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$\frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i}$$

$$\Delta S = (1.00 \text{ mol}) \left[ \frac{3}{2} (8.314 \text{ J/mol} \cdot \text{K}) \right] \ln \left( \frac{(2.00)(0.0400)}{(1.00)(0.0250)} \right) + (1.00 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K}) \ln \left( \frac{0.0400}{0.0250} \right)$$

$$\therefore \Delta S = 18.4 \text{ J/K}$$

إلى اللقاء مع المحاضرة (٢٧)

***Pure Substances***



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# Thermodynamics

Dr. Hazem Falah Sakeek  
Al-Azhar University - Gaza

## Unit 5: Pure Substance

### Lecture 27: Enthalpy, Helmholtz and Gibbs functions

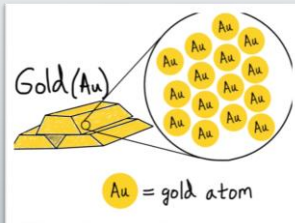
## Unit 5: Pure Substance

- ❑ **Enthalpy**
- ❑ **The Helmholtz functions**
- ❑ **Gibbs functions**
- ❑ **Maxwell's Equations**
- ❑ The Tds equations
- ❑ Energy equations
- ❑ Heat-capacity equations

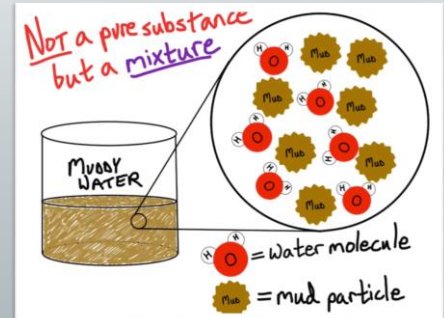
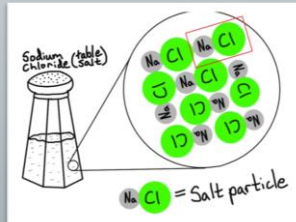
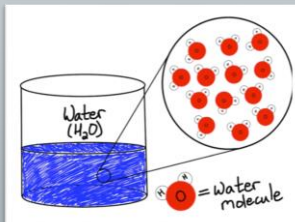
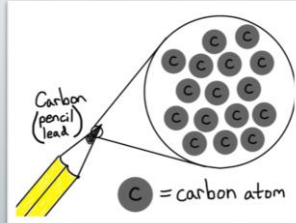


## Pure Substance

A substance that has a **fixed chemical composition** throughout is called pure substance. Water, helium carbon dioxide, nitrogen are examples.



Pure Substances



NOT Pure Substances

## The Enthalpy

الانثالبي enthalpy او المحتوى الحراري يرمز له بـ H وهو يعبر عن مقدار الطاقة الكلية لنظام ديناميكي حراري، بالإضافة إلى كمية الشغل اللازم لإفساح مكان او اعطاء حجم محدد للنظام خلال الوسط المحيط فيحصل النظام على حجمه وضغطه.

# Enthalpy

In discussing some of the properties of gases, the sum of  $U$  and  $PV$  appeared several times. It has been found very useful to define a new **function  $H$** , called the **enthalpy** by the relation

$$H = U + PV$$

In order to study the properties of this function, consider the change in enthalpy that takes place from an initial equilibrium state to a final equilibrium state.

$$dH = dU + PdV + VdP$$

but

$$dQ = dU + PdV$$

Therefore,

$$dH = dQ + VdP$$

Dividing both sides by  $dT$

$$\frac{dH}{dT} = \frac{dQ}{dT} + V \frac{dP}{dT}$$

- At constant  $P$

$$\left( \frac{dH}{dT} \right)_P = \left( \frac{dQ}{dT} \right)_P = C_P$$

- Since

$$dH = dQ + VdP$$

- the change in enthalpy during an **isobaric process** is equal to the heat that is transferred. That is

$$\left. \begin{aligned} H_f - H_i &= Q \\ H_f - H_i &= \int_i^f C_P dT \end{aligned} \right\} \text{ (isobaric)}$$

- Since isobaric processes are much more important in engineering and chemistry than isochoric processes, the enthalpy is of greatest use in these branches of science.

## اهمية الانثالبي enthalpy (المحتوى الحراري)

- الانثالبي enthalpy او المحتوى الحراري يرمز له بـ  $H$  وهو يعبر عن مقياس الطاقة الكلية لنظام ديناميكي حراري والتي تشتمل على الطاقة الداخلية  $U$  المسؤولة عن انشاء النظام، بالإضافة إلى كمية الشغل اللازم لإفساح مكان او اعطاء حجم محدد للنظام خلال الوسط المحيط فيحصل النظام على حجمه وضغطه. وحدة الانثالبي هي الجول.
- لا يمكن قياس الانثالبي الكلي  $H$  للنظام انما نقيس التغير في الانثالبي  $\Delta H$ .
- يعبر التغير في الانثالبي  $\Delta H$  عن الشغل الغير ميكانيكي الذي نزوده للنظام او كمية الحرارة التي نعطيها للنظام.
- عند ثبوت الضغط يكون التغير في الانثالبي مساويا للتغير في الطاقة الداخلية للنظام بالإضافة إلى مقدار الشغل الذي يبذله النظام على المحيط. وهذا يعني انه خلال تفاعل كيميائي يكون التغير في الانثالبي مساويا لكمية الحرارة التي يحررها النظام (التفاعل) إلى المحيط او التي يمتصها منه.
- تغير  $\Delta H$  موجب الإشارة: فيكون تفاعل يمتص الحرارة endothermic
- تغير  $\Delta H$  سالب الإشارة: فيكون تفاعل طارد للحرارة exothermic

