Lectures notes on Thermodynamics

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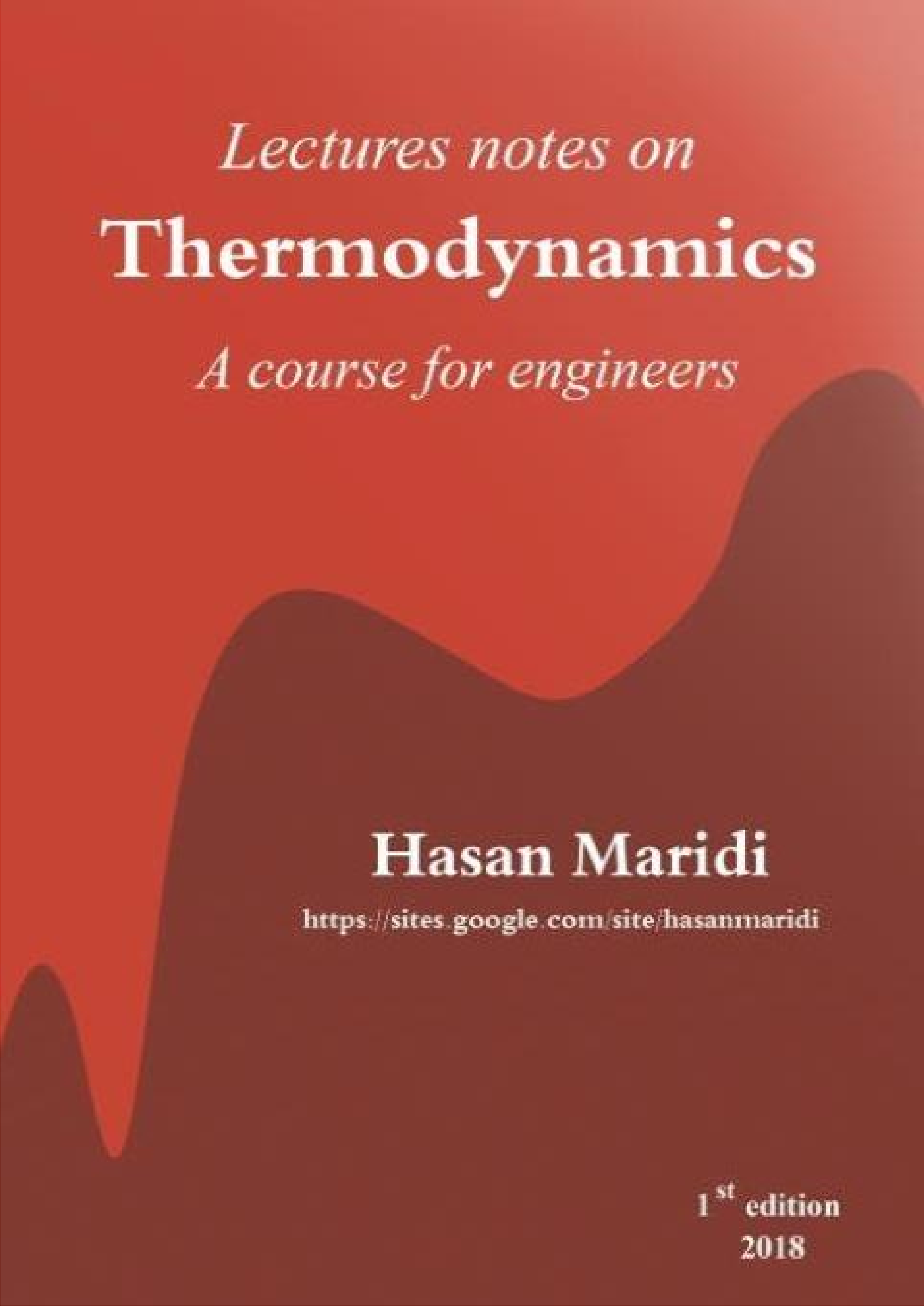

Lectures notes on

Thermodynamics

A course for engineers

Hasan Maridi

https://sites.google.com/site/hasanmaridi

1st edition
2018

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By

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Preface

This course is about thermodynamics which is concerned with the studies of transformation of energy from heat to work and vice versa. Thermodynamics allows chemists to predict whether a chemical process will occur under a given set of conditions.

Thermodynamics is immense importance in chemistry – energy output of chemical reactions, why reactions reach equilibrium, what their composition is at equilibrium, how reactions in electrochemical (and biological) cells can generate electricity.

In our study of thermodynamics we shall be looking at the first and second laws of thermodynamics as they apply to volume-pressure processes and energy changes associated with chemical reactions. In molecular kinetic theory, we shall be looking at explaining the general behaviour of gases from a molecular point of view.

Thermodynamics involves situations in which the temperature or state of a system changes due to energy transfers. It is very successful in explaining the bulk properties of matter. Also, it is successful in explaining the correlation between these properties and the mechanics of atoms and molecules. Historically, the development of thermodynamics paralleled the development of atomic theory.

Thermodynamics with its branches (Thermochemistry, Electrochemistry, Equilibrium chemistry, …) also addresses practical questions:

- How a refrigerator is able to cool its contents?
- What types of transformations occur in a power plant?
- What happens to the kinetic energy of an object as it comes to a rest?

HASAN MARIDI

SANAA, YEMEN, 02 MAR 2018

CONTENTS

PREFACE..3

CONTENTS 5

1 **CHAPTER 1 TEMPERATURE**.. 7

1.1 TEMPERATURE...

1.2 THERMAL EQUILIBRIUM..

1.3 ZEROTH LAW OF THERMODYNAMICS ....

1.4 THERMOMETERS ....

1.5 TEMPERATURE SCALES ....

1.6 THERMAL EXPANSION...

2 **CHAPTER 2 KINETIC MOLECULAR THEORY OF IDEAL GAS**.............................. 21

2.1 PROPERTIES OF GASES..

2.2 THE GAS LAWS ....

2.3 KINETIC MOLECULAR THEORY ....

2.4 REAL GASES ....

3 CHAPTER 3 HEAT.. 47

3.1 HEAT..

3.2 SPECIFIC HEAT ....

3.3 CALORIMETRY...

3.4 LATENT HEAT ....

3.5 HEAT TRANSFER ....

4 **CHAPTER 4 WORK AND FIRST LAW OF THERMODYNAMICS**............................. 67

4.1 INTERNAL ENERGY ....

4.2 SYSTEMS AND SURROUNDINGS...

4.3 VOLUME- PRESSURE WORK...

4.4 FIRST LAW OF THERMODYNAMICS ....

4.5 SPECIAL PROCESSES ....

5 **CHAPTER 5 THERMOCHEMISTRY** 87

5.1 ENTHALPY ....

5.2 MOLAR SPECIFIC HEATS..

5.3 MEASUREMENTS OF ENTHALPY CHANGES ....

5.4 CONSTANT VOLUME CALORIMETER..

5.5 CONSTANT PRESSURE CALORIMETER ....

5.6 THE STANDARD REACTION ENTHALPY ....
5.7 HESS'S LAW ....
6 **CHAPTER 6 SECOND LAW OF THERMODYNAMICS** 107
6.1 SPONTANEOUS PROCESSES ....
6.2 SECOND LAW OF THERMODYNAMICS ....
6.3 ENTROPY ....
6.4 THIRD LAW OF THERMODYNAMICS ....
6.5 GIBBS FREE ENERGY...
7 **CHAPTER 7 HEAT ENGINES** 123
7.1 HEAT ENGINE ....
7.2 THERMAL EFFICIENCY OF A HEAT ENGINE...
7.3 PERFECT HEAT ENGINE ....
7.4 CARNOT ENGINE ....
7.5 CARNOT CYCLE...
8 **CHAPTER 8 CHEMICAL EQUILIBRIUM**...145
8.1 CHEMICAL EQUILIBRIUM ....
8.2 THE LAW OF MASS ACTION ....
8.3 THE REACTION QUOTIENT...
8.4 FREE ENERGY AND EQUILIBRIUM CONSTANT ....
9 **CHAPTER 9 ELECTROCHEMISTRY** 155
9.1 ELECTROCHEMICAL CELLS ....
9.2 THE CELL POTENTIAL ....
9.3 STANDARD ELECTRODE POTENTIALS...
9.4 THE THERMODYNAMICS OF ELECTROCHEMICAL CELLS ....
APPENDIX A KEY CONCEPTS 167
REFERENCES..171

Chapter 1 *by Dr. Hasan Maridi*

Temperature

Temperature

We associate the concept of temperature with how hot or cold an object feels.
Our senses provide us with a qualitative indication of temperature.
Our senses are unreliable for this purpose.
We need a reliable and reproducible method for measuring the relative hotness or coldness of objects. We need a technical definition of temperature.

Thermal Contact and Thermal Equilibrium

Two objects are in **thermal contact** with each other if energy can be exchanged between them. The exchanges we will focus on will be in the form of heat or electromagnetic radiation.
The energy is exchanged due to a temperature difference.
Thermal equilibrium is a situation in which two objects would not exchange energy by heat or electromagnetic radiation if they were placed in thermal contact. The thermal contact does not have to also be physical contact.

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.
Let object C be the thermometer. Since they are in thermal equilibrium with each other, there is no energy exchanged among them.

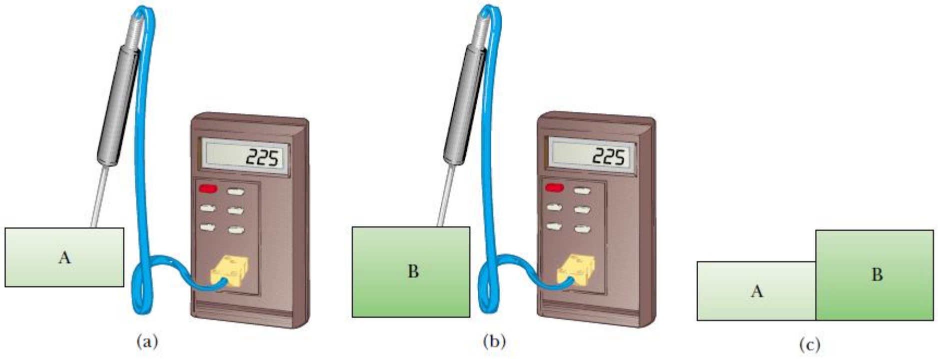


Figure 1.1 The zeroth law of thermodynamics. (a) and (b) If the temperatures of A and B are measured to be the same by placing them in thermal contact with a thermometer (object C), no energy will be exchanged between them when they are placed in thermal contact with each other (c).

- Object C (thermometer) is placed in contact with A until they achieve thermal equilibrium.
- The reading on C is recorded.
- Object C is then placed in contact with object B until they achieve thermal equilibrium.
- The reading on C is recorded again.
- If the two readings are the same, we can conclude that A and B are in thermal equilibrium with each other.

Temperature – Definition

Temperature can be thought of as the property that determines whether an object is in thermal equilibrium with other objects.
Two objects in thermal equilibrium with each other are at the same temperature. If two objects have different temperatures, they are not in thermal equilibrium with each other.
Temperature is something that determines whether or not energy will transfer between two objects in thermal contact.

Thermometers

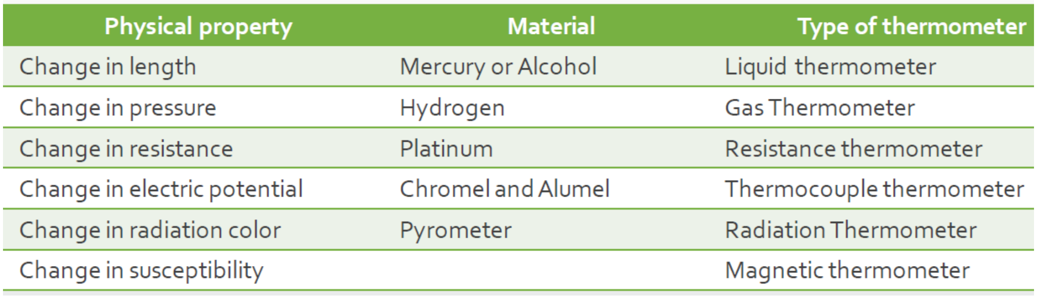
A **thermometer** is a device that is used to measure the temperature of a system.

Thermometers are based on the principle that some physical property of a system changes as the system's temperature changes.

These properties include:

- The volume of a liquid
- The dimensions of a solid
- The pressure of a gas at a constant volume
- The volume of a gas at a constant pressure
- The electric resistance of a conductor
- The color of an object

A temperature scale can be established on the basis of any of these physical properties.



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

Thermometer, Liquid in Glass

A common type of thermometer is a liquid-in-glass. The material in the capillary tube expands as it is heated. The liquid is usually mercury or alcohol.

Figure 1.2 As a result of thermal expansion, the level of the mercury in the thermometer rises as the mercury is heated by water in the test tube.

Calibrating a Thermometer

A thermometer can be calibrated by placing it in contact with some natural systems that remain at constant temperature.
Common systems involve water as:

- A mixture of ice and water at atmospheric pressure called the ***ice point*** of water

- A mixture of water and steam in equilibrium called the ***steam point*** of water

Once these points are established, the length between them can be divided into a number of segments.

Celsius Scale

The ice point of water is defined to be 0^{o} C.
The steam point of water is defined to be 100^{o} C.
The length of the column between these two points is divided into 100 increments, called degrees.

Problems with Liquid-in-Glass Thermometers

An alcohol thermometer and a mercury thermometer may agree only at the calibration points. The discrepancies between thermometers are especially large when the temperatures being measured are far from the calibration points. The thermometers also have a limited range of values that can be measured.

- Mercury cannot be used under –39° C
- Alcohol cannot be used above 85° C

Table 3.1 Types of thermometric liquids

Liquid	**Temperature range, °C**	
	From	**To**
Mercury	-35	750
Toluene	-90	200
Ethanol	-80	70
Kerosene	-60	300
Petroleum Ether	-120	25
Pentane	-200	20

Constant-Volume Gas Thermometer

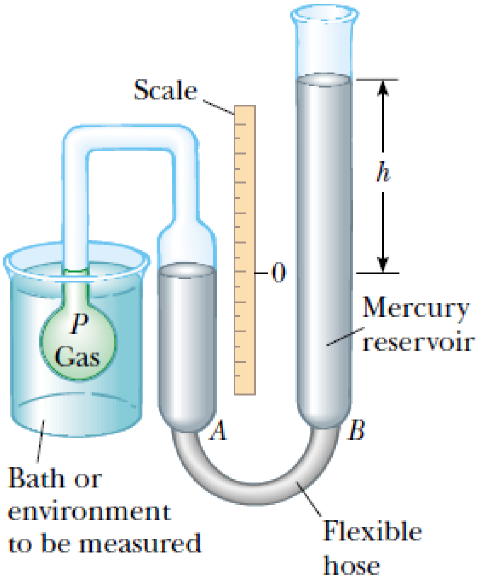


Figure 1.3 A constant-volume gas thermometer measures the pressure of the gas contained in the flask immersed in the bath. The volume of gas in the flask is kept constant by raising or lowering reservoir *B* to keep the mercury level in column *A* constant.

The physical change exploited is the variation of pressure of a fixed volume gas as its temperature changes.
The volume of the gas is kept constant by raising or lowering the reservoir B to keep the mercury level at A constant.
The pressure is indicated by the height difference between reservoir B and column A.

- The thermometer is calibrated by using an ice water bath and a steam water bath.
- The pressures of the mercury under each situation are recorded.
- The volume is kept constant by adjusting A.
- The information is plotted.

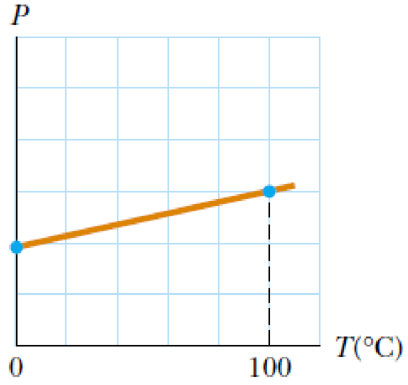


Figure 1.4 A typical graph of pressure versus temperature taken with a constant-volume gas thermometer. The two dots represent known reference temperatures (the ice and steam points of water).

To find the temperature of a substance, the gas flask is placed in thermal contact with the substance. The pressure is found on the graph and the temperature is read from the graph.

Absolute Zero

The thermometer readings are virtually independent of the gas used. If the lines for various gases are extended, the pressure is always zero when the temperature is –273.15° C. This temperature is called **absolute zero.**

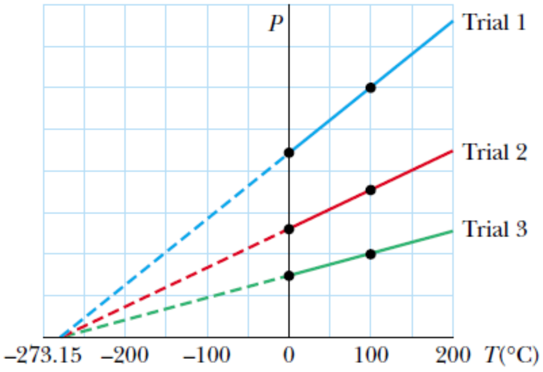


Figure 1.5 Pressure versus temperature for experimental trials in which gases have different pressures in a constant-volume gas thermometer. Note that, for all three trials, the pressure extrapolates to zero at the temperature -273.15°C.

The thermometer readings are virtually independent of the gas
Absolute zero is used as the basis of the **absolute temperature scale.** The size of the degree on the absolute scale is the same as the size of the degree on the Celsius scale.
To convert: $T_C = T - 273.15$.

Absolute Temperature Scale

The absolute temperature scale is now based on two new fixed points adopted by in 1954 by the International Committee on Weights and Measures. One point is absolute zero.The other point is the **triple point** of water. This is the combination of temperature and pressure where ice, water, and steam can all coexist.
The triple point of water occurs at *0.01° C and 4.58 mm of mercury.* This temperature was set to be 273.16 on the absolute temperature scale. This made the old absolute scale agree closely with the new one. The units of the absolute scale are **kelvins,** No degree symbol is used with kelvins.
The absolute scale is also called the Kelvin scale. **It is** named for William Thomson, Lord Kelvin.
The kelvin is defined as 1/273.16 of the difference between

absolute zero and the temperature of the triple point of water.
The temperature of absolute zero cannot be achieved. Experiments have come close.