- If a pure substance undergoes an infinitesimal reversible process,

$$dH = dQ + VdP \quad \longrightarrow \quad dH = TdS + VdP$$

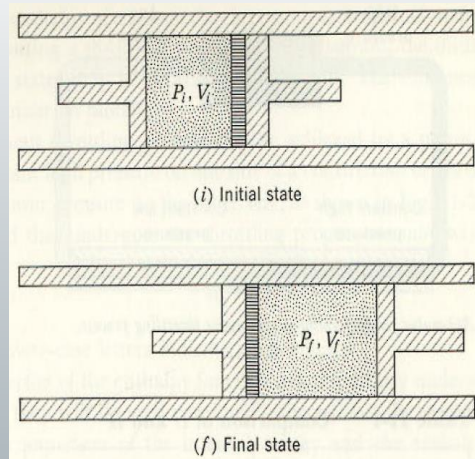
$$\left(\frac{dH}{dS}\right)_P = T \quad \text{and} \quad \left(\frac{dH}{dP}\right)_S = V$$

- One of the most interesting properties of the enthalpy function is in connection with a throttling process.

العملية التي دخلت في دروة الثلاجة  
لتحويل سائل التبريد refrigerant عند  
ضغط مرتفع إلى غاز عند ضغط  
منخفض

## Throttling Process

- Imagine a cylinder thermally insulated and equipped with two nonconducting pistons on opposite sides of a porous wall.
- Between the left-hand piston and the wall there is a gas at a pressure  $P_i$  and a volume  $V_i$ , since the right-hand piston is against the wall, with any gas being prevented from seeping through, the initial state of the gas is an equilibrium state.
- Now imagine moving both pistons simultaneously in such a way that a constant pressure  $P_i$  is maintained on the left-hand side of the wall and a constant lower pressure  $P_f$  is maintained on the right-hand side.
- After all the gas has seeped through the porous wall, the final equilibrium state of the system will be as shown in Fig. f. Such a process is a throttling process.



- Applying the first law to the throttling process

$$Q = U_f - U_i + W$$

- But  $Q = 0$  and

$$W = \int_0^{V_f} P dV + \int_{V_i}^0 P dV$$

- Since both pressures remain constant,

$$W = P_f V_f - P_i V_i$$

- The above expression is known in engineering as flow work, since it represents the work necessary to keep the gas flowing.

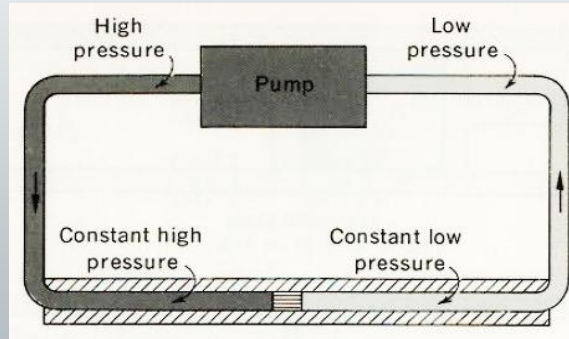
$$0 = U_f - U_i + P_f V_f - P_i V_i$$

$$U_i + P_i V_i = U_f + P_f V_f$$

$$H_i = H_f$$

$$H_i = H_f$$

In a **throttling process**, therefore, the initial and final enthalpies are equal.



A continuous throttling process may be achieved by a **pump** that maintains a constant high pressure on one side of a porous wall and a constant lower pressure on the other side.

## Comparison between **internal energy** and **enthalpy**

Internal Energy U	Enthalpy H	Internal Energy U	Enthalpy H
<b>In general</b> $dU = dQ + PdV$ $\left(\frac{dU}{dT}\right)_V = C_V$	<b>In general</b> $dH = dQ + VdP$ $\left(\frac{dH}{dT}\right)_P = C_P$	<b>Free expansion</b> $U_i = U_f$	<b>Throttling Process</b> $H_i = H_f$
<b>Isochoric Process</b> $U_f - U_i = Q$ $U_f - U_i = \int_i^f C_V dT$	<b>Isobaric Process</b> $H_f - H_i = Q$ $H_f - H_i = \int_i^f C_P dT$	<b>For an ideal gas</b> $U = \int C_V dT + const$	<b>For an ideal gas</b> $H = \int C_P dT + const$
<b>Adiabatic Process</b> $U_f - U_i = \int_i^f P dV$	<b>Adiabatic Process</b> $H_f - H_i = \int_i^f V dP$	<b>Reversible Process</b> $dU = T dS - P dV$ $T = \left(\frac{dU}{dS}\right)_V$ $P = \left(\frac{dU}{dV}\right)_S$	<b>Reversible Process</b> $dH = T dS - V dP$ $T = \left(\frac{dH}{dS}\right)_P$ $V = \left(\frac{dH}{dP}\right)_S$

# The Helmholtz Function

تعبّر دالة هلمهولتز عن مقدار الشغل الممكن أن نحصل عليه من نظام ديناميكي حراري مغلق.  
تساوي طاقة هلمهولتز الطاقة الداخلية للنظام  $U$  مطروحاً منها حاصل ضرب درجة الحرارة المطلقة  $T$  في الانتروبي  $S$ .

## The Helmholtz Function

The Helmholtz function (sometimes called the Helmholtz free energy) is defined

$$F = U - TS$$

For an infinitesimal reversible process,

$$dF = dU - TdS - SdT$$

and

$$TdS = dU - PdV$$

Hence

$$dF = -SdT + PdV$$

From this it follows: (1) For a reversible isothermal process,  $dF = PdV$  or

$$F_f - F_i = \int_i^f PdV$$

i.e. the change of the Helmholtz function during a reversible isothermal process equals the work done on the system.

(2) For a reversible isothermal and isochoric process,

$$dF = 0$$

And

$$F = \text{const}$$

These properties are of interest in chemistry and are useful in considering chemical reactions that take place isothermally and isochorically. The main importance of the Helmholtz function, however, is in statistical mechanics, where it is closely associated with the partition function  $Z$  defined by the equation

$$Z = \sum g_i e^{-\epsilon_i/kT}$$

where  $\epsilon$ , and  $g$ , represent the energy values and degeneracies, respectively, of the various energy levels of the system of particles.

$$dF = -SdT + PdV$$

the entropy and the pressure may then be calculated by performing the simple differentiations:

$$S = -\left(\frac{dF}{dT}\right)_V \quad \text{and} \quad P = \left(\frac{dF}{dV}\right)_T$$

# The Gibbs Function

دالة تعبر الطاقة الحرة التي لها القدرة على التحرر من النظام والقيام بشغل ميكانيكي أو تصدر كحرارة من النظام. مثل طاقة احتراق البنزين تعمل على تسيير سيارة أو تشغيل آلة

## The Gibbs Function

The Gibbs Junction (also called the Gibbs free energy) is defined as

$$G = H - TS$$

For an infinitesimal reversible process,

$$dG = dH - TdS - SdT$$

but

$$dH = TdS + VdP$$

$$dG = -SdT + VdP$$

In the case of a reversible isothermal and isobaric process,

$$dG = 0$$

And

$$G = \text{Constant}$$

- This is a particularly important result in connection with processes involving a change of phase. **Sublimation, fusion, and vaporization** take place isothermally and isobarically and can be considered to be occurring reversibly.
- Hence, during such processes, the Gibbs function of the system remains constant.
- The Gibbs function is of the utmost importance in chemistry, since chemical reactions can be conceived of as taking place at constant  $P$  and  $T$ . It is also of some use in engineering.

## Summery

Internal Energy

•  $U$

Enthalpy

•  $H = U + PV$

Helmholtz Function

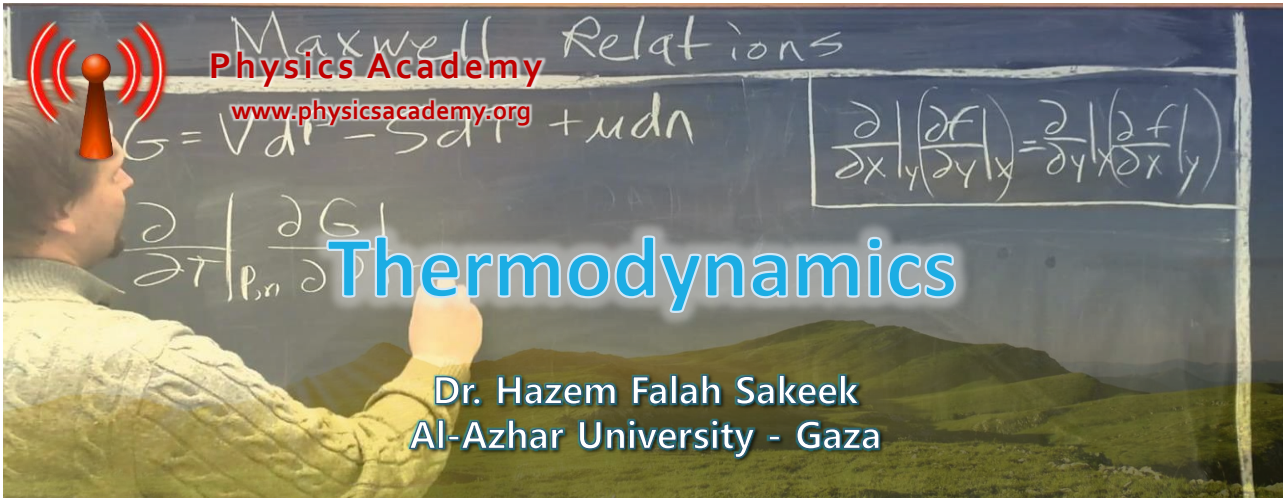
•  $F = U - TS$

Gibbs Function

•  $G = H - TS$

إلى اللقاء مع المحاضرة (٢٨)