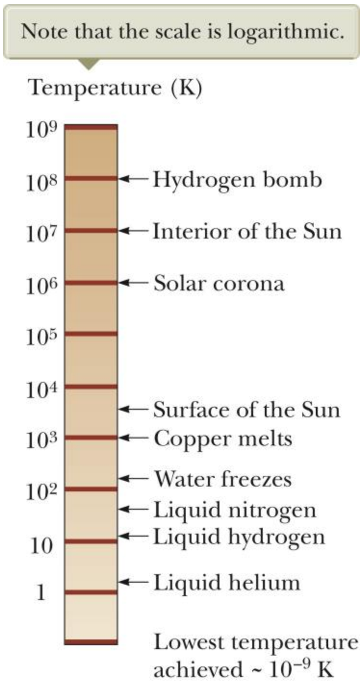


Figure 1.6 Absolute temperatures at which various physical processes occur. Note that the scale is logarithmic.

Fahrenheit Scale

A common scale in everyday use in the US, it is named for Daniel Fahrenheit. Temperature of the ice point is 32°F and temperature of the steam point is 212°. There are 180 divisions (degrees) between the two reference points.

Comparison of Scales

Celsius and Kelvin have the same size degrees, but different starting points.
$T_C = T_k - 273.15$ (1.1)
Celsius and Fahrenheit have different sized degrees and different starting points.

$$T_F = \frac{9}{5} T_C + 32^\circ F \tag{1.2}$$

To compare changes in temperature

$$\Delta T_C = \Delta T = \frac{5}{9} \Delta T_F$$

Ice point temperatures: 0°C = 273.15 K = 32° F
Steam point temperatures: 100°C = 373.15 K = 212° F.

Example 1.1

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

$$T_C = \tfrac{5}{9}(T_F - 32) = \tfrac{5}{9}(50 - 32)$$

$$= 10^\circ\mathrm{C}$$

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

Example 1.2

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

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

$$\Delta T_F = \tfrac{9}{5}\,\Delta T_C = \tfrac{9}{5}(55^\circ\mathrm{C}) = 99^\circ\mathrm{F}$$

Problem 1.1

Liquid nitrogen has a boiling point of -195.81°C at atmospheric pressure. Express this temperature (a) in degrees Fahrenheit and (b) in kelvins.

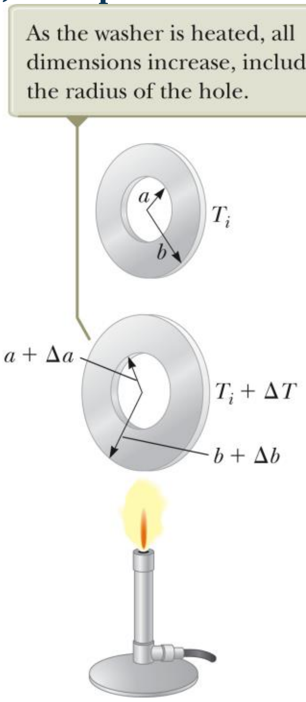
Thermal Expansion

Materials expand when heated and contract when cooled. This is true for all three states of matter however gases expand more than liquids which expand more than solids.

Different solids e.g metals expand by different amounts when heated through the same temperature range.

Solids expand in length, area, and volume. Thermal expansion is the increase in the size of an object with an increase in its temperature. Thermal expansion is a consequence of the change in the average separation between the atoms in an object. If the expansion is small relative to the original dimensions of the object, the change in any dimension is, to a good approximation, proportional to the first power of the change in temperature.

Thermal Expansion, example



As the washer is heated, all dimensions increase, including the radius of the hole.

Figure 1.7 Thermal expansion of a homogeneous metal washer. As the washer is heated, all dimensions increase. (The expansion is exaggerated in this figure.)

As the washer shown at right is heated, all the dimensions will increase. A cavity in a piece of material expands in the same way as if the cavity were filled with the material.

Linear Expansion

Assume an object has an initial length L. That length increases by ΔL as the temperature changes by ΔT. We define the **coefficient of linear expansion** α as

$$\alpha = \frac{\Delta L / L_i}{\Delta T}$$

or

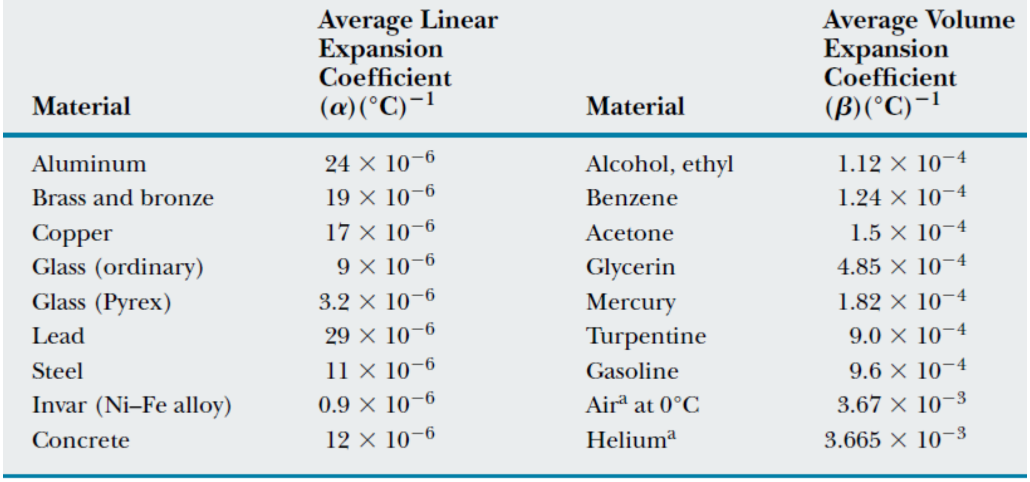
$$\Delta L = \alpha L_i \Delta T \qquad (1.3)$$

This equation can also be written in terms of the initial and final conditions of the object:

$L_f - L_i = \Delta L_i (T_f - T_i)$

The coefficient of linear expansion, α, has units of $(^{o}\mathrm{C})^{-1}$

Table 1.2 Some expansion coefficients



Material	Average Linear Expansion Coefficient $(\alpha)(^\circ\mathrm{C})^{-1}$	Material	Average Volume Expansion Coefficient $(\beta)(^\circ\mathrm{C})^{-1}$
Aluminum	24×10^{-6}	Alcohol, ethyl	1.12×10^{-4}
Brass and bronze	19×10^{-6}	Benzene	1.24×10^{-4}
Copper	17×10^{-6}	Acetone	1.5×10^{-4}
Glass (ordinary)	9×10^{-6}	Glycerin	4.85×10^{-4}
Glass (Pyrex)	3.2×10^{-6}	Mercury	1.82×10^{-4}
Lead	29×10^{-6}	Turpentine	9.0×10^{-4}
Steel	11×10^{-6}	Gasoline	9.6×10^{-4}
Invar (Ni–Fe alloy)	0.9×10^{-6}	Air[a] at 0°C	3.67×10^{-3}
Concrete	12×10^{-6}	Helium[a]	3.665×10^{-3}

Some materials expand along one dimension, but contract along another as the temperature increases. Since the linear dimensions change, it follows that the surface area and volume also change with a change in temperature.

A hole in a piece of material expands in the same way as if the cavity were filled with the material.

The notion of thermal expansion can be thought of as being similar to a photographic enlargement.

Example 1.3 Expansion of a Railroad Track

A segment of steel railroad track has a length of 30.0 m when the temperature is 0.0°C.

i- What is its length when the temperature is 40.0°C?

$$\Delta L = \alpha L_i \, \Delta T = [11 \times 10^{-6} (°\text{C})^{-1}](30.000 \text{ m})(40.0°\text{C})$$

$$= 0.013 \text{ m}$$

If the track is 30.0 m long at 0.0°C, its length at 40.0°C is 30.013 m.

ii- Suppose that the ends of the rail are rigidly clamped at 0.0°C so that expansion is prevented. What is the thermal stress set up in the rail if its temperature is raised to 40.0°C?

$$\text{Tensile stress} = \frac{F}{A} = Y\frac{\Delta L}{L_i}$$

Because *Y* for steel is 20 x 10^{10} N/m^2

$$\frac{F}{A} = (20 \times 10^{10} \text{ N/m}^2)\left(\frac{0.013 \text{ m}}{30.000 \text{ m}}\right) = 8.7 \times 10^7 \text{ N/m}^2$$

Volume Expansion

The change in volume is proportional to the original volume and to the change in temperature.

$$\Delta V = \beta V_i \, \Delta T \qquad (1.4)$$

where γ is the coefficient of volume expansion.

- For a solid, β= 3α, This assumes the material is isotropic, the same in all directions.

- For a liquid or gas, γ is given in the table

Problem 1.2

Prove that $\beta = 3\alpha$ for a solid

Hint: Consider a solid box of dimensions L, w, and h. Its volume at some temperature T_i is $V_i = Lwh$. Consider $\alpha \Delta T \ll 1$

Area Expansion

The change in area is proportional to the original area and to the change in temperature:

$$\Delta A = 2\alpha A_i \Delta T \qquad (1.5)$$

Bimetallic Strip

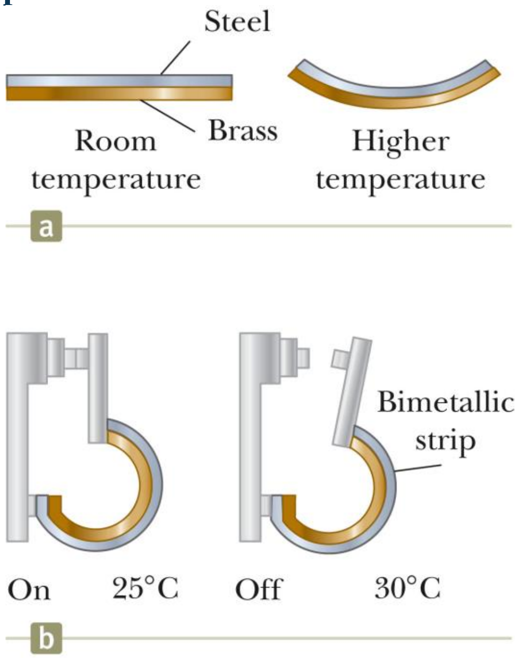


Figure 1.8 (a) A bimetallic strip bends as the temperature changes because the two metals have different expansion coefficients. (b) A bimetallic strip used in a thermostat to break or make electrical contact.

Each substance has its own characteristic average coefficient of expansion. This can be made use of in the device shown, called a bimetallic strip.

As the temperature of the strip increases, the two metals expand by different amounts. Then, the strip bends. It can be used in a thermostat.

Water’s Unusual Behavior

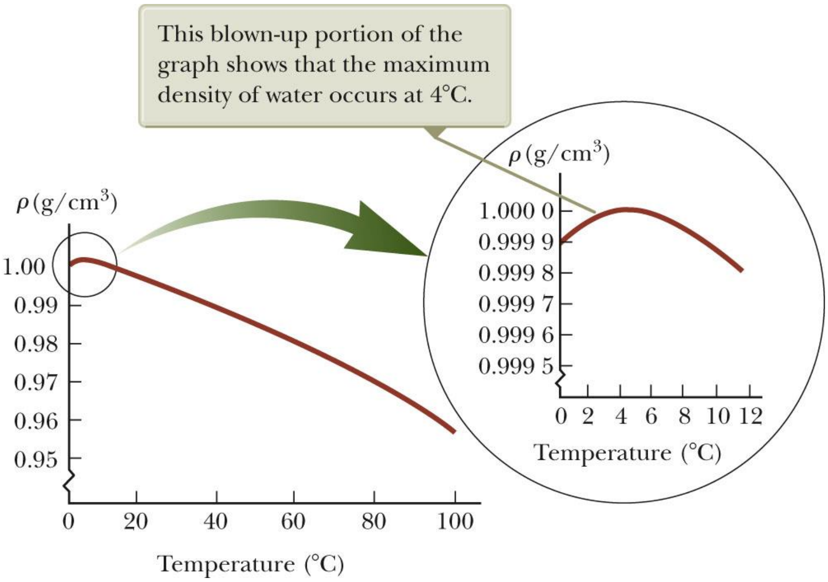

This blown-up portion of the graph shows that the maximum density of water occurs at 4°C.

Figure 1.11 The variation in the density of water at atmospheric pressure with temperature. The inset at the right shows that the maximum density of water occurs at 4°C.

As the temperature increases from 0°C to 4°C, water contracts. Its density increases.

Above 4°C, water expands with increasing temperature. Its density decreases.

The maximum density of water (1.000 g/cm^3) occurs at 4°C.

Chapter 2 *by Dr. Hasan Maridi*

Kinetic Molecular Theory of ideal gas

Three basic states of matter

Gas: Fills a container, taking on the shape of the container. Similar to a liquid, except that particles are very widely spaced from one another, and inter-particle interactions are minimal.

Liquid: Does not fill a container, but takes the shape of the container. Similar to gases except particles are very closely spaced.

Solid: Does not fill a container, and does not conform to the shape of the container. Particles are very closely packed – still much dynamic motion in a solid which increases with heating.

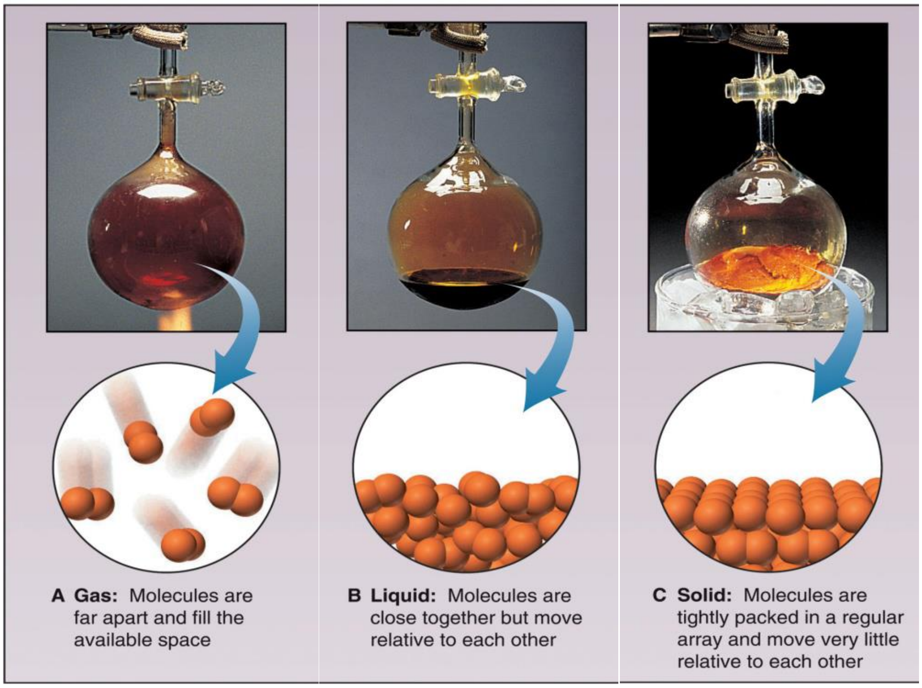


Figure 2.1 Three basic states of matter.

General properties of gases

- A gas is a state of matter which fills any container it occupies.
- Molecular picture of gas: Collection of widely separated molecules in random chaotic motion. Hence molecules move through space freely to fill any volume.
- Gases are highly compressible hence readily confined to smaller volume.
- Gases respond readily to changes in temperature and occupy a larger volume when heated and a smaller volume when cooled.
- Fundamental properties of gases described in terms of pressure P (units: Nm^{-2}, atm etc), Volume V (units: L (or dm^3), m^3 etc), temperature T (unit: K, ^oC) and amount (unit: mol).
- General properties of gases are described in terms of three empirical laws developed by Boyle, Charles and Avogadro which may be used to predict the behaviour of gas under given conditions of temperature, pressure and volume.

Ideal Gas

- An Ideal gas is pictured as a collection of molecules or atoms which undergo continuous random motion (Brownian motion).
- The speeds of the gas particles increase as the temperature increases.
- The molecules are widely separated from one another, with the only interactions being with the side walls of the container and other molecules during infrequent collisions.
- The molecules are unaffected by intermolecular forces (e.g. dipole/dipole, van der Waals etc).
- The state of a gas is defined by its pressure P, volume V, temperature T and amount n.

Pressure (P) is the force exerted by gas against the walls of the container. The SI unit of P is pascal
$1Pa = 1Nm^{-2} = 1\ kg\ m^{-1}\ s^{-2}$.
There are several non-SI units of pressure; the *atmosphere* (atm), the *torr*, and the *bar*.
1 atm = 101325 Pa = 760 torr = 760 mmHg

1 bar =100000 Pa

Volume (V) is the space occupied by the gas. The SI unit of volume is m^3. Other unit is Liter (L) where
$1\ L = 1\ dm^3 = 10^3\ cm^3 = 10^{-3}\ m^3$

Temperature (T) determines the kinetic energy and rate of motion of the gas particles. The SI unit of temperature is the *kelvin* (K). Other non-SI unit is Celsius (^0C)
$K = {}^0C + 273.15$

Amount (n) is the quantity of gas present in a container. The SI unit of n is the *mole* (mol).
$n = N/N_A$
where $N_A = 6.023x10^{23}$ (Avogadro's number). N is the number of molecules. Also,
$n = M/M_w$
where M is the mass of molecules and M_w is the molecular weight (molar mass) of one molecule.

The gas laws

Boyle's law (1661)

At constant temperature, the pressure of a fixed amount of gas is inversely proportional to its volume: $p \propto 1/V$
By treating n and T as constant, it becomes
PV = constant (at constant n and T) (2.1)

If we compress a fixed amount of gas at constant temperature into half of its original volume, then its pressure will double. The graph is obtained by plotting experimental values of P against V for a fixed amount of gas at different temperatures and the curves predicted by Boyle's law. Each curve is called an isotherm because it depicts the variation of a property (in this case, the pressure) at a single constant temperature.