***Maxwell's Equations***



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Maxwell Relations

$$G = VdP - SdT + \mu dn$$

$$\left. \frac{\partial}{\partial T} \right|_{P,n} \left. \frac{\partial G}{\partial P} \right|_{T,n} = \left. \frac{\partial}{\partial P} \right|_{T,n} \left. \frac{\partial G}{\partial T} \right|_{P,n}$$

# Thermodynamics

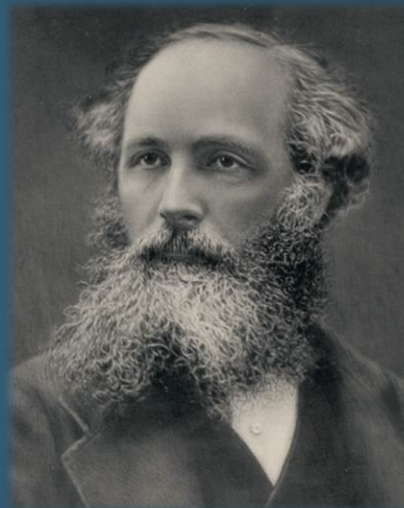
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## Unit 5: Pure Substance

### Lecture 28: Maxwell's Equations

## Unit 5: Pure Substance

- ☐ Enthalpy
- ☐ The Helmholtz functions
- ☐ Gibbs functions
- ☐ **Maxwell's Equations**
- ☐ The Tds equations
- ☐ Energy equations
- ☐ Heat-capacity equations



## Example 1

One mole of ice is converted to water at 273 K in atmospheric pressure, the change in volume is  $1.64 \times 10^{-6} \text{ m}^3$ . If the latent heat of fusion is 6030 J/mole, **calculate the change in internal energy, change in entropy, change in Gibb's function.**

(i) The change in internal energy  $\Delta U = Q + W$

$$\Delta U = Q + P\Delta V = 6030 + 1 \times 10^5 (1.6 \times 10^{-6}) = 6030.16 \text{ J}$$

(ii) The change in entropy  $\Delta S = \frac{\Delta Q}{T}$

$$= \frac{6030}{273} = 22 \text{ J/K}$$

(iii) The change in Gibb's function  $\Delta G = V\Delta P - S\Delta T = 0$

Since  $\Delta P = 0$  (isobaric process) and  $\Delta T = 0$  (isothermal process)

## Example 2

Prove that the change in pressure with respect to the temperature in phase change is given by

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

For phase change  $dG = 0$

Therefore,  $G = \text{constant}$

Then,

$g' = g''$  for fusion curve

$g'' = g'''$  for vaporization curve

$g' = g'''$  for sublimation curve

Where  $g'$  for gas phase,  $g''$  for liquid phase,  $g'''$  for solid phase

$$dG = VdP - SdT$$

عند زيادة درجة الحرارة من  $T$  إلى  $T + dT$  فإن الضغط يزداد من  $P$  إلى  $P + dP$  وكذلك تزداد دالة جيبس من  $g'$  إلى  $g' + dg'$  ومن  $g''$  إلى  $g'' + dg''$

ولكن في حالة الاتزان يكون التغير في دالة جيبس ثابتا اي ان

$$g' = g''$$

$$g' + dg' = g'' + dg''$$

$$dg' = dg''$$

$$dg' = V_1 dP - S_1 dT$$

$$dg'' = V_2 dP - S_2 dT$$

**معادلة كلاوزيوس-كلايرون**  
Clausius–Clapeyron relation

بمساواة المعادلتين نحصل على ما يلي:

$$(V_2 - V_1) dP = (S_2 - S_1) dT$$

ما هو الضغط اللازم لانصهار الثلج عند درجة حرارة أقل بمقدار  $\Delta T$  من الصفر المئوي؟

$$\frac{dP}{dT} = \frac{\Delta S}{(V_f - V_i)} = \frac{L}{T(V_f - V_i)}$$

## Maxwell's Equations

A set of equations in thermodynamics which are derivable from the symmetry of second derivatives and from the definitions of the thermodynamic potentials. These relations are named for the nineteenth-century physicist James Clerk Maxwell.

## Theorem: Condition for an exact differential

If a relation exists among  $x$ ,  $y$ , and  $z$ , we may imagine  $z$  expressed as a function of  $x$  and  $y$ ; hence,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

If we let

$$M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

then

$$dz = Mdx + Ndy$$

where  $z$ ,  $M$ , and  $N$  are all functions of  $x$  and  $y$ .

Partially differentiating  $M$  with respect to  $y$ , and  $N$  with respect to  $x$ , we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial^2 z}{\partial y \partial x}\right) \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

Since the two second derivatives of the right-hand terms are equal, it follows that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

This is known as the condition for an exact differential.

## Maxwell's Equations

The properties of a pure substance are conveniently represented in terms of these four functions

Internal Energy •  $U$

Enthalpy •  $H = U + PV$

Helmholtz Function •  $F = U - TS$

Gibbs Function •  $G = H - TS$

Any one of these may be regarded as a function of any two of  $P$ ,  $V$ , and  $T$ .

Suppose for example that both  $U$  and  $S$  are expressed as functions of  $V$  and  $T$ , thus

$$U = \text{function of } (V, T) \quad \text{and} \quad S = \text{function of } (V, T)$$

The second equation  $S = \text{function of } (V, T)$  may be imagined to be solved for  $T$  in terms of  $S$  and  $V$ ;

Substituting this value of  $T$  in the first equation  $U = \text{function of } (V, T)$ , we should then have

$$U = \text{function of } (S, V)$$

Now imagine a hydrostatic system undergoing an infinitesimal reversible process from one equilibrium state to another

1 The internal energy changes by an amount

$$dU = TdS - PdV$$

2 The enthalpy changes by an amount

$$dH = TdS + VdP$$

3 The Helmholtz function changes by an amount

$$dF = -SdT - PdV$$

4 The Gibbs function changes by an amount

$$dG = -SdT + VdP$$

Since  $U$ ,  $H$ ,  $F$ , and  $G$  are actual functions, their differentials are exact differentials of the type

$$dz = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

# Maxwell's equations

Applying this result to the four exact differentials  $dU$ ,  $dH$ ,  $dF$ , and  $dG$ :

$$dz = Mdx + Ndy$$

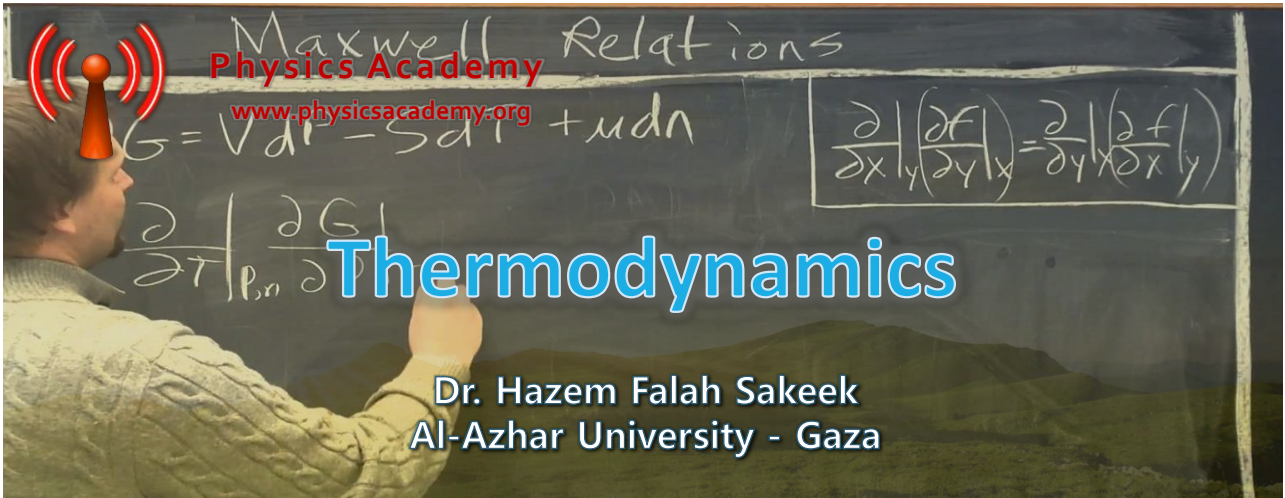
$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

1	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
2	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
3	$dF = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
4	$dG = -SdT + VdP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Maxwell's equations are extremely useful, because they provide relationships between measurable quantities and those which either cannot be measured or are difficult to measure.

إلى اللقاء مع المحاضرة (٢٩)

*The Tds equations*



Maxwell Relations

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$$G = \int V dp - \int S dT + \int \mu dn$$

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right)$$

# Thermodynamics

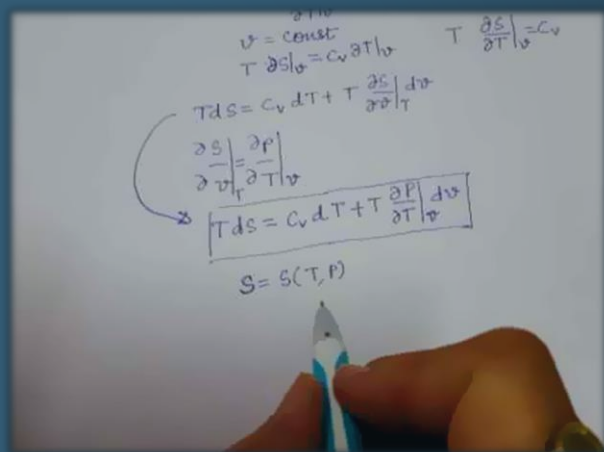
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## Unit 5: Pure Substance