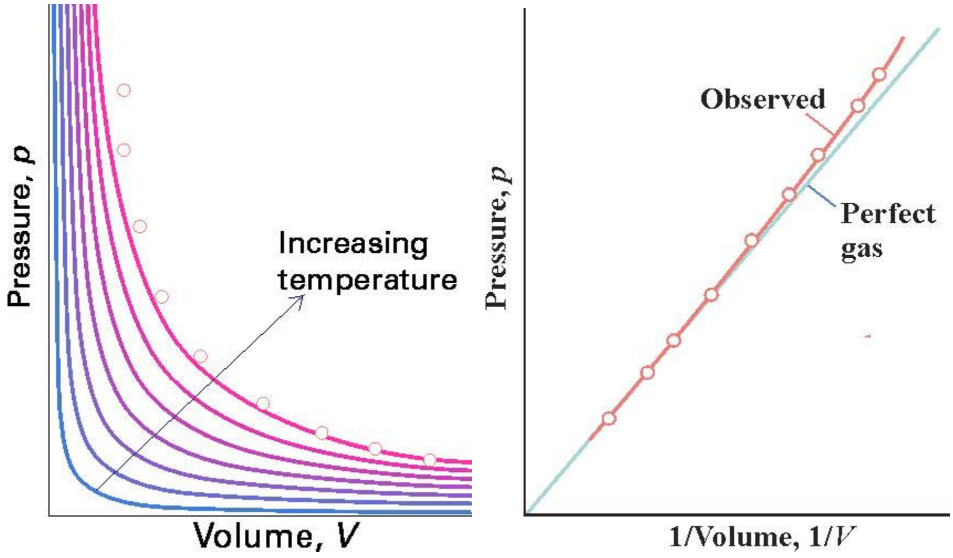


Figure 2.2 (a) Boyels law (b) Experimental verification of Boyle’s law.

Example 2.1

Consider a gas of 100 mL confined to a cylinder under a pressure of 1 atm. What would be the volume of the same gas at a pressure of 1.3 atm?

Solution

Boyle’s law states that the pressure of a gas (P) is inversely proportional to the volume (V) for a given of gas at constant temperature.

$PV = k$ where k is a constant, then, $P_1V_1 = P_2V_2$

$V_2=P_1V_1 / P_2$

P_1 = 1 atm, V_1 = 0.1 atm, P_2 = 1.3 atm, V_2 = ?

$V_2 = 1 atm \times 1.0 L / 1.3 atm$ = 0.0769 L

Practice problem 2.1

A gas bubble has a volume of 0.500 cm^3 at the bottom of the lake where the pressure is 3.49 atm. What is the volume of the bubble at the surface of the lake where the pressure is 1 atm? Assume that the temperature is constant.

(a) 10 dm^3 (b) 1.7 x 10^3 dm^3 (c) 1.7 dm^3 (d) 1.7 cm^3

Charles's law (Gay-Lussac's law)

At constant pressure, the volume of a fixed amount of gas varies linearly with the temperature: V = constant x (θ + 273.15)

θ- the temperature on the Celsius scale. Typical plots of volume against temperature for a series of samples of gases at different pressures. At low pressures and for temperatures that are not too low the volume varies linearly with the Celsius temperature.

All the volumes extrapolate to zero as θ approaches the same very low temperature (-273.15 ^{o}C). A volume cannot be negative – this common temperature must represent the absolute zero of temperature, a temperature below which it is impossible to cool an object. The Kelvin scale ascribes the value $T = 0$ to this absolute zero of temperature. Charles's law takes the simpler form: At constant pressure, $V \propto T$.

V / T= constant (at constant p and n)   (2.2)

An alternative version of Charles's law, in which the pressure of a sample of gas is monitored under conditions of constant volume, is

p / T= constant   (at constant V and n)   (2.3)

Example 2.2

A balloon is inflated to a volume of 2.5 L in a warm living room (24 ^{0}C). Then it is taken outside on a very cold winter's day (– 25 ^{0}C). Assume that the quantity of air in the balloon and its pressure both remain constant. What will be the volume of the balloon when it is taken outdoors?

Solution

The volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature.

$V \propto T$

$V = kT$

$V/T = k$

where k is a constant.

$V_1/T_1 = V_2/T_2$

Solving for V_2 with temperature in Kelvin scale gives us

$V_2=V_1T_2/T_1$

$V_1 = 2.5$ L, $T_1 = 297$ K, $T_2 = 248$ k, $V_2 = (?)$

$V_2 = 2.5$ L . 248 k / 297 K = 2 L

Avogadro's principle

At a given temperature and pressure, equal volumes of gas contain the same numbers of molecules. If we double the number of molecules but keep the temperature and pressure constant, then the volume of the sample will double.

Avogadro's principle: at constant temperature and pressure, $V \propto n$. This result follows from the perfect gas law by treating p and T as constants.

Avogadro's suggestion is a principle rather than a law (a direct summary of experience) because it is based on a model of a substance, in this case as a collection of molecules.

The molar volume, V_m, of any substance is the volume the substance occupies per mole of molecules.

Molar volume = (volume of sample) / (amount of substance)

$V_\mathrm{m} = V / n \quad (2.4)$

Avogadro's principle implies – the molar volume of a gas should be the same for all gases at the same temperature and pressure.

Example 2.3

Cyclopropane (C_3H_6) is a gas used as an anesthetic. What would be the mass of 1.0 L of the gas measured at standard temperature and pressure?

The law states that at a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas. At STP 1 mol of gas = 22.414 L.

Solution

Mass gas =1.00 L x1 mol x42.8 gmol^{-1} / 22.414 L = 1.88g

Practice problem 2.2

A car travelling at 16 km/h produces 150 g CO per kilometer. How many moles of CO are produce per kilometer?

(a) 5.4 (b) 3.4 (c) 5.0 (d) 53.6

The ideal gas law

In the previous sections we have looked at three historical laws that relate to two physical properties keeping all other properties constant. These laws and their mathematical expressions are shown below:

Boyle's law $P \propto 1/V$ where T and n are constant

Charles's law $V \propto T$ where P and n are constant

Avogadro's law $V \propto n$ where P and T are constant

The three gas laws can be combined to give a single general gas law

$PV/T \propto n$

We can replace the proportionality symbol $\propto$ with an equal sign by introducing proportionality constant. If the constant is given the symbol R, then

$PV/T = nR$

R is called the universal gas constant. The value and units of R depend on the units that are used for pressure, volume, temperature, and number of moles. The equation can be rearranged to the expression

$$PV = nRT \qquad (2.5)$$

called the ***ideal gas equation***. An ideal gas is one whose behavior can be accurately described by the ideal gas equation.

The constant of proportionality was found experimentally to be the same for all gases, is denoted R and called gas constant.

$R = 8.31451\ \text{J K}^{-1}\ \text{mol}^{-1}$

$= 8.31451\ \text{kPa L K}^{-1}\ \text{mol}^{-1}$

$= 0.082058\ \text{L atm K}^{-1}\ \text{mol}^{-1}$

$= 62.364\ \text{L Torr K}^{-1}\ \text{mol}^{-1}$

$= 1.98722\ \text{Cal K}^{-1}\ \text{mol}^{-1}$

the ***ideal gas equation*** can be rewritten as

$PV = nRT = (N/N_A)\ RT = Nk_BT$

where $k_B = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant. Sometimes k.

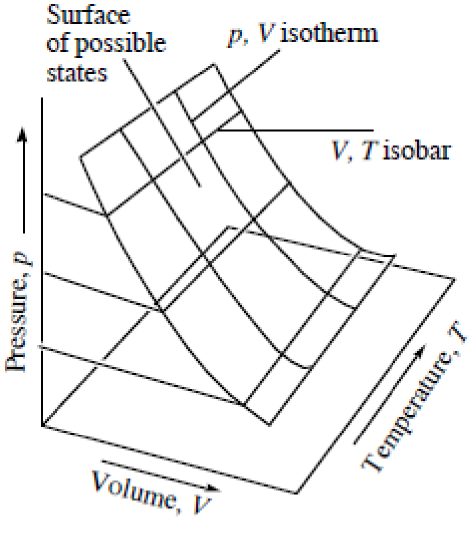


Figure 2.3 A plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature. The surface depicts only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface.

Determination of Universal Gas Constant R

Assume 1 mole gas (n = 1). At STP, P = 1 atm, T = 273.15 K, V_M = 22.414 $dm^{3.}$ In SI units: n = 1, P = 1 atm = 1.013 x 10^5 N m^{-2}, V_M= 22.414 x 10^{-3} m^3 since 1 dm^3 = 1 L = 10^{-3} m^3.

$$\boxed{R=\frac{\left(1.013\times10^{5}Nm^{-2}\right)\times\left(22.414\times10^{-3}m^{3}\right)}{\left(1mol\right)\times\left(273.15K\right)}=8.314\,Nm\,mol^{-1}K^{-1}=8.314\,\overset{\downarrow}{J}\,mol^{-1}K^{-1}}$$

Example 2.4

How many moles of hydrogen are present in a 50 L vessel if the pressure is 10 atm and the temperature is 25 °C?

Solution

The volume, pressure and temperature are given. The ideal gas law relates all the quantities given.

PV = nRT

P = 10 x 101325 Nm^{-2} =1.01 x 10^6 Nm^{-2}, V = 50 x10^{-3} m^3, T = 298 K, R = 8.314 J K^{-1} mol^{-1}

n = 50 x10^{-3} m^3 x1.01 x 10^6 Nm^{-2} / 8.314 J K^{-1} mol^{-1}x298 K = 20

Example 2.5

A chemist is investigating the conversion of atmospheric nitrogen to usable form by bacteria and needs to know the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 mL at 20°C.

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

$$p=\frac{(1.25/28.02)mol\times(8.31451kPaLK^{-1}mol^{-1})\times(20+273.15K)}{0.250L}$$

$$=435kPa$$

$$n_{N_2}=\frac{m}{M_{N_2}}=\frac{1.25g}{28.02gmol^{-1}}=\frac{1.25}{28.02}mol \qquad T/K=20+273.15$$

For a given temperature and pressure all gases have the same molar volume. An earlier set of standard conditions – standard temperature and pressure (STP) - °C and 1 atm. The molar volume of a perfect gas at STP is 22.41 L mol^{-1}. It is convenient to report data in chemical research at a particular set of standard conditions. Standard ambient temperature and pressure (SATP) – a temperature of 25ºC (more precisely, 298.15 K) and a pressure of 1 bar. The molar volume of a perfect gas at SATP is 24.79 L mol^{-1}.

Dalton's law of partial pressures

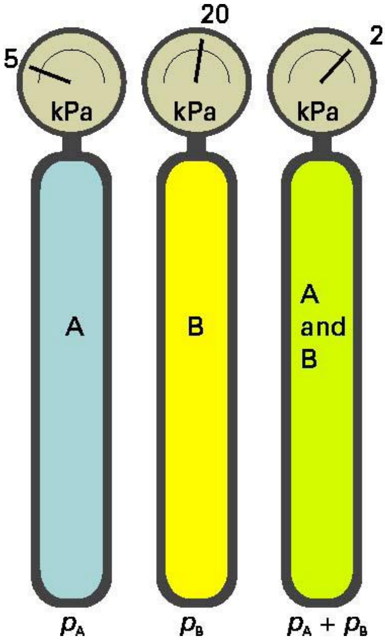


Figure 2.4 Mixture of perfect gases.

Dalton's law: The pressure exerted by a mixture of perfect gases is the sum of pressures that each gas would exert if it were alone in the container at the same temperature:

$$p = p_A + p_B + \ldots = (n_A + n_B + \ldots) RT/V = nRT/V \qquad (2.6)$$

p_J – the pressure that a gas J would exert if it were alone in the container at the same temperature.

For each gas: $p_J = n_J RT/V$ (2.7)

Dalton's law is strictly valid only for mixtures of perfect gases but it can be treated as valid for most conditions we encounter.

For any type of gas in a mixture, the partial pressure, p_J, is defined as

$$p_J = x_J \times p \qquad (2.8)$$

x_J – the mole fraction of J in the mixture. The mole fraction of J is the amount of J molecules expressed as a fraction of the total amount of molecules in the mixture.

In a mixture that consist of n_A A molecules, n_B B molecules, and so on, the mole fraction of J is

Mole fraction of J = (amount of J molecules)/(total amount of molecules)

$$x_J = n_J /n, \quad n = n_A + n_B + \ldots, \text{ and } \quad x_A + x_B + \ldots = 1 \qquad (2.9)$$

and

$$p_A + p_B + \ldots = (x_A + x_B + \ldots)p = p$$

For a binary mixture consisting of two species:

$$x_A = n_A /(n_A + n_B), \quad x_B = n_B /(n_A + n_B), \quad x_A + x_B = 1 \qquad (2.10)$$

For a mixture of perfect gases, we can identify the partial pressure of J with the contribution that J makes to the total pressure.

$$p_J = x_J\, p = x_J\, nRT/V = n_J\, RT/V \qquad (2.11)$$

The value of n_JRT/V is the pressure that an amount n_J of J would exert in the otherwise empty container.

Example 2.6

A container of volume 10.0 L holds 1.00 mol N_2 and 3.00 mol H_2 at 298 K. What is the total pressure in atmospheres if each component behaves as a perfect gas?

Solution

$p = p_A + p_B = (n_A + n_B)\ RT/V$

Use $R = 8.206\text{x}10^{-2}$ L atm K^{-1} mol^{-1}.

$p = (1.00\text{mol} + 3.00\text{mol})\ 8.206\text{x}10^{-2}$ L atm K^{-1} mol^{-1} x (298K) /10.0L

$p = 9.78$ atm

Example 2.7

The mass percentage composition of dry air at sea level is approximately N_2: 75.5; O_2: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1 atm?

Solution

We expect species with a high mole fraction to have a proportionally high partial pressure, as partial pressures are defined by $p_J = x_J\ p$. To calculate mole fractions, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J / M_J$. The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (for simplicity of calculations).

n(N2) = 0.755 x100 g / 28.02 g mol^{-1} = 2.69 mol

n(O2) = 0.232 x100 g / 32.00 g mol^{-1} = 0.725 mol

n(Ar) = 0.013 x100 g / 39.95 g mol^{-1} = 0.033 mol

n = n(N2) + n(O2) + n(Ar) = 3.448 mol

x(N2) = n(N2) / n = 2.69 mol / 3.448 mol = 0.780

x(O2) = n(O2) / n = 0.725 mol / 3.448 mol = 0.210

x(Ar) = n(Ar) / n = 0.033 mol / 3.448 mol = 0.0096

p(N2) = x(N2) p = 0.780 x1 atm = 0.780 atm

p(O2) = x(O2) p = 0.210 x1 atm = 0.210 atm

p(Ar) = x(Ar) p = 0.0096 x1 atm = 0.0096 atm

We have not had to assume that the gases are perfect: p_J are defined as $p_J = x_J\ p$ for any kind of gas.

Practice problem 2.3

In an experiment a mixture of oxygen and nitrogen gas is collected over water at 30 ^{0}C and 700 torr pressure. What is the partial pressure of oxygen, if the partial pressure of nitrogen is 550 torr? (Vapour pressure H_2O at 30 ^{0}C, 4.2455 kPa).

(a) 118 torr (b) 120 (c) 115 (d) 119

Kinetic molecular theory of gases

Chiefly Rudolf Clausius (1822-1906), James Clerk Maxwell (1831-1879) and Ludwig Boltzmann (1844-1888) developed the kinetic molecular theory. Their theory is based on the following assumptions about the nature of gases at molecular level.

1. Molecules in a gas are in constant random motion and frequently collide with each other.

2. A gas consists of a large number of particles that are so small and separated by such large distances that their size is negligible. Attractive and repulsive forces between gas molecules are negligible.

3. Each molecule acts independent of the other molecules and is unaffected by their presence. At sufficiently low temperatures, all gases will condense into liquids suggesting the presence of intermolecular forces that become significant at low temperatures. Attractive forces are responsible for holding liquid and solid molecules together. The tendency for a gas to expand and fill the volume in which it occupies suggests the presence of negligible forces of attraction between molecules. Increasing pressure of a gas results in decrease of inter- particle distance and therefore more interaction between molecules.

4. Molecules collide with each other and the walls of the container. In these collisions, individual molecules may gain or lose energy. However, in a collection of molecules at constant temperature the total energy remains constant. The assumption is valid in the sense that if it were not true, then the pressure of a gas would decrease gradually as it is a consequence of collisions with the wall of the container.

5. The average kinetic energy of the molecules which is proportional to the temperature of the gas in Kelvin. Any two gases at the same temperature will have the same average kinetic energy.

Gas pressure derived from KMT analysis (Kinetic Equation of Gases)

The pressure of a gas can be explained by KMT as arising from the force exerted by gas molecules impacting on the walls of a container (assumed to be a cube of side length L and hence of Volume L^3. In addition, area of each side is L^2 and the total area is 6 L^2).

We consider a gas of N molecules each of mass m contained in cube of volume $V = L^3$.

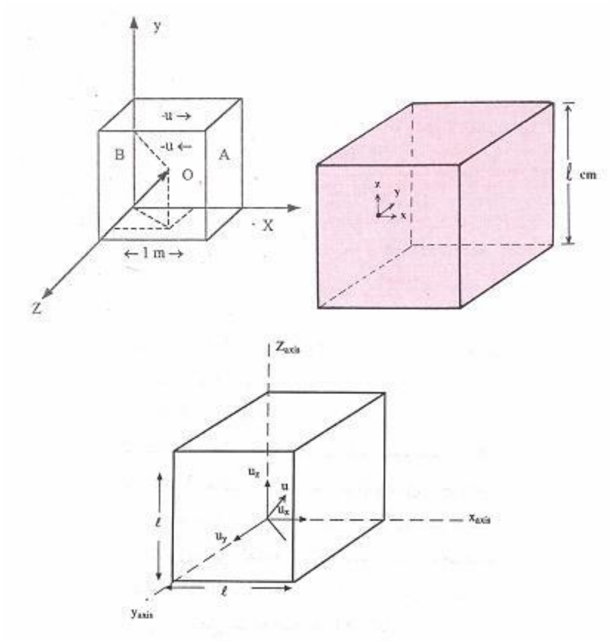


Figure 2.5 A gas container (assumed to be a cube of side length L and hence of Volume L^3.