### Lecture 29: The Tds equations and Energy equations

## Unit 5: Pure Substance

- ☐ Enthalpy
- ☐ The Helmholtz functions
- ☐ Gibbs functions
- ☐ Maxwell's Equations
- ☐ **The Tds equations**
- ☐ **Energy equations**
- ☐ Heat-capacity equations



$$v = \text{const}$$

$$T \left. \frac{\partial S}{\partial T} \right|_v = C_v$$

$$T ds = C_v dT + T \left. \frac{\partial S}{\partial T} \right|_v dv$$

$$\left. \frac{\partial S}{\partial T} \right|_v = \left. \frac{\partial P}{\partial T} \right|_v$$

$$T ds = C_v dT + T \left. \frac{\partial P}{\partial T} \right|_v dv$$

$$S = S(T, P)$$

## The first $TdS$ Equation

The entropy of a pure substance can be imagined as a function of  $T$  and  $V$ , i.e.  $S = f(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

$TdS = dQ$  for a reversible process, then

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_v$$

And, from Maxwell's third equation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

**The first  $Tds$  equation**

## Example 1

1 mole of a **van der Waals gas** undergoes a reversible **isothermal expansion** from a volume  $V_i$  to a volume  $V_f$ . How much heat has been transferred?

For 1 mole

$$TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

Using molar van der Waals equation of state.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$TdS = C_v dT + RT \frac{dV}{V-b}$$

Since  $T$  is constant,  $C_v dT = 0$ ; and since the process is reversible,  $Q = \int TdS$ , Therefore,

$$Q = RT \int_{V_i}^{V_f} \frac{dV}{V-b}$$

$$Q = RT \ln \frac{V_f - b}{V_i - b}$$

## The Second $TdS$ Equation

The entropy of a pure substance can be imagined as a function of  $T$  and  $P$ , i.e.  $S = f(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$TdS = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$T \left(\frac{\partial S}{\partial T}\right)_P = C_P$$

And, from Maxwell's fourth equation,

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

$$TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{The second } Tds \text{ equation}$$

### Case 1: Reversible isothermal change of pressure

$$TdS = C_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$TdS = -T \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$Q = -T \int \left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{But} \quad \boxed{\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P} \Rightarrow \boxed{V\beta = \left(\frac{\partial V}{\partial T}\right)_P}$$

$$Q = -T \int V\beta dP$$

which can be integrated when the dependence of  $V$  and  $\beta$  on the pressure is known. In the case of a solid or liquid, **neither  $V$  nor  $\beta$  is very sensitive to a change in pressure.**

**For example,** in the case of mercury, as the pressure is increased from zero to 1000 atm at 0°C the volume of 1 mole of mercury changed 0.3%, and  $\beta$  changed by 4%.

Therefore the volume and expansivity of solid and liquid assumed to be constant.

$$Q = -T \int V \beta dP$$

$$Q = -TV\beta \int_{P_i}^{P_f} dP$$

$$Q = -TV\beta(P_f - P_i)$$

It is seen from this result that, as the pressure is increased isothermally, heat will flow out if  $\beta$  is positive but, for a substance with a negative expansivity (such as water between 0 and 4°C), an isothermal increase of pressure causes an absorption of heat.

If the pressure on  $2 \times 10^{-5} \text{ m}^3$  of mercury at 0°C is increased reversibly and isothermally from zero to 1000 atm, the heat transferred will be

$$Q = -TV\beta P_f$$

Where  $T = 293\text{K}$ ,  $V = 2 \times 10^{-5} \text{ m}^3$ ,  $\beta = 1.81 \times 10^{-4} \text{ K}^{-1}$ ,  $P_f = 1.01 \times 10^8 \text{ Pa}$

$$Q = -(293) \times (2 \times 10^{-5})(1.81 \times 10^{-4})(1.01 \times 10^8) = -80.3 \text{ J}$$

i.e. 80.1 J of heat leaves the system in order to keep the temperature constant as the pressure increased.

## Case 2: Reversible adiabatic change of pressure

Then the entropy is constant in this process

$$TdS = 0 = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$dT = \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_P dP \quad \text{But} \quad \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$dT = \frac{TV\beta}{C_p} dP$$

In the case of a solid or liquid, an increase of pressure of as much as 1000 atm produces only a small temperature change.

Also, experiment shows that  $C_p$  hardly changes even for an increase of 10,000 atm. The above equation, when applied to a solid or a liquid, may therefore be written

$$\Delta T = \frac{TV\beta}{C_p} (P_f - P_i)$$

$$\Delta T = \frac{TV\beta}{C_p}(P_f - P_i)$$

It is clear from the above that an adiabatic **increase of pressure** will produce an **increase of temperature** in any substance with a positive expansivity and a **decrease in temperature** in a substance with a negative expansivity.