When gas molecule collides (with speed v_x) with wall of the container perpendicular to x co-ordinate axis and bounces off in the opposite direction with the same speed (an elastic collision) then the momentum lost by the particle and gained by the wall is Δp_x

$$\Delta P_x = mv_x - (-mv_x) = 2mv_x$$

The particle impacts the wall once every $2L/v_x$ time units

$$\Delta t = \frac{2L}{v_x}$$

The number of collisions in 1 second is $v_x/2L$ collisions.

The force F due to the particle can then be computed as the rate of change of momentum with respect to time (Newton Second Law).

$$F = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

The force of the two sides along X-axis is

$$F = 2\frac{m}{L}v_x^2$$

The magnitude of the velocity v of any particle j can also be calculated from the relevant velocity components v_x, v_y, and v_z.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Force acting on the six walls is

$$F = 2\frac{m}{L}(v_x^2 + v_y^2 + v_z^2) = 2\frac{m}{L}v^2$$

Force acting on the six walls from all N molecules can be computed by summing forces arising from each individual molecule j.

$$F = 2\frac{m}{L}\sum_{i=1}^{N} v_i^2$$

Assuming that a large number of particles are moving randomly then the force on each of the walls will be approximately the same.

$$< v^2 >= v_{rms}^2 = \frac{1}{N}\sum_{i=1}^{N} v_i^2$$

Then,

$$F = 2\frac{m}{L}Nv_{rms}^2$$

The force can also be expressed in terms of the average velocity v^2_{rms} where v_{rms} denotes the root mean square velocity of the collection of particles.

The pressure can be readily determined once the force is known using the definition P = F/A where $A=6L^2$ denotes the area of the wall over which the force is exerted.

$$P = \frac{F}{A} = \frac{2}{L}\frac{Nmv_{rms}^2}{6L^2} = \frac{1}{3}\frac{Nmv_{rms}^2}{V}$$

$$PV = \tfrac{1}{3}Nmv_{rms}^2 \qquad (2.11)$$

Internal energy of an ideal gas

We have average kinetic energy of a gas molecule is given by

$$< KE >= \tfrac{1}{2}mv_{rms}^2 \qquad (2.12)$$

Then,

$$PV = \frac{1}{3}Nmv_{rms}^2 = \frac{2}{3}\;\frac{1}{2}\;\; Nmv_{rms}^2 = \frac{2}{3}N\left(\frac{1}{2}mv_{rms}^2\right) = \frac{2}{3}N < KE >$$

$$nRT = \frac{2}{3}N < KE >$$

$$< KE >= \frac{3}{2}\frac{nRT}{N}$$

For N molecules

$$KE = N < KE >= \frac{3}{2} nRT \qquad (2.13)$$

Root-mean-square speed

We can derive a useful equation for u_{rms}. One of the results of the kinetic theory of gases is that the average kinetic energy of a gas is We have n=N/N_A and m=M/ N_A where M is the total mass of one mole of molecules and N_A is Avogadro's number. M_w is the molecular weight or mass of one mole.

$$KE = N < KE >= \frac{1}{2} Nmv_{rms}^2 = \frac{1}{2} nN_A \ \ mv_{rms}^2 = \frac{1}{2} nM_w v_{rms}^2$$
$$= \frac{3}{2} nRT$$
$$M_w v_{rms}^2 = 3RT$$

$$v_{rms} = \sqrt{\frac{3RT}{M_w}} \qquad (2.14)$$

Note that M_w must be taken in Kg/mol.

Example 2.8

Calculate the root-mean-square speed in meters per second for $Cl_2(g)$ molecules at 30 ^{0}C.

Solution

The expression for u_{rms} is used

$$v_{rms} = \sqrt{\frac{3RT}{M_w}}$$

For chlorine M_w = 70.91 g = 7.09 x 10 $^{-2}$ kg mol^{-1}, T = 303 K, R = 8.314 J K^{-1} mol^{-1}

Substituting in the equation

$$v_{rms} = \sqrt{\frac{3 \times 8.314 \times 303}{7.09 \times 10^{-2}}} = 326 \ \ \mathrm{m/\ \ s}$$

Practice problem 2.4

At what temperature would the u_{rms} for Ne (g) be expected to be the same as that for He (g) at 300 K?

(a) 1000 (b) 150 (c) 1500 (d) 1600

Distribution of molecular speeds

In a real gas sample at a given temperature T, all molecules do not travel at the same speed. Some move more rapidly than others.

- In a real gas the speeds of individual molecules span wide ranges with constant collisions continually changing the molecular speeds.

Maxwell and independently Boltzmann analysed the molecular speed distribution in an ideal gas, and derived a mathematical expression for the speed distribution f(v).

This formula enables one to calculate various statistically relevant quantities such as the average velocity of a gas sample, the rms velocity, and the most probable velocity of a molecule in a gas sample at a given temperature T.

$$F(v) = 4\pi v^2 \left\{\frac{m}{2\pi k_B T}\right\}^{3/2} \exp\left[-\frac{mv^2}{2k_B T}\right] \qquad (2.15)$$

In Figure 2.6, the peak of the most probable speed increases as temperature increases. Also, it flattens out increasing with increasing temperature.

In Figure 2.7 light molecules have high average speed and a wide spread of speeds.

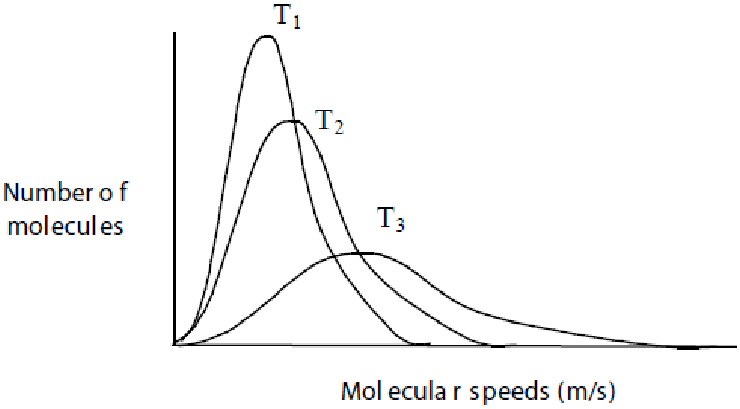


Figure 2.6 Maxwell-Boltzmann distributions of molecular speeds at three temperatures.

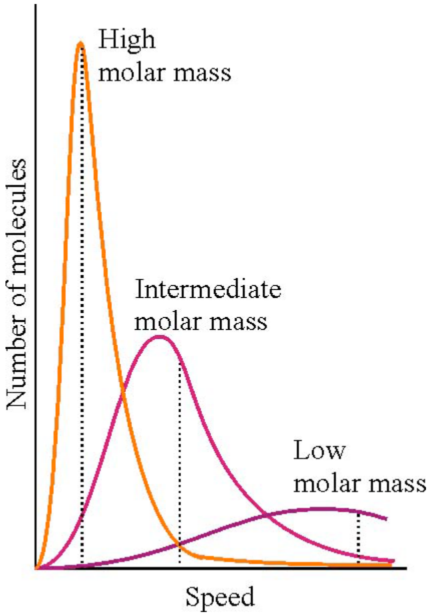


Figure 2.7 Maxwell-Boltzmann distributions of molecular speeds at three molar masses.

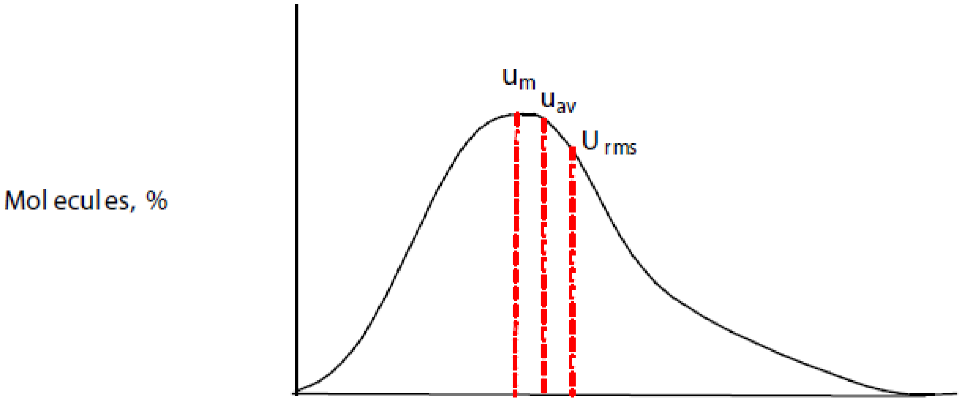


Figure 2.8 Diagram showing the different characteristics speeds for a sample of gas Molecules, %

Three characteristic speeds are shown in the diagram. More molecules have the speed u_m, known as the most probable or modal speed, than the other two. The simple average speed is u_{av} whilst u_{rms}

is the square root of the average of the squares of speeds of all molecules in a sample.

Diffusion and effusion of gases

Diffusion is the migration of molecules of different substances as a result of the random motion of molecules. Although gas molecules are consistently having collisions resulting in frequent changes in direction, the net rate at which a gas moves in a particular direction depends on the average speed. Diffusion always proceeds from a region of higher concentration to one of lower concentration.

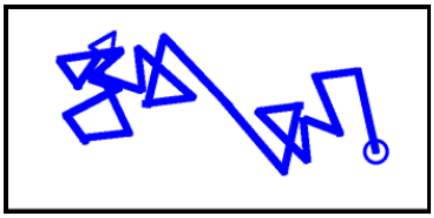


Figure 2.9 Path travelled by a single gas molecule in which each change in direction represents a collision.

Effusion is a process related to diffusion, it is the escape of gas molecules from their container through an orifice (pinhole). Consider the effusion of a mixture of gases through an orifice as shown in the figure below.

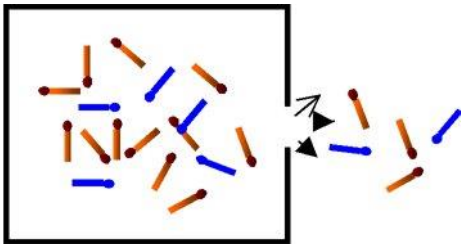


Figure 2.10 Path travelled by a single gas molecule in which each change in direction represents a collision.

The rates at which the two effusions can be compared are given below

$$\frac{\text{Rate effusion of A}}{\text{Rate effusion of B}} = \frac{u_{rms}\ (\text{A})}{u_{rms}\ (\text{B})} = \sqrt{\frac{3\text{RT} / \text{M}_A}{3\text{RT} / \text{M}_B}} \tag{2.16}$$

This result is a statement of Graham's law, which states that the rate of effusion (or diffusion) of two different gases are inversely proportional to the square roots of their molar masses.

In considering the equation above it is evident that lighter gases will effuse faster than the heavier gases. The consequences of the above theory maybe summarised that ratios of the root-mean-square speeds are equal to the ratios of

- rates of effusion
- effusion times
- amount of gas effused
- distance travelled by the molecules
- amount of gas effused
- molecular speeds

Example 2.9

Calculate the ratio of the diffusion rate for H_2O and D_2O (D is deuterium an isotope of hydrogen).

Molar mass H_2O = 18.01 g mol $^{-1}$, D_2O = 19.01 g mol $^{-1}$

$$\frac{\text{Rate diffusion } \text{H}_2\text{O}}{\text{Rate diffusion } \text{D}_2\text{O}} = \sqrt{\frac{\text{M}_{\text{H}_2\text{O}}}{\text{M}_{\text{D}_2\text{O}}}} = \sqrt{\frac{19.01\ \text{g mol}^{-1}}{18.01\ \text{g mol}^{-1}}}$$

$$= 1.02$$

Practice problem 2.6

Two gases, HBr and CH_4, effuse through a small opening. HBr effuses through the opening at a rate of 4 $cm^3\,s^{-1}$, at what rate will the CH_4 molecules effuse through the same opening.

(a) 9 $cm^3\,s^{-1}$ (b) 10 $cm^3\,s^{-1}$ (c) 8.5 $cm^3\,s^{-1}$ (d) 9 $m^3\,s^{-1}$

Real gases: deviation from ideal gas

Real gases do not conform to ideal gas behaviour. A plot of *PV* against pressure shows that whereas the *PV* is constant for an ideal gas, this is not true for real gases.

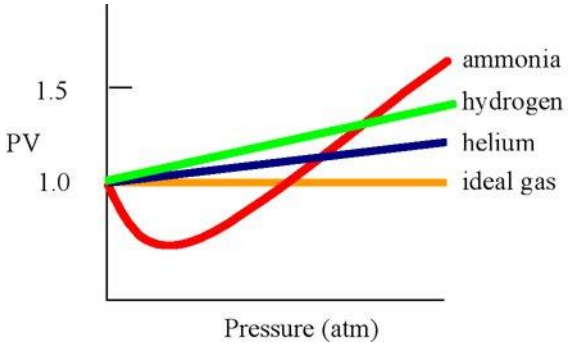


Figure 2.10 Plot of *PV* against pressure showing the behaviour for an ideal gas and real gases. Plot for NH_3, H_2, and He show deviation from the ideal gas curve.

Real gases do not follow the assumptions of the ideal gas behaviour. Deviations from ideal gas behaviour of varying degrees are seen when *PV* is plotted against *P*. Gases with only weak intermolecular forces give straight lines at low pressure and are close to the ideal gas behaviour. Significant deviation is observed for gases with strong intermolecular forces such as oxygen and nitrogen. Another assumption made when dealing with ideal gases is that molecules have no volume whereas real gases have a defined volume.

The compression factor

We can express the extent of deviation from ideal behaviour as a function of pressure (which is related to the density of the gas) by introducing a quantity called the Compressibility or Compression factor Z.

$$Z = \frac{PV}{nRT} = \frac{PV_m}{RT} \qquad (2.17)$$

For an ideal gas Z = 1, and real gases exhibit Z values different from unity. Z values may be explained in terms of the operation of intermolecular forces.

At low pressures the molecules are far apart and the predominant intermolecular interaction is **attraction**. The molar volume V_m is less than that expected for an ideal gas: intermolecular forces tend to draw the molecules together and so reduce the space which they occupy. Under such conditions we expect that $Z < 1$.

As the pressure is increased the average distance of separation between molecules decreases and **repulsive** interactions between molecules become more important. Under such conditions we expect that $Z > 1$. When $Z > 1$, the molar volume is greater than that exhibited by an ideal gas: repulsive forces tend to drive the molecules apart.

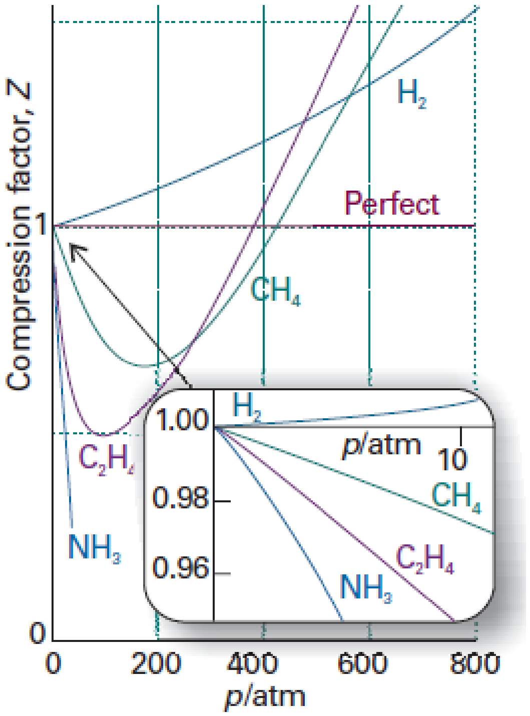


Figure 2.11 The variation of the compression factor, *Z*, with pressure for several gases at 0°C. A perfect gas has *Z* = 1 at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

The virial equation of state

The observation of a Z factor different from unity can be used to construct an empirical or observation based equation of state, by supposing that the ideal gas equation of state is only the first term of a more complex expression which can be expressed in terms of a mathematical power series. This is called the Virial equation of state.

$$Z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ... = 1 + B'P + C'P^2 \qquad (2.18)$$

Note that the virial coefficients B, C, B’ and C’ are obtained by fitting the experimental Z vs P data to the virial equation of state. Their values depend on the identity of the gas and reflect the presence of intermolecular forces and interactions.

When the pressure P is small the molar volume V_m will be very large and so the second and third terms in the virial series will be very small and to a good approximation the virial equation of state reduces to the ideal gas equation of state.

The van der Waals equation of state

The ideal gas equation has been modified with corrections so that it fits with experimental data corresponding to real gases. One such effort was made by van der Waals. The van der Waals equation is the form

$$\{P + a\left(\frac{n}{V}\right)^2\}(V - nb) = nRT \qquad (2.19)$$

where *a* and *b* are known as van der Waals constants. The constants are determined experimentally by measuring *P*, *V* and *T* under a set of different conditions.

The repulsive interactions between molecules are taken into account by supposing that they cause the molecules to behave as small but impenetrable spheres. The nonzero volume of the molecules implies that instead of moving in a volume *V* they are restricted to a smaller volume *V* - *nb*, where *nb* is approximately the total volume taken up by the molecules themselves.

The closest distance of two hard-sphere molecules of radius *r*, and volume $V_{molecule} = 4\pi r^3/3$, is 2*r*, so the volume excluded is $= 4\pi(2r)^3/3$, or $8V_{molecule}$. The volume excluded per molecule is one-half this volume, or $4V_{molecule}$, so $b \approx 4V_{molecule} N_A$.

The pressure depends on both the frequency of collisions with the walls and the force of each collision. Both the frequency of the collisions and their force are reduced by the attractive forces, which act with a strength proportional to the molar concentration, n/V, of molecules in the sample. Therefore, because both the frequency and the force of the collisions are reduced by the attractive forces, the pressure is reduced in proportion to the square of this concentration. If the reduction of pressure is written as $-a(n/V)^2$, where a is a positive constant characteristic of each gas, the combined effect of the repulsive and attractive forces is the van der Waals equation of state.

Example 2.10

Use the van der Waals equation to calculate the pressure of nitrogen gas at 273.15 K and a molar volume of 22.414 L mol^{-1}. Compare with the pressure of an ideal gas at the same temperature and molar volume.

Solution

$$P = \frac{\left(8.134\ \mathrm{J\ K^{-1} mol^{-1}}\right)(273.15\ \mathrm{K})}{0.022414\ \mathrm{m^3\ mol^{-1}} - 0.0000391\ \mathrm{m^3\ mol^{-1}}} - \frac{0.1408\ \mathrm{Pa\ m^3\ mol^{-1}}}{\left(0.022414\ \mathrm{m^3\ mol^{-1}}\right)^2}$$

$$= 1.0122 \times 10^5\ \mathrm{Pa} = 0.9990\ \mathrm{atm}$$

For the ideal gas

$$P = \frac{RT}{V_\mathrm{m}} = \frac{\left(8.134\ \mathrm{J\ K^{-1} mol^{-1}}\right)(273.15\ \mathrm{K})}{0.022414\ \mathrm{m^3\ mol^{-1}}} = 1.0132 \times 10^5\ \mathrm{Pa} = 1.0000\ \mathrm{atm}$$

Chapter 3

Heat

by Dr. Hasan Maridi

Internal Energy

Internal energy is all the energy of a system that is associated with its microscopic components.

- These components are its atoms and molecules.
- The system is viewed from a reference frame at rest with respect to the center of mass of the system.

The kinetic energy due to its motion through space is not included but Internal energy does include kinetic energies due to:

- Random translational motion
- Rotational motion
- Vibrational motion

Internal energy also includes potential energy between molecules.

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.

The term heat will also be used to represent the amount of energy transferred by this method.

There are many common phrases that use the word “heat” incorrectly.

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

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 14.5ºC to 15.5ºC. 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 63ºF to 64ºF.

The standard in the text is to use Joules.

Mechanical Equivalent of Heat

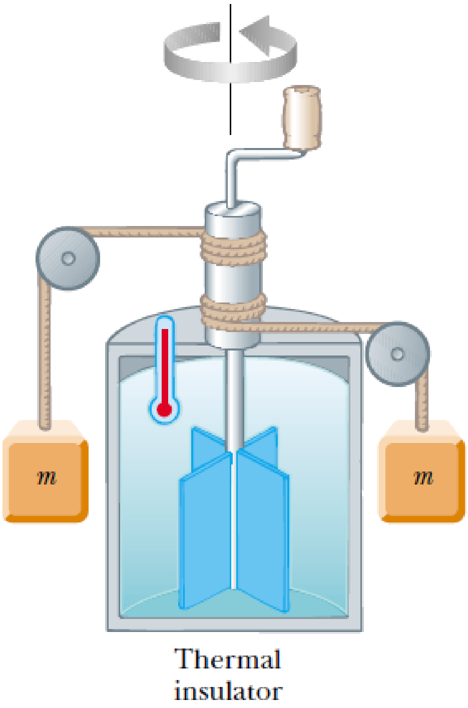


Figure 3.1 Joule's experiment for determining the mechanical equivalent of heat. The falling blocks rotate the paddles, causing the temperature of the water to increase.

Joule, 1818 – 1889, British physicist, 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. 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.

$$1 \text{ cal} = 4.186 \text{ J} \qquad (3.1)$$

This is known as the **mechanical equivalent of heat.**

Heat Capacity

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°C.

If energy Q produces a change of temperature of ΔT, then,

$$Q = C\,\Delta T.$$

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 ΔT, then the specific heat is

$$c \equiv \frac{Q}{m\,\Delta T} \qquad (3.2)$$

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.

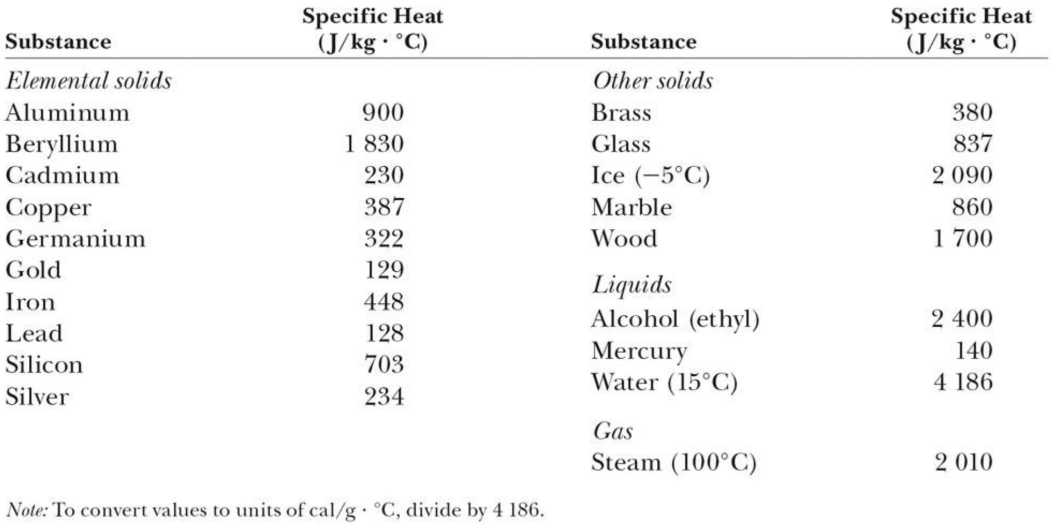
The equation is often written in terms of Q:

$$Q = m\,c\,\Delta T \qquad (3.3)$$

The change in internal energy of a system can be identified with $m\,c\,\Delta\,t$ if we ignore any thermal expansion or contraction of the system. Then $\Delta U = Q$.

The internal energy of a system can be changed by transferring energy into the system by any mechanism. This also indicates temperature is related to the energy of the molecules of a system.

Table 3.1 Specific Heats of Some Substances at 25°C and Atmospheric Pressure



Substance	Specific Heat (J/kg · °C)	Substance	Specific Heat (J/kg · °C)
Elemental solids		*Other solids*	
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	*Liquids*	
Iron	448	Alcohol (ethyl)	2 400
Lead	128	Mercury	140
Silicon	703	Water (15°C)	4 186
Silver	234	*Gas*	
		Steam (100°C)	2 010

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

Specific Heat Varies With Temperature

Technically, the specific heat varies with temperature.
The corrected equation is

$$Q = m\int_{T_i}^{T_f} c\, dT \qquad (3.4)$$

However, if the temperature intervals are not too large, the variation can be ignored and c can be treated as a constant. For example, for water there is only about a 1% variation between 0^o and 100^oC. These variations will be neglected unless otherwise stated.

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.

Conservation of Energy gives a mathematical expression of this:

$$Q_{cold} = -Q_{hot} \qquad (3.5)$$

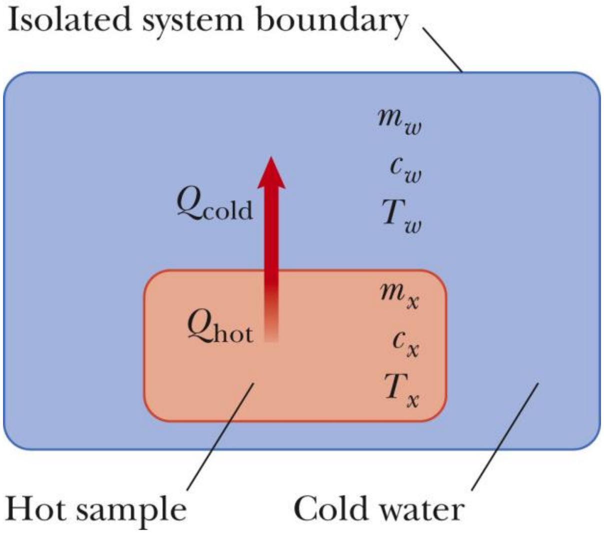
If the temperature increases:

- Q and ΔT are positive
- Energy transfers into the system

If the temperature decreases:

- Q and ΔT are negative
- Energy transfers out of the system

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



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 spcific heat is to be determined.
Since each Q = mcΔT, 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.

$$c_x = \frac{m_w c_w (T_f - T_w)}{m_x (T_x - T_f)} \qquad (3.6)$$

Technically, the mass of the container should be included, but if $m_w >> m_{container}$ it can be neglected.

Example 3.1 Cooling a Hot Ingot

A 0.050 0-kg ingot of metal is heated to 200.0°C and then dropped into a calorimeter containing 0.400 kg of water initially at 20.0°C. The final equilibrium temperature of the mixed system is 22.4°C. Find the specific heat of the metal.

Soluation

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

$$(0.400 \text{ kg})(4\,186 \text{ J/kg} \cdot {}^\circ\text{C})(22.4^\circ\text{C} - 20.0^\circ\text{C})$$
$$= -(0.050\,0 \text{ kg})(c_x)(22.4^\circ\text{C} - 200.0^\circ\text{C})$$

Solve for the specific heat of the metal:

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

Example 3.2

A quantity of hot water at 91°C and another cold one at 12°C. How much kilogram of each one is needed to make an 800 liter of water bath at temperature of 35°C.

Solution

Assume the mass of hot water m_H and cold one is m_C,
800 liter of water is equivalent to 800 kg, *So* $m_H + m_C = 800$,

From the conservation of energy

$$m_H C_w (T_H - T_f) = m_C C_w (T_f - T_C)$$

$$T_H = 92°C, \quad T_C = 12°C, \quad T_f = 35°C.$$

$$56\, m_H = 23\, m_C,$$

- *So*

$$m_C = 2.43\, m_H$$

- So by substitution

$$3.43\, m_H = 800,$$

$$m_H = 233\, kg, \text{ and } m_C = 567\, kg$$

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

If an amount of energy Q is required to change the phase of the mass m of the substance is

$$L \equiv Q/m$$

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.

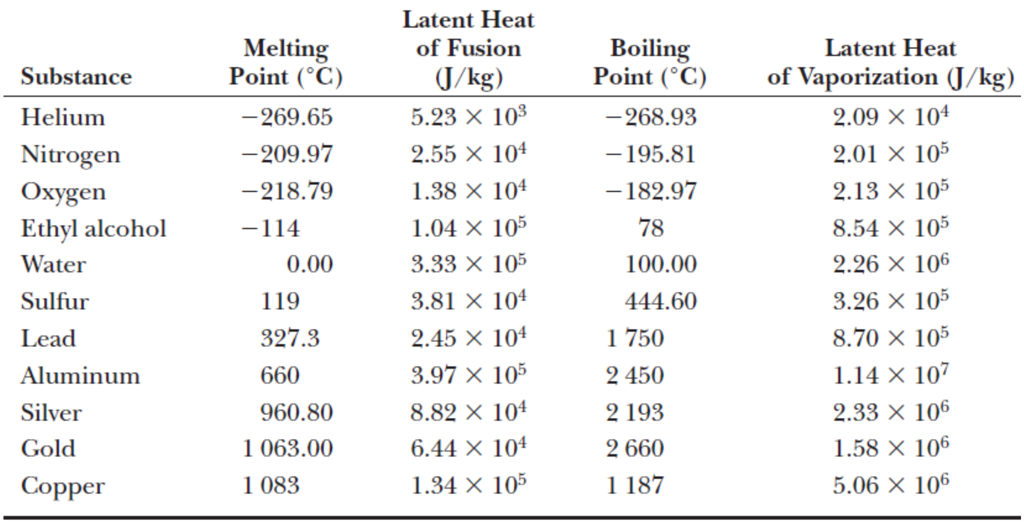
The energy required to change the phase of a given mass m of a pure substance is

$$Q = \pm mL \qquad (3.7)$$

The positive sign in Equation is used when energy enters a system, causing melting or vaporization. The negative sign corresponds to energy leaving a system such that the system freezes or condenses.

Latent heat of fusion L_f is the term used when the phase change is from solid to liquid (*to fuse* means “to combine by melting”), and **latent heat of vaporization** L_v is the term used when the phase change is from liquid to gas. The latent heats of various substances vary considerably as data in Table 3.2 show.

Table 3.2 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	5.23×10^3	−268.93	2.09×10^4
Nitrogen	−209.97	2.55×10^4	−195.81	2.01×10^5
Oxygen	−218.79	1.38×10^4	−182.97	2.13×10^5
Ethyl alcohol	−114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

If energy is enters the system:

- This will result in melting or vaporization

- The amount of the higher-phase material will increase
- 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
- m and Q are negative

Graph of Ice to Steam

To understand the role of latent heat in phase changes, consider the energy required to convert a 1.00-g cube of ice at -30.0°C to steam at 120.0°C. Figure 20.2 indicates the experimental results obtained when energy is gradually added to the ice.

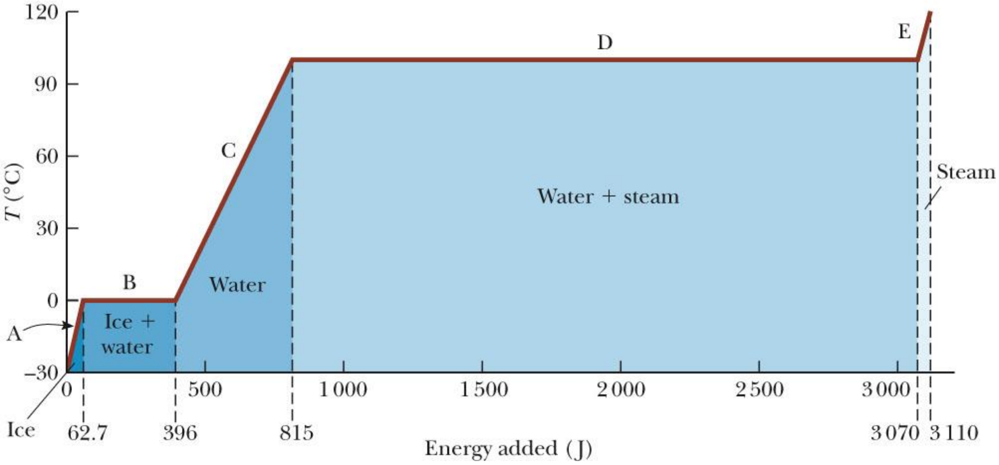


Figure 3.2 A plot of temperature versus energy added when 1.00 g of ice initially at -30.0°C is converted to steam at 120.0°C.

Warming Ice, Graph Part A

Start with one gram of ice at –30.0ºC.
During phase A, the temperature of the ice changes from –30.0ºC to 0ºC. Use $Q = m_i c_i \Delta T$

$$Q = m_i c_i \, \Delta T = (1.00 \times 10^{-3} \text{ kg})(2\,090 \text{ J/kg} \cdot {}^\circ\text{C})(30.0^\circ\text{C}) = 62.7 \text{ J}$$

In this case, 62.7 J of energy are added.

Melting Ice, Graph Part B

Once at 0ºC, the phase change (melting) starts.
The temperature stays the same although energy is still being added. Use $Q = L_f \quad \Delta m_w = L_f\, m_i$

$$Q = m_i L_f = (1.00 \times 10^{-3}\ \mathrm{kg})(3.33 \times 10^{5}\ \mathrm{J/kg}) = 333\ \mathrm{J}$$

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 0ºC and 100ºC, the material is liquid and no phase changes take place.
Energy added increases the temperature. Use $Q = m_w c_w\, \Delta T$

$$Q = m_w c_w\ \Delta T = (1.00 \times 10^{-3}\ \mathrm{kg})(4.19 \times 10^{3}\ \mathrm{J/kg\cdot{}^\circ C})(100.0^\circ\mathrm{C}) = 419\ \mathrm{J}$$

419 J are added. The total is now 815 J

Boiling Water, Graph Part D

At 100ºC, a phase change occurs (boiling).
Temperature does not change. Use $Q = L_v\, \Delta m_s = L_v\, m_w$

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

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 $Q = m_s c_s \Delta T$

$$Q = m_s c_s\ \Delta T = (1.00 \times 10^{-3}\ \mathrm{kg})(2.01 \times 10^{3}\ \mathrm{J/kg\cdot{}^\circ C})(20.0^\circ\mathrm{C}) = 40.2\ \mathrm{J}$$

In this case, 40.2 J are needed. The temperature is increasing from 100º C to 120º C. The total is now 3110 J.

The total amount of energy that must be added to change 1 g of ice at -30.0°C to steam at 120.0°C is the sum of the results from all five parts of the curve, which is 3110 J. Conversely, to cool 1 g of steam at 120.0°C to ice at- 30.0°C, we must remove 3110 J of energy.

Example 3.3

A quantity of hot water at 91°C and another cold one at 12°C. How much kilogram of each one is needed to make an 800 liter of water bath at temperature of 35°C.

Solution

Assume the mass of hot water m_H and cold one is m_C, 800 liter of water is equivalent to 800 kg, *So* $m_H+m_C=800$, From the conservation of energy

$$m_H C_w(T_H-T_f) = m_C C_w(T_f-T_C)$$

$$T_H = 92°C,\quad T_C=12°C,\quad T_f=35°C,$$

$$56\, m_H = 23\, m_C,$$

- So

$$m_C = 2.43\, m_H$$

- So by substitution

$$3.43\, m_H = 800,$$

$$m_H = 233\ kg,\ \text{and}\ m_C = 567\ kg$$

Supercooling

If liquid water is held perfectly still in a very clean container, it is possible for the temperature to drop below 0^o C without freezing. This phenomena is called **supercooling.**

It arises because the water requires a disturbance of some sort for the molecules to move apart and start forming the open ice crystal structures. This structure makes the density of ice less than that of water. If the supercooled water is disturbed, it immediately freezes and the energy released returns the temperature to 0^o C.

Superheating

Water can rise to a temperature greater than 100° C without boiling. This phenomena is called **superheating.**

The formation of a bubble of steam in the water requires nucleation site. This could be a scratch in the container or an impurity in the water. When disturbed, the superheated water can become explosive. The bubbles will immediately form and hot water is forced upward and out of the container.