### Example

If the pressure on 15 cm<sup>3</sup> of mercury ( $C_p=139$  J/kg.K and specific volume  $V=7.38 \times 10^{-5}$  m<sup>3</sup>/kg) at 20°C is increased at constant entropy from zero to 1000 atm, the temperature change will be

$$\Delta T = \frac{TV\beta}{C_p}P_f$$

$$\Delta T = \frac{(293)(7.38 \times 10^{-5})(1.81 \times 10^{-4})}{139}(1.01 \times 10^8) = 2.84K$$

# Energy Equation

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## The first Energy Equation the dependence of volume

If a pure substance undergoes an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = TdS - PdV$$

Dividing by  $dV$ , we get

$$\frac{dU}{dV} = T \frac{dS}{dV} - P$$

where  $U$ ,  $S$ , and  $P$  are regarded as functions of  $T$  and  $V$ . If  $T$  is held constant, then the derivatives become partial derivatives, and

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

Using Maxwell's third equation,  $(\partial S / \partial V)_T = (\partial P / \partial T)_V$ , we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{the first energy equation}$$

### Case 1: Ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$P = \frac{nRT}{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{nR}{V} - P = 0$$

Therefore,  $U$  does not depend on  $V$ , but is a function of  $T$  only in an ideal gas

## Case 2: Van der Wools gas $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \frac{R}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

$$dU = C_V dT + \frac{a}{V^2} dV \Rightarrow U = \int (C_V dT) - \frac{a}{V} + \text{constant}$$

The internal energy of a van der Waals gas increases as the volume increases, with the temperature remaining constant.

## The second Energy Equation the dependence of pressure

$$dU = TdS - PdV$$

divide by  $dP$

$$\frac{dU}{dP} = T \frac{dS}{dP} - P \frac{dV}{dP}$$

where  $U$ ,  $S$ , and  $V$  are imagined to be functions of  $T$  and  $P$ . If  $T$  is held constant, then the derivatives become partial derivatives, and

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T$$

Using Maxwell's fourth equation,  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ , we get

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T \quad \text{the second energy equation}$$

## Problem to solve by yourself

Derive the third  $TdS$  Equation


$$T dS = C_V \left( \frac{\partial T}{\partial P} \right)_V dP + C_P \left( \frac{\partial T}{\partial V} \right)_P dV$$

and show that the three  $TdS$  equations may be written as follows

$$\begin{aligned} (a) \quad T dS &= C_V dT + \frac{\beta T}{\kappa} dV. \\ (b) \quad T dS &= C_P dT - V \beta T dP. \\ (c) \quad T dS &= \frac{C_V \kappa}{\beta} dP + \frac{C_P}{\beta V} dV. \end{aligned}$$

إلى اللقاء مع المحاضرة (٣٠)

***Heat-capacity equations***



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Maxwell Relations

$$G = VdT - SdT + \mu dn$$

$$\left. \frac{\partial}{\partial x} \right|_y \left( \left. \frac{\partial f}{\partial y} \right|_x \right) = \left. \frac{\partial}{\partial y} \right|_x \left( \left. \frac{\partial f}{\partial x} \right|_y \right)$$

# Thermodynamics

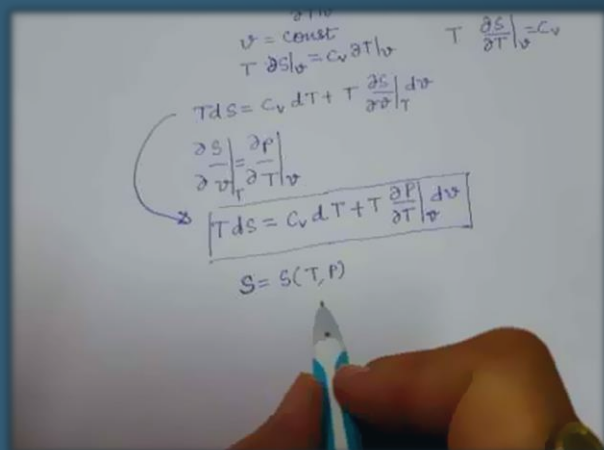
Dr. Hazem Falah Sakeek  
Al-Azhar University - Gaza

## Unit 5: Pure Substance

### Lecture 30: Heat-capacity equations

## Unit 5: Pure Substance

- ☐ Enthalpy
- ☐ The Helmholtz functions
- ☐ Gibbs functions
- ☐ Maxwell's Equations
- ☐ The Tds equations
- ☐ Energy equations
- ☐ **Heat-capacity equations**



$$v = \text{const} \quad T \left. \frac{\partial S}{\partial T} \right|_v = C_v$$

$$TdS = C_v dT + T \left. \frac{\partial S}{\partial v} \right|_T dv$$

$$\left. \frac{\partial S}{\partial v} \right|_T = \left. \frac{\partial p}{\partial T} \right|_v$$

$$TdS = C_v dT + T \left. \frac{\partial p}{\partial T} \right|_v dv$$

$$S = S(T, v)$$

## Heat-capacity Equations

$$T dS = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_V dV \quad \text{The first } Tds \text{ equation}$$

$$T dS = C_P dT - T \left( \frac{\partial V}{\partial T} \right)_P dP \quad \text{The second } Tds \text{ equation}$$

Equating the first and second  $T dS$  equations,

$$C_P dT - T \left( \frac{\partial V}{\partial T} \right)_P dP = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_V dV$$

solving for  $dT$

$$dT = \frac{T \left( \frac{\partial P}{\partial T} \right)_V}{C_P - C_v} dV + \frac{T \left( \frac{\partial V}{\partial T} \right)_P}{C_P - C_v} dP$$