State Variables

State variables describe the state of a system. Variables may include: Pressure, temperature, volume, internal energy

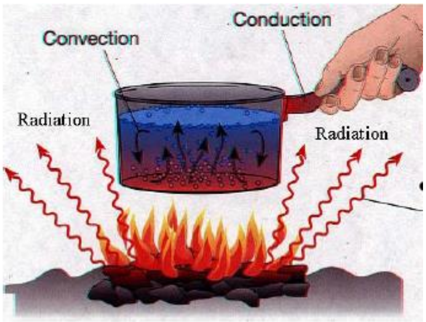
The state of an isolated system can be specified only if the system is in thermal equilibrium internally. For a gas in a container, this means every part of the gas must be at the same pressure and temperature.

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.

Heat Transfer



We want to know the rate at which energy is transferred.
There are various mechanisms responsible for the transfer:

- Conduction
- Convection
- Radiation

Conduction

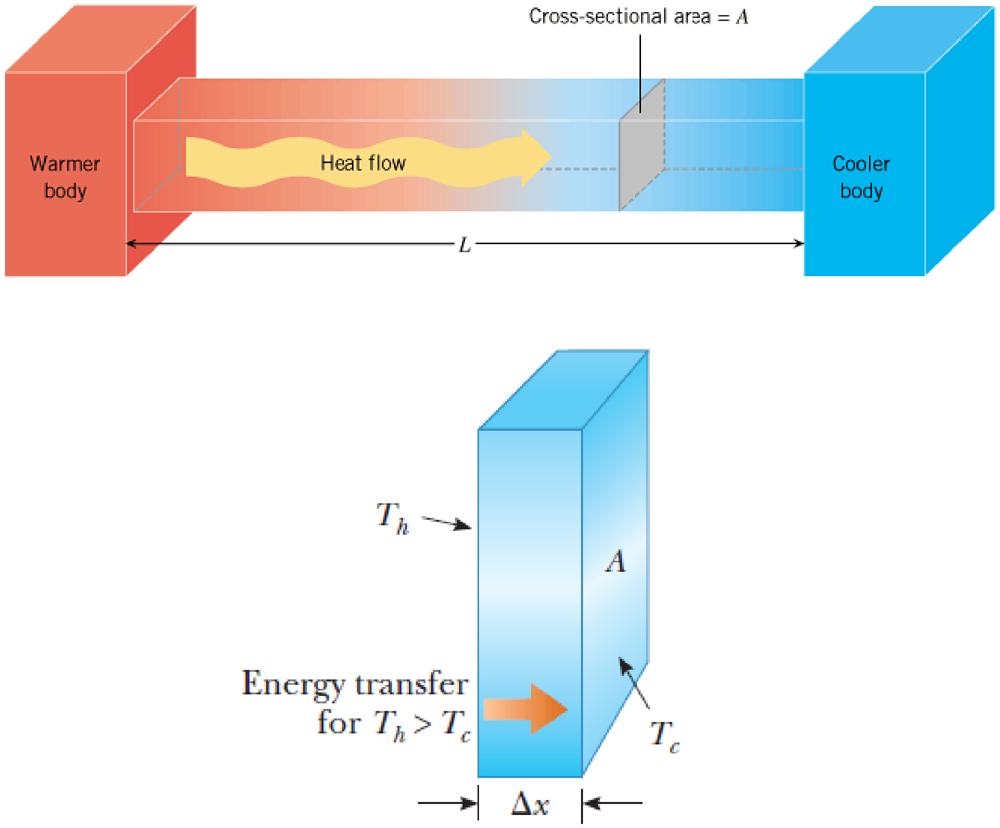
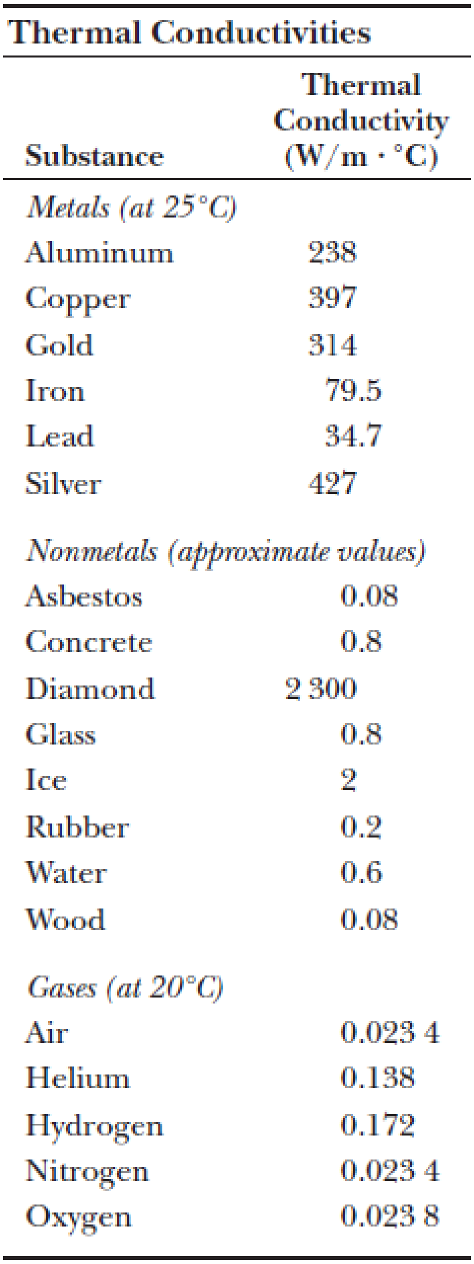


Figure 3.3 Energy transfer through a conducting slab with a cross-sectional area A and a thickness Δx. The opposite faces are at different temperatures T_c and T_h.

The transfer can be viewed on an atomic scale. **Conduction** is an exchange of kinetic energy between microscopic particles by collisions. The microscopic particles can be atoms, molecules or free electrons. Less energetic particles gain energy during collisions with more energetic particles.

Table 3.3 Thermal Conductivities



Thermal Conductivities

Substance	**Thermal Conductivity (W/m · °C)**
Metals (at 25°C)	
Aluminum	238
Copper	397
Gold	314
Iron	79.5
Lead	34.7
Silver	427
Nonmetals (approximate values)	
Asbestos	0.08
Concrete	0.8
Diamond	2 300
Glass	0.8
Ice	2
Rubber	0.2
Water	0.6
Wood	0.08
Gases (at 20°C)	
Air	0.023 4
Helium	0.138
Hydrogen	0.172
Nitrogen	0.023 4
Oxygen	0.023 8

Rate of conduction depends upon the characteristics of the substance. In general, metals are good thermal conductors. They contain large numbers of electrons that are relatively free to move through the metal. They can transport energy from one region to another. Poor conductors include asbestos, paper, and gases.

Conduction can occur only if there is a difference in temperature between two parts of the conducting medium.

The slab at right allows energy to transfer from the region of higher temperature to the region of lower temperature.

The rate of transfer ***P*** or ***H*** is given by:

$$P = \frac{Q}{\Delta t} = kA\left|\frac{dT}{dx}\right| \qquad (3.8)$$

or

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

where *A* is the cross-sectional area, dT is the temperature difference, and dx is the thickness of the slab or the length of a rod.

P is in Watts when *Q* is in Joules and t is in seconds.

k is the thermal conductivity of the material. Good conductors have high k values and good insulators have low k values.

Temperature Gradient

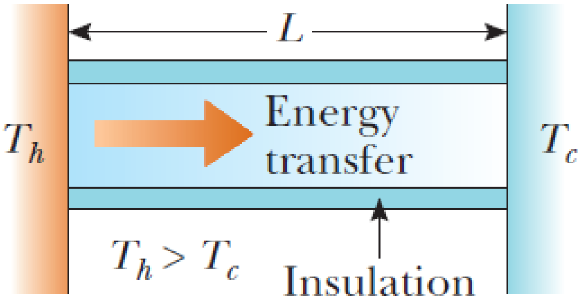


Figure 3.4 Conduction of energy through a uniform, insulated rod of length *L*. The opposite ends are in thermal contact with energy rese.

The quantity $|dT / dx|$ is called the **temperature gradient** of the material. It measures the rate at which temperature varies with position.

For a rod, the temperature gradient can be expressed as:

$$\left|\frac{dT}{dx}\right| = \frac{T_h - T_c}{L}$$

Using the temperature gradient for the rod, the rate of energy transfer becomes:

$$P = kA\left(\frac{T_h - T_c}{L}\right) \qquad (3.9)$$

Example 3.4

An aluminum pot contains water that is kept steadily boiling (100ºC). The bottom surface of the pot, which is 12 mm thick and $1.5\text{x}10^4$ 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

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

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

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

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

Compound Slab

For a compound slab containing several materials of various thicknesses (L_1, L_2,…) and various thermal conductivities (k_1, k_2, …) the rate of energy transfer depends on the materials and the temperatures at the outer edges:

$$P = \frac{A\left(T_h - T_c\right)}{\sum_i \left(L_i / k_i\right)}$$

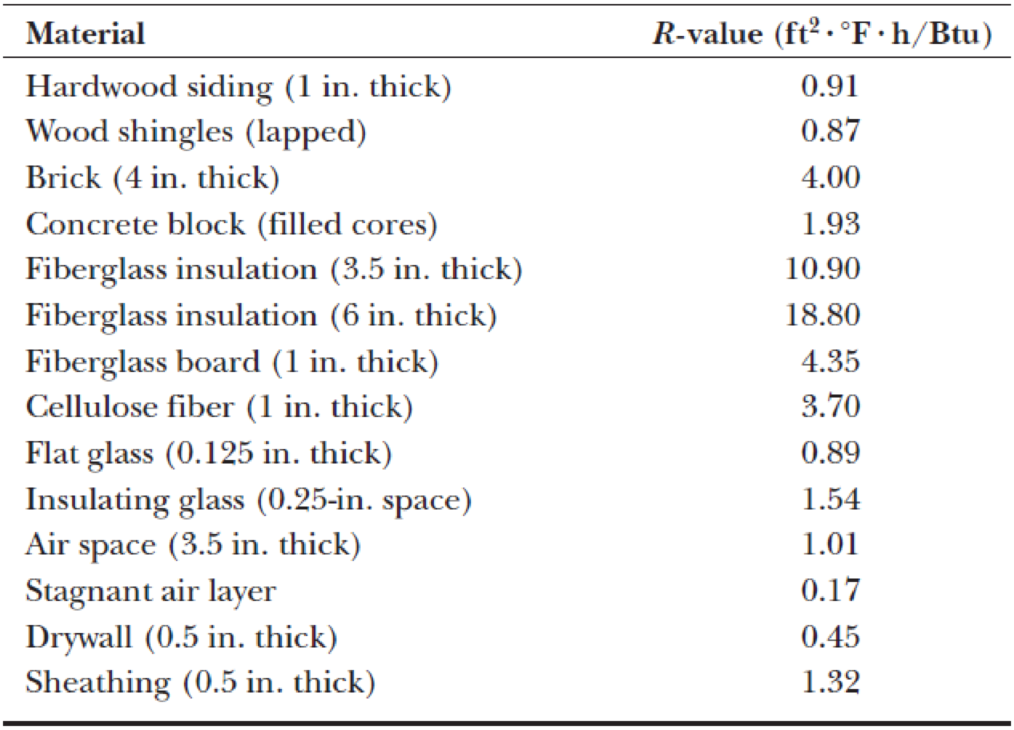
Home Insulation

Substances are rated by their R-values. R = L / k and the rate becomes:

$$P = \frac{A\left(T_h - T_c\right)}{\sum_i R_i} \qquad (3.10)$$

For multiple layers, the total R value is the sum of the R values of each layer. Wind increases the energy loss by conduction in a home.

Table 3.4 R-Values for Some Common Building Materials



Material	R-value (ft$^2\cdot$°F$\cdot$h/Btu)
Hardwood siding (1 in. thick)	0.91
Wood shingles (lapped)	0.87
Brick (4 in. thick)	4.00
Concrete block (filled cores)	1.93
Fiberglass insulation (3.5 in. thick)	10.90
Fiberglass insulation (6 in. thick)	18.80
Fiberglass board (1 in. thick)	4.35
Cellulose fiber (1 in. thick)	3.70
Flat glass (0.125 in. thick)	0.89
Insulating glass (0.25-in. space)	1.54
Air space (3.5 in. thick)	1.01
Stagnant air layer	0.17
Drywall (0.5 in. thick)	0.45
Sheathing (0.5 in. thick)	1.32

Convection

Energy transferred by the movement of a substance. It is a form of matter transfer:

- When the movement results from differences in density, it is called *natural convection.*

- When the movement is forced by a fan or a pump, it is called *forced convection.*

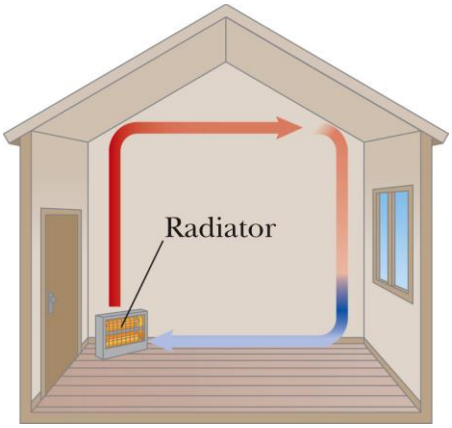


Figure 3.5 Convection currents are set up in a room warmed by a radiator.

Air directly above the radiator is warmed and expands. The density of the air decreases, and it rises. A continuous air current is established.

Radiation

Radiation does not require physical contact. All objects radiate energy continuously in the form of electromagnetic waves due to thermal vibrations of their molecules. Rate of radiation is given by **Stefan's law.**

$$P= \sigma AeT^4$$

- P is the rate of energy transfer, in Watts.
- $\sigma = 5.6696 \times 10^{-8}\ W/m^2 \cdot K^4$
- A is the surface area of the object.
- e is a constant called the emissivity. e varies from 0 to 1. The emissivity is also equal to the absorptivity.
- T is the temperature in Kelvins.

An *ideal absorber* ($e = 1$) is defined as an object that absorbs all of the energy incident on it. This type of object is called a **black body.** An ideal absorber is also an ideal radiator of energy.

Energy Absorption and Emission by Radiation

With its surroundings, the rate at which the object at temperature T with surroundings at T_o radiates is

$P_{net} = \quad \sigma A e \, (T^4 - T_o^4)$

When an object is in equilibrium with its surroundings, it radiates and absorbs at the same rate and its temperature will not change.

Example 3.5

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^2.

Solution

Using the Stefan-Boltzmann's law

$$P_{net} = e\,\sigma\,A\,(T^4 - T_s^4) = (5.67\times10^{-8})(0.9)(1.5)(310^4 - 293^4) = 143\,watt.$$

The total energy lost during 10 min is

$$Q = P_{net}\,\Delta t = 143\times600 = 85.8\,kJ$$

The Dewar Flask

A Dewar flask is a container designed to minimize the energy losses by conduction, convection, and radiation. It is invented by Sir James Dewar (1842 – 1923). It is used to store either cold or hot liquids for long periods of time. A Thermos bottle is a common household equivalent of a Dewar flask.

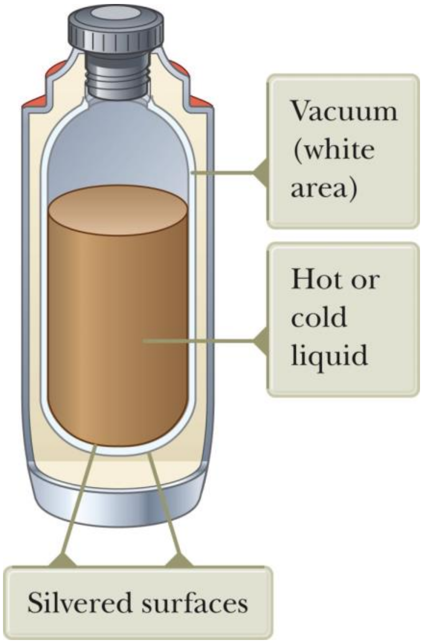


Figure 3.6 A cross-sectional view of a Dewar flask, which is used to store hot or cold substances.

The space between the walls is a vacuum to minimize energy transfer by conduction and convection. The silvered surface minimizes energy transfers by radiation. Silver is a good reflector. The size of the neck is reduced to further minimize energy losses.

Chapter 4

by Dr. Hasan Maridi

Work and First law of thermodynamics

The energy

Energy is usually defined as the capacity to do work. Various processes in the body produce energy to operate the muscle and to maintain the body temperature. Energy is produced in some chemical processes while some chemical reactions require energy to take place.

The energy determines what molecules may form what reaction may occur, how fast they may occur, in which direction a reaction has a tendency to occur.

A gas at high temperature has more energy than at low temperature – it has a higher pressure and can do more work in driving out a piston.

Conservation of energy – the energy can be neither created nor destroyed but merely converted from one form to another or moved from place to place.

There are two forms of energy: kinetic energy and potential energy.

Kinetics energy – is the energy associated with motion of matter. A body of mass m moving with a velocity v will have a kinetic energy of $\frac{1}{2} m v^2$

Potential energy – is the energy a body has by virtual of its position in a force field. Typical examples of force fields include gravitational, electrical and magnetic fields. Consider a man drawing water from well through a height h. The process involves moving object of mass m against the force of gravity, g, through a distance h. The potential energy change involved is given by mgh where g is the acceleration due to gravity.

Internal energy (*U*)

Internal energy represents the total energy of the system comprising two components: kinetic energy and potential energy. Kinetic energy is the energy associated with various types of molecular motion and movement of molecules. Potential energy arises from the attractive and repulsive forces within atoms or molecules. The internal energy from a chemistry point is the sum of the total kinetic and potential energy of the system.

Units of Energy

From the expression of kinetic energy it can be seen that energy has units of kg m^2 s^{-2}
SI unit is Joule (J)
1 J = 1 kg m^2 s^{-2}
Another unit of energy commonly used in nutrition is the calorie (cal). It is defined as the energy required to raise the temperature of 1 g of water by 1 ^{0}C.
1 cal = 4.18 J

Example 4.1
What is the kinetic energy of a truck carrying yams with a mass of 2000 kg travelling at 50 km/h?
Solution

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2} \times 2000kg \times \left(\frac{50000m}{3600s}\right)^2 = 193 \quad \text{KJ}$$

Practice problem 4.1
How much potential energy does 1kg of water at the top of a waterfall that is 500 m deep possess? How much kinetic energy is converted in falling from the top to the base? Give the answer in joules and calories.

Thermodynamic systems and surroundings

The systems is that part of the universe that we choose to focus on or study (in an experiment – a reaction flask) whilst **the surroundings** is everything else outside the system (area of focus). Three types of system:

An open system – can exchange both energy and matter with its surroundings. (A flask that is not stoppered).

A closed system – can exchange energy but not matter with its surroundings. (A stoppered flask).

An isolated system – can exchange neither energy nor matter with its surroundings. (A sealed flask that is thermally, mechanically, and electrically insulated from its surroundings.

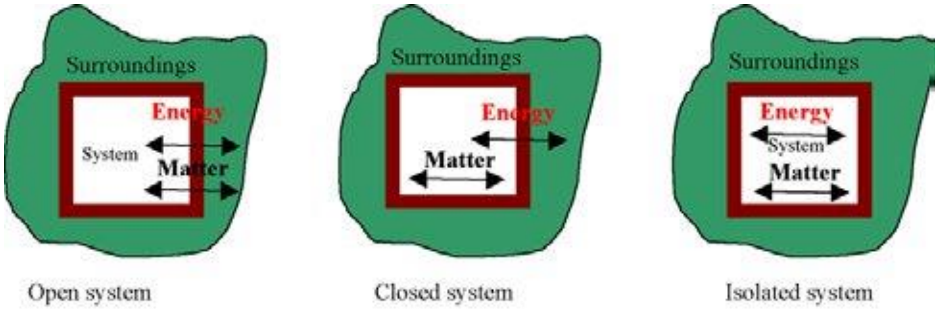


Figure 6.1 Different types of thermodynamic systems showing the types of energy and matter interactions with the surrounding.

Example 4.2

What type of system does a boiling kettle represent?

Solution

Both energy and matter can be transferred between a system and its surroundings. It is therefore an open system.

Practice problem 4.2

The vacuum flask is often used to illustrate one type of thermodynamics system. Which type is this?

(a) Open system (b) Closed system

(c) Isolated system (d) Closed-isolated system

State functions and non-state functions

Thermodynamics is concerned with changes in the state of the system as defined by macroscopic parameters such as composition, volume, pressure, temperature and energy. These properties are said to be state functions. Such properties depend only on the initial and final the states of the system and not on the path used to reach a certain condition. Work and heat on the other hand are examples of functions that depend on the route taken. Heat and work are therefore non-state functions.

Energy, work and heat

Energy can be exchanged between a closed system and its surroundings as work or as heat.

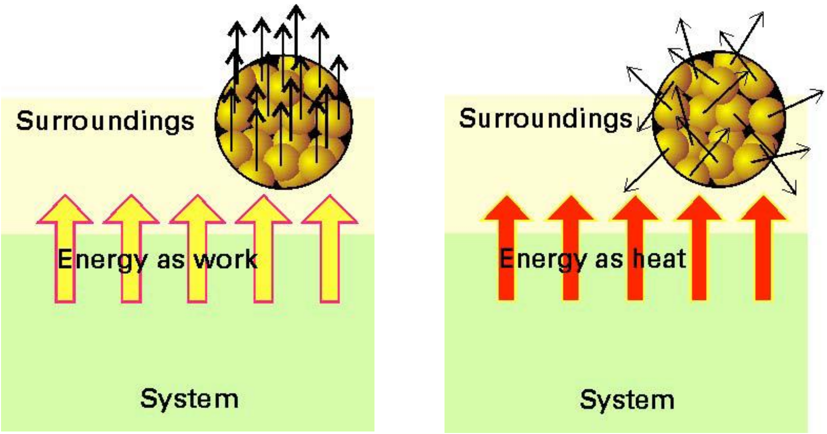


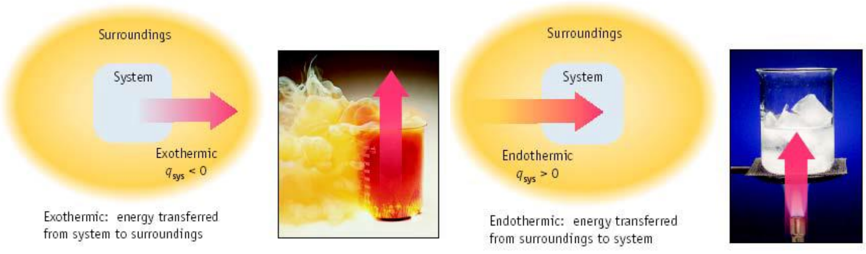
Figure 4.2 Molecular nature of work:
(a) Work is the transfer of energy that achieves or utilizes uniform motion in the surroundings.
(b) Heat is the transfer of energy that achieves or utilizes disorderly motion in the surroundings.

Work (*w*) is a transfer of energy that can cause motion against an opposing force. A process produces work if it can be used to change the height of a weight somewhere in the surroundings.

In simple language, work is said to have taken place when we do something. When an object is moved against an opposing force, work is done. Raising an object is an example of doing work. In chemistry, however, the most common work encountered is related to pressure-volume changes accompanying chemical reactions.

Heat (*q*) is a transfer of energy as a result of a temperature difference between the system and its surroundings. When two bodies are in thermal contact, energy flows from the warmer body to the cooler one – thermal energy is transferred. The molecular explanation for this process is that the molecules are in constant random motion and have kinetic energy associated them. When two objects are in contact, thermal energy is transferred until the average kinetic energy between the two bodies is the same (thermal equilibrium).

Directionality of energy transfers



(a) **(b)**

Figure 4.3 Directionality of Energy Transfers: (a) exothermic: heat transfers from the system to the surroundings. (b) endothermic: heat transfers from the surroundings to the system.

Chemical changes involve release or gain of heat from the system to the surroundings. An **exothermic process** is one that releases heat to the surroundings. For example, combustion reactions are exothermic while a process such as vaporisation of water is endothermic.

Energy is absorbed by the system in an **endothermic process** where thermal energy is transferred from the surroundings to the system

The conservation of energy

The total energy of a system – **internal energy**, U (or E): the total kinetic and potential energy of the molecules in the system. The change in internal energy:

$\Delta U = U_f – U_i$

Where Uf is internal energy at a final state and Ui is internal energy at an initial state.

The internal energy is a state function: its value depends only on the current state of the system and is independent on how this state was prepared. It is a function of properties that determine the physical state of the system, i.e., pressure, volume, temperature, and amount of substance. Changing any of these variables changes U. The internal energy is an extensive property – it depends on the amount of substance. **The molar internal energy**, Um = U/n – intensive property, does not depend on the amount of substance, but depends on the temperature and pressure.

Internal energy, heat, and work are all measured in the same units, the joule (J):

$1 J = 1 kg m^2 s^{-1}$.

Changes in molar internal energy ΔU_m are typically expressed in kilojoules per mole (kJ mol^{-1}).

An energy of 1 cal is enough to raise the temperature of 1 g of water by 1^0C:

1 cal = 4.184 J

Experimental finding: the internal energy of a system may be changed either by doing work on the system or by heating it. Heat and work are equivalent ways of changing a system’s internal energy. It is also found experimentally that, if a system is isolated from the surroundings, then no change in internal energy takes place. Suppose we consider an isolated system. It can neither do work nor supply heat – the internal energy cannot change.

Volume- pressure work

The work often encountered with chemical processes is that associated with the formation or disappearance of gaseous substances. This type of work is called pressure-volume work, expansion work or PV-work.

Expansion work

To illustrate the relationship between volume-pressure changes and work, consider the following system consisting of a piston. The system comprises a gas confined to a cylinder in which the external pressure is viewed as weights against the gas.

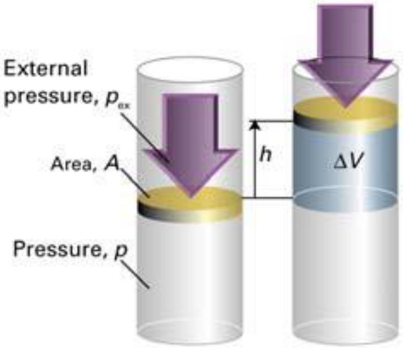


Figure 4.4 Pressure-volume work. Expanding gas against an object through a distance *h*.

Recall that pressure is the force per unit area. Force therefore is the product of pressure and area, $F = P_{ex}A$.

From classical physics, work= force x distance. Then, the work required moving an object through a distance *h* (or *dz*) against an opposing force *F* is

$dw = -Fdz$

where the negative sign is indicative that when the system does work against an opposing force, the internal energy of the system doing work will decrease.

The work done is then expressed as

$dw = -P_{ex}dV$ (4.2)

where $dV=Adz$.

- 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:

$$W = -\int_{V_i}^{V_f} P\, dV \qquad (4.3)$$

PV Diagrams

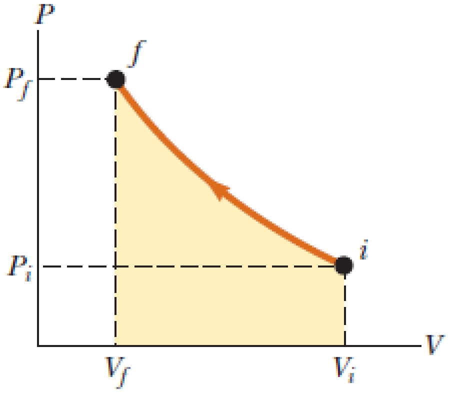


Figure 4.5 A gas is compressed quasi-statically (slowly) from state *i* to state *f*. The work done on the gas equals the negative of the area under the *PV* curve. The volume is decreasing, so this area is negative. Then the work done on the gas is positive. An outside agent must do positive work on the gas to compress it.

PV diagrams are 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. The work done does depend on the path taken.

Work Done By Various Paths

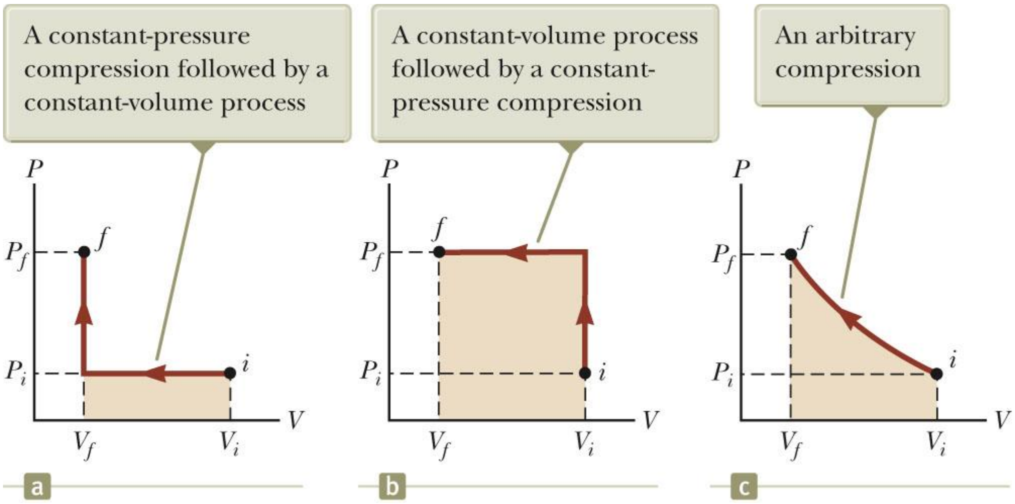


Figure 4.6 The work done on a gas as it is taken from an initial state to a final state depends on the path between these states.

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.

Example (Figure 4.6 a): 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.

$W = -P_i (V_f - V_i)$

Example (Figure 4.6 b): 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 .

$W = -P_f(V_f - V_i)$

Example (Figure 4.6 b): 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.

Expansion against external pressure

Consider the expansion of a gas confined in a cylinder as shown below.

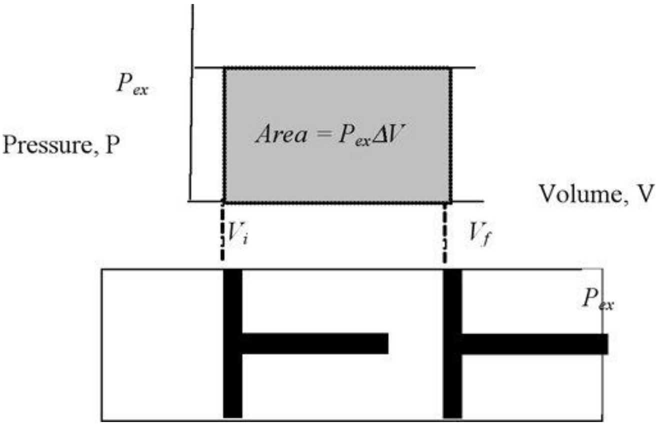


Figure 4.7 Work of expansion by a gas expanding against an external pressure.

The total work done in moving from an initial state 1 to 2 will involve a change in volume from V_i to V_f against a constant pressure P_{ex}. We can then write that

$$W = -\int_{Vi}^{Vf} \mathrm{P}_{ex}\, dV = -\mathrm{P}_{ex} \int_{Vi}^{Vf} dV = -\mathrm{P}_{ex}(V_f - Vi) \qquad (4.4)$$

or

$$W = -\mathrm{P}_{ex}\,\Delta V \qquad (4.5)$$

The area under the curve in Figure 4.6 represents the work done by the gas. A common example of this type of work is in an internal combustion engine of car where expanding gases are able to drive a piston. The lifting-off of rockets and space vehicles such as the space shuttle also involve expansion of gases

Example 4.3

A gas expands by 0.5 L against a constant pressure of 1 atm at 25 ^{0}C. How much work is done in joules by the system against the surroundings?

Solution

The work done is given by

$w = -P\Delta V$,

$P = 1$ atm, $\Delta V = 0.5$ L

$w = -101325\ Nm^{-2} \times 5 \times 10^{-4}\ m^3 = -50.6\ Nm = -50.6\ J$

Example 4.4

A hydrocarbon is burned in a container with a movable piston with a cross-section area of 0.5 m^2. If the piston moved a distance of 30 cm against a pressure of 1 atm, how much work is done in the expansion?

Solution

In expanding, the piston sweeps through a volume = cross section area x distance covered.

Change in volume $\Delta V = 0.5\ m^2 \times 0.3\ m = 0.15\ m^3$,

From equation (4.5), $P = 1\ atm = 101325\ Nm^{-2}$

$w = -P_{ex}\Delta V = -(101325\ Nm^{-2} \times 0.15\ m^3) = -15\,199\ J = -15.2\ kJ$

Practice problem 4.4

A sample of gas is compressed from an initial volume of 4.0 L to a final volume of 1.0 L. What is the work done if the external pressure is 5 atm?

(a) 5.0×10^3	(b) 1.8×10^3
(c) 1.5×10^3	(d) 1.6×10^2

First Law of thermodynamics

The first law of thermodynamics is essentially a statement of the law of the conservation of energy. It states that energy can neither be created nor destroyed. It also can be stated as: the internal energy of an isolated system is constant. It can only be redistributed or converted from one form to another. A useful way to express this in chemistry is through the equation

$$\Delta U = q + w \qquad (4.6)$$

where q is the heat absorbed and w is the work done by the system. Although the internal energy cannot be directly measured, the two quantities heat and work are measurable quantities. If heat flows into the system (or the surroundings do work on the system), the internal energy of the system increases – the sign of w or q is positive. Conversely, if the heat flows out of the system or work is done by the system (at the expense of the system), the internal energy of the system will be negative.

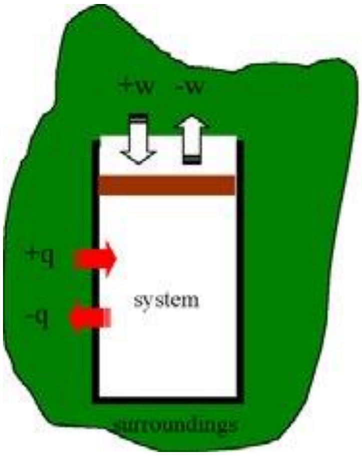


Figure 4.8 Summary of sign convention involving heat and work.

Reversible expansion of a gas

Suppose that the gas expands or contracts in such way that the external pressure equals the pressure of the gas. Such expansion/compression is said to take place in a reversible manner. A ***reversible process*** is one in which the system and surroundings are continuously in equilibrium. This implies that the process takes place infinitesimally slowly so that there is plenty of time at each stage for equilibration with the surroundings.

Isothermal reversible expansion of a gas

The process described above could be done reversibly and under isothermal conditions (e.g. constant temperature water bath). Using the equation for an ideal case and equation (4.4), we can evaluate the work done during this process.

$$W = -nRT \int_{Vi}^{Vf} \frac{dV}{V} = -\,\mathrm{n}RT \ln \frac{V_f}{V_i} \qquad (4.7)$$

The above expression will be positive if the initial volume, V_i, is greater than the final volume, V_f, indicating a compression process. The work done during the process may be drawn using an indicator diagram in Figure 4.9.

In comparing the two areas (a and b), it is clear that more work is done during a reversible expansion against a constant external pressure than during an irreversible expansion process. Maximum work is obtained during a reversible expansion because maximum work is ensured at every step – no wastage.

In Isothermal reversible expansion of a gas

$\Delta U = 0$! since $T_2 = T_1$.

$q_{rev} = -w_{rev}$, from first law.

Practice problem 4.5

Prove that equation (4.7) can be rewritten as

$$W = -\mathrm{n}RT \ln \frac{P_i}{P_f}$$

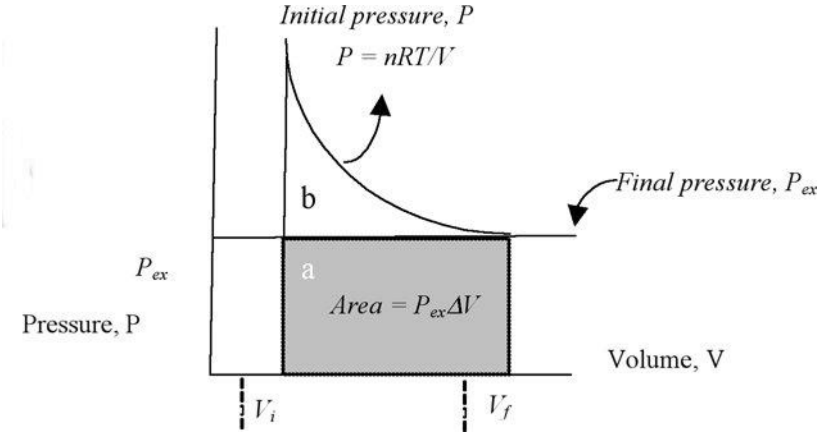


Figure 4.9 Indicator diagram for expansion at constant pressure and for the reversible process.