But

$$dT = \frac{T \left( \frac{\partial P}{\partial T} \right)_V}{C_P - C_v} dV + \frac{T \left( \frac{\partial V}{\partial T} \right)_P}{C_P - C_v} dP$$

$$dT = \left( \frac{\partial T}{\partial V} \right)_P dV + \left( \frac{\partial T}{\partial P} \right)_V dP$$

Therefore,

$$\left( \frac{\partial T}{\partial V} \right)_P = \frac{T \left( \frac{\partial P}{\partial T} \right)_V}{C_P - C_v}$$

$$\left( \frac{\partial T}{\partial P} \right)_V = \frac{T \left( \frac{\partial V}{\partial T} \right)_P}{C_P - C_v}$$

Both the above equations yield the result that

$$C_P - C_v = T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V$$

It was shown

$$\left( \frac{\partial P}{\partial T} \right)_V = - \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T$$

$$C_P - C_v = -T \left( \frac{\partial V}{\partial T} \right)_P^2 \left( \frac{\partial P}{\partial V} \right)_T$$

Heat-capacity Equations

This is one of the most important equations of thermodynamics, and it shows that:

## Remarks

$$C_P - C_v = -T \left( \frac{\partial V}{\partial T} \right)_P^2 \left( \frac{\partial P}{\partial V} \right)_T$$

Heat-capacity Equations

- Since  $\left( \frac{\partial P}{\partial V} \right)_T$  is always negative for all known substances and  $\left( \frac{\partial V}{\partial T} \right)_P^2$  must be positive, then  $C_P - C_v$  can never be negative, or  $C_P$  can never be less than  $C_v$ .
- As  $T \rightarrow 0$ ,  $C_P \rightarrow C_v$ ; or at absolute zero, the two heat capacities are equal.
- $C_P = C_v$  when  $\left( \frac{\partial V}{\partial T} \right)_P = 0$ . For example at  $4^\circ\text{C}$ , the temperature at which the density of water is maximum,  $C_P = C_v$ .

## Remarks

- Laboratory measurements of the heat capacity of solids and liquids usually take place at **constant pressure** and therefore yield **values of  $C_p$** .
- It would be extremely difficult to measure with any degree of accuracy the  $C_v$  of a solid or liquid.
- Values of  $C_v$ , however, must be known for purposes of comparison with theory. The equation for the difference in the heat capacities is very useful in calculating  $C_v$  in terms of  $C_p$  and other measurable quantities. **Remembering that**

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

Volume expansivity

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

Isothermal compressibility

## Heat-capacity Equations (Practical form)

Heat-capacity Equations  $C_p - C_v = -T \left( \frac{\partial V}{\partial T} \right)_P^2 \left( \frac{\partial P}{\partial V} \right)_T$

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$C_p - C_v = \frac{TV \left[ \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \right]^2}{-\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T}$$

$$C_p - C_v = \frac{TV\beta^2}{\kappa}$$

## Example

Calculate  $C_v$  of mercury at 20°C and atmospheric pressure, where  $C_p=139\text{J/kg.K}$ ,  $T=293\text{K}$ ,  $V = 7.38 \times 10^{-5}\text{m}^3/\text{kg}$ ,  $\beta = 1.81 \times 10^{-4}\text{K}^{-1}$ ,  $\kappa = 4.01 \times 10^{-11}\text{Pa}^{-1}$

$$C_p - C_v = \frac{TV\beta^2}{\kappa}$$

$$139 - C_v = \frac{(293)(7.38 \times 10^{-5})(1.81 \times 10^{-4})^2}{4.01 \times 10^{-11}}$$

$$= 17.7.3\text{J/kg.K}$$

$$C_v = 121.3\text{J/kg.K}$$

The ratio  $\frac{C_p}{C_v} = \gamma$ ,

$$\gamma = \frac{C_p}{C_v} = \frac{139}{121.3} = 1.15$$

## Heat-capacity in adiabatic compressibility

The two  $TdS$  equations are

$$TdS = C_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dV \quad \text{The first } Tds \text{ equation}$$

$$TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_p dP \quad \text{The second } Tds \text{ equation}$$

At constant  $S$

$$C_p dT_S = T \left( \frac{\partial P}{\partial T} \right)_p dP_S$$

$$C_v dT_S = -T \left( \frac{\partial P}{\partial T} \right)_v dV_S$$

$$\Rightarrow \frac{C_p}{C_v} = - \left[ \frac{\left( \frac{\partial V}{\partial T} \right)_p}{\left( \frac{\partial P}{\partial T} \right)_v} \right] \left( \frac{\partial P}{\partial V} \right)_S$$

$$\frac{C_P}{C_V} = - \left[ \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial P}{\partial T} \right)_V} \right] \left( \frac{\partial P}{\partial V} \right)_S$$

But

$$\left[ \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial P}{\partial T} \right)_V} \right] = - \left( \frac{\partial V}{\partial P} \right)_T$$

And

$$\kappa_S = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S$$

Isentropic compressibility

$$\kappa = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

Isothermal compressibility

Therefore

$$\gamma = \frac{C_P}{C_V} = \frac{\kappa}{\kappa_S}$$

From which  $\kappa_S$  can be calculated

إلى اللقاء في سلسلة محاضرات  
فيزيائية أخرى  
مع خالص دعواتي لكم بالتوفيق

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