Free expansion

Free expansion involves expansion with no opposing force. For example if the gas were to expand into a vacuum. In such a case $P_{ex}=0$, so that the work done is equal to zero ($dw = 0, w = 0$) i.e. no work is done during free expansion of a gas.

Constant pressure and constant volume proces

These are the most common processes encountered in chemical reactions. It is thus instructive to consider the behaviour of the first law of thermodynamics in relation to such processes.

Constant volume processes

To carry out a reaction at constant volume we would need a sealed vessel to contain any gaseous products produced. Typical equipment used to perform such measurements is the bomb calorimeter, frequently used to carry out combustion reactions.

In the previous sections, we have seen that the change in internal energy U is given by

$\Delta U = q + w$ (4.8)

If work is done by the system then

$w = - P_{ex}\Delta V$ (4.9)

Thus,

$\Delta U = q + (- P_{ex}\Delta V)$

In the case of constant volume, ΔV is zero therefore

$\Delta U = q_v$ (4.10)

where q_v indicates that heat involved is at constant volume. The result is significant as it shows that the heat change at constant volume is equal to the change in internal energy of the system. Thus, we can experimentally determine the internal energy change for a reaction by measuring energy absorb or released in the process.

Example 4.5

An ideal monoatomic gas is expanded at 298 K from an initial pressure of 1 atm to a final pressure of 5 atm isothermally and reversibly. Calculate the heat absorbed by the gas (q), work done on the gas (w) and the change in internal energy (ΔU).

Solution

Since the process is taking place isothermally and at constant pressure, $T_1 = T_2$, $\Delta T = 0$ and $\Delta U = 0$.

For a reversible process, the work done by the gas expanding isothermally and reversibly equation (12) can be used where the inverse relationship of pressure and volume is utilised i.e.

$W=-RT \ln (V_f / V_i) =-RT \ln (P_i / P_f)$

$W=8.314 \text{ J K}^{-1} \text{mol}^{-1} \text{x}298 \text{ K} \ln 5 = -3990 \text{ J mol}^{-1}$

From the first law of thermodynamics, $\Delta U = q + w$. But $\Delta U = 0$, therefore q = -w. Then, $q = - w = 3990 \text{ J mol}^{-1}$

Example 4.5 An Isothermal Expansion

A 1.0-mol sample of an ideal gas is kept at 0.0°C during an expansion from 3.0 L to 10.0 L.

- **i.** How much work is done on the gas during the expansion?

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

$$= (1.0\ \text{mol})(8.31\ \text{J/mol}\cdot\text{K})(273\ \text{K})\ \ln\left(\frac{3.0\ \text{L}}{10.0\ \text{L}}\right)$$

$$= \boxed{-2.7\times10^{3}\ \text{J}}$$

ii. How much energy transfer by heat occurs between the gas and its surroundings in this process?

from the first law:

$$0 = Q + W$$

$$Q = -W = \boxed{2.7\times10^{3}\ \text{J}}$$

iii. If the gas is returned to the original volume by means of an isobaric process, how much work is done on the gas?

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

$$= -\frac{(1.0\ \text{mol})(8.31\ \text{J/mol}\cdot\text{K})(273\ \text{K})}{10.0\times10^{-3}\ \text{m}^3}(3.0\times10^{-3}\ \text{m}^3 - 10.0\times10^{-3}\ \text{m}^3)$$

$$= \boxed{1.6\times10^{3}\ \text{J}}$$

Practice problem 4.6

Find the work done on the surroundings when 12 litres of an ideal gas, initially at a pressure of 10 atm is allowed to expand at constant pressure to 10 litres: (a) by reducing the external pressure to 1 atm; (b) by reducing pressure first to 5 atm, and then 1 atm; (c) allowing gas to expand into an evacuated space so that its total volume is 10 litres.

Constant pressure processes: enthalpy of reactions

Most chemical reactions take place at constant pressure, for example in the laboratory at atmospheric pressure. In such processes, volume changes do occur.

$q_p = \Delta U + P_{ex}\Delta V$ at constant pressure (4.11)

Heat evolved or absorbed at constant pressure, q_p, is known as enthalpy (H), $q_p = \Delta H$.

Summary of processes

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.
- $q = W = 0$, so $\Delta U = 0$

The internal energy of an isolated system remains constant.

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 since it is a state variable.

If $\Delta U = 0$, $q = -W$

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.

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 $q = 0$, $\Delta U = W$

If the gas is compressed adiabatically, W is positive so ΔU 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

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 $W = 0$, $\Delta U = 0$ and the initial and final states are the same. No change in temperature is expected.

Isobaric Processes

An ***isobaric process*** is one that occurs at a constant pressure. It 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.

Isovolumetric 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, $\Delta U = q$

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.

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, $\Delta U = 0$. Therefore, q = - W. Any energy that enters the system by heat must leave the system by work.

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.
- Because 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.

Summary of Special Processes

Adiabatic

- No heat exchanged
- $q = 0$ and $\Delta U = W$

Isobaric

- Constant pressure
- $W = P(V_f - V_i)$ and $\Delta U = q + W$

Isothermal

- Constant temperature
- $\Delta U = 0$ and $q = -W$

Chapter 5 *by Dr. Hasan Maridi*

Thermochemistry

Thermochemistry

Systems that are unstable (high potential energy) have a higher tendency to undergo chemical change than systems that are stable (lower potential energy). Chemical reactions whenever possible tend to spontaneously move from a state of higher potential energy to one of lower potential energy.

The study of the heat produced or required by chemical reactions is the thermochemistry. It is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and surroundings.

Enthalpy

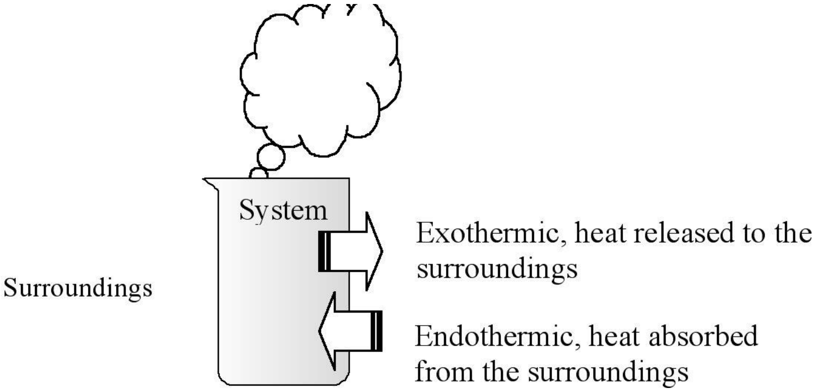


Figure 5.1 Diagram showing a reactions taking place in an open beaker. System in relations to its surroundings.

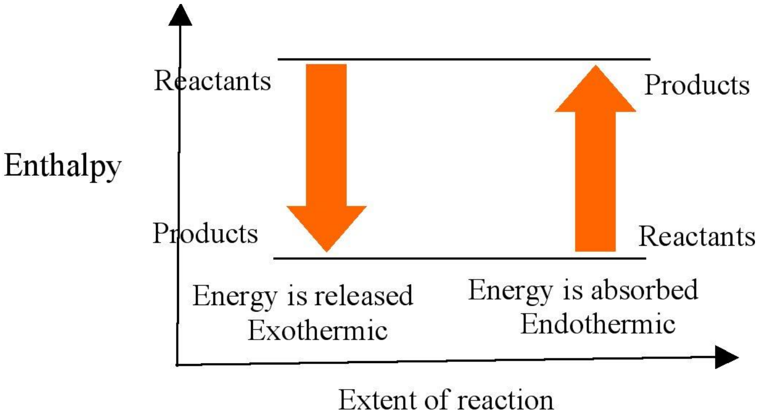


Figure 5.2 Diagram showing relative energy changes for an exothermic and endothermic reaction.

Chemical reactions involve either release or absorption of heat from the surroundings.

- When a chemical reaction occurs in which the system absorbs heat, the process is ***endothermic*** (it feels cold)
- When a chemical reaction occurs in which the system produces heat it is ***exothermic*** (it feels hot)

The heat of reaction is the quantity of heat exchanged between the system and its surroundings when chemical reactions occur. Heat will tend to flow until the system and surroundings are at the same temperature.

Many chemical and biological processes take place at constant pressure. The heat released under conditions of constant pressure is a thermodynamic function known as enthalpy (H), sometimes referred to as “heat content".

The enthalpy (*heat inside*), H, of a system is defined as

$H = U + pV$ (5.1)

The enthalpy of a system is always greater than its internal energy.

Enthalpy is an extensive property.

Molar enthalpy, $H_m = H/n$

$H_m = U_m + pV_m$

For a perfect gas, $H_m = U_m + RT$

The difference between the molar enthalpy and molar internal energy of a perfect gas increases with temperature.

A property that depends only on its initial and final state is known as a state function. Enthalpy is a state function. The enthalpy depends on the amount of substances reacting. Its magnitude depends on the amounts of reactants that are consumed. Reversing thermochemical equations also results in reverse of enthalpy sign but with the same magnitude. Enthalpy change is also dependent on the state of the reactants and products i.e. must be specified.

The change in enthalpy, ΔH, is defined as the sum of the change in internal energy, ΔU, and the pressure-volume work done by the system.

The change in enthalpy ΔH, when a system changes from one state to another is independent of the path between two states.

The change in enthalpy (described or labeled as ΔH) is not measured directly but through the energy released as heat. The enthalpy change (ΔH) depends only on the initial and final states i.e.

$\Delta H = H_f - H_i$

Whether a reaction is exothermic or endothermic depends on the initial and final enthalpies of the reactants and products respectively.

- For ***endothermic*** reactions $H_{final} > H_{initial}$ ***and ΔH is positive ($+\Delta H$)***
- For **exothermic** reactions $H_{final} < H_{initial}$ ***and ΔH is negative ($-\Delta H$)***

The diagram in Figure 5.2 summaries exothermic and endothermic reactions. The diagram shows that for exothermic reactions, the products are lower in energy than the reactants whilst in endothermic reaction the energy of the products is higher than that of the reactants. The increase in enthalpy and extent of reaction are depicted on the y and x axes respectively.

At constant pressure,

$$\Delta H = \Delta U + P\Delta V \qquad (5.2)$$

If it is assumed that the gases produced in a reaction behave as ideal gases, we can solve for V using the perfect gas equation to give us

$$V = \frac{nRT}{P} \qquad (5.3)$$

For a change in volume we can write

$$\Delta V = \Delta(nRT / P) \qquad (5.4)$$

If the reaction is taking place at constant temperature and pressure

$$\Delta V = \Delta n(RT / P) \qquad (5.5)$$

The change in volume for the reaction is essentially a change in number of moles of the species involved. Substituting equation (5.5) in equation (5.2), the enthalpy expression becomes

$$\Delta H = \Delta U + \Delta n_{gas}RT \qquad (5.6)$$

where Δn_{gas} is given by $\Delta n_{gas} = \sum\Delta n_{gas,\ products} - \sum \Delta n_{gas,\ reactants}$ and represents the change in number of moles between the reactants and products.

Example 5.1

Carbon monoxide poisoning sometimes occurs during the cold season due to in-door use of charcoal braziers for heating. This occurs when the amount of oxygen is limited. With sufficient air (oxygen) the carbon monoxide reacts with oxygen to form carbon dioxide which is somewhat less harmful. Calculate ΔH for the reaction at 25 ^{0}C given that the change in internal energy for the reaction is - 281.7 kJ.

Solution

$CO\ (g) + 1/2\ O_2\ (g) \rightarrow CO_2\ (g)$

The enthalpy change enthalpy, ΔH, is defined as the sum of the change in internal energy, ΔU, and the pressure-volume work done by the system.

$\Delta H = \Delta U + P\Delta V$

Since there is no indication of pressure and volume an alternative method is used to work out the problem as shown in equation (4.20).

$\Delta H = \Delta U + \Delta n_{gas}RT$

Δn_{gas} = 1 mol CO_2 - (1 mol C0 + 0.5 mol O_2) = - 0.5,

ΔU = -281.7 kJ, R = 8.314 J $K^{-1}mol^{-1}$, T = 298 K

Substituting the equation (23)

$\Delta H = -2.817 \times 10^5 \text{ J} + (-0.5 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$

$= -2.817 \times 10^5 - 1.238 \times 10^3$

$= - 282.9$ kJ

Practice problem 5.1

One mole of methane reacted with oxygen at constant volume and at 298 K temperature according to the equation below.

$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (l)$

What is the change in enthalpy, ΔH, for the reaction if 886 kJ of energy is liberated during the reaction?

(a) - 881 kJ (b) - 891 kJ

(c) 891 kJ (d) - 886 kJ

Heat capacity

The heat capacity of an object is defined as the amount of heat energy required to raise its temperature by 1 K (or °C), mathematically expressed as

$$C = \frac{q}{\Delta T} \qquad (5.7)$$

The heat capacity (C) measures the temperature change experienced by a substance as a result of heat flow. The heat capacity of 1 mole of a substance is called its ***molar heat capacity*** (C_m =C/n) where n is the number of moles.

Several processes can change the temperature of an ideal gas. Since ΔT is the same for each process, ΔU is also the same. The work done on the gas is different for each path.

The heat associated with a particular change in temperature is **not** unique.

We define specific heats for two processes that frequently occur:

- Changes with constant pressure, isobaric
- Changes with constant volume, isovolumic

The heat capacity depends on whether a sample is maintained at constant volume ($C = C_V$) or constant pressure ($C = C_P$). The respective molar quantities are $C_{V,m}$ and $C_{P,m}$.

Specific heat (c) is the heat capacity of 1 gram of a substance or it is the quantity of the heat required to change the temp of 1g of a substance by 1 K (or °C).

$$c = \frac{q}{m\Delta T} \qquad (5.8)$$

The specific heat of a substance can be determined experimentally by measuring the temperature change ($\Delta \boldsymbol{T}$) of a known mass ($\boldsymbol{m}$) of the substance when it gains or loses a specific amount of heat ($\boldsymbol{q}$).

The measurement of heat flow (q) is known as ***calorimetry.***

Molar specific heats

- $q = n\, C_{V,m}\, \Delta T$ for constant-volume processes
- $q = n\, C_{P,m}\, \Delta T$ for constant-pressure processes

Q (constant pressure) must account for both the increase in internal energy and the transfer of energy out of the system by work.

$Q_{\text{constant P}} > Q_{\text{constant V}}$ for given values of n and ΔT

$C_P > C_V$

Ideal Monatomic Gas

A monatomic gas contains one atom per molecule.

When energy is added to a monatomic gas in a container with a fixed volume, all of the energy goes into increasing the translational kinetic energy of the gas. There is no other way to store energy in such a gas.

Therefore, $\Delta U = 3/2\ nRT$

ΔU is a function of T only

In general, the internal energy of an ideal gas is a function of T only.

- The exact relationship depends on the type of gas.
- At constant volume, $q = \Delta U = nC_{V,m}\ \Delta T$
- This applies to all ideal gases, not just monatomic ones.

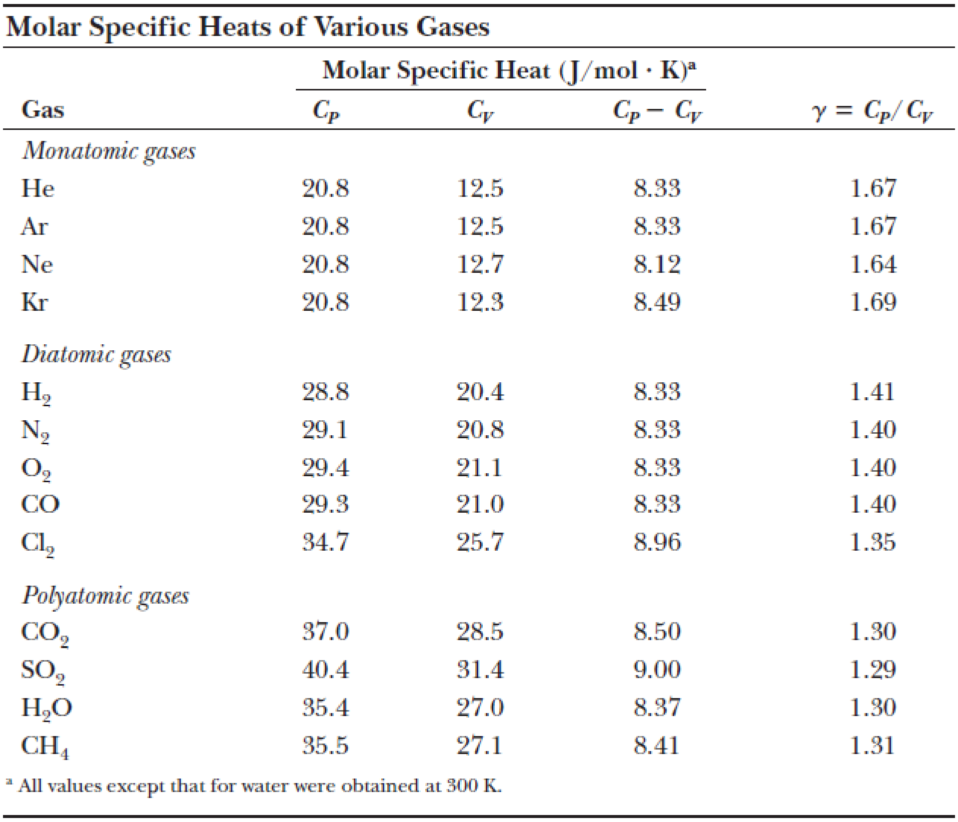
Solving for $C_{V,m}$ gives $C_{V,m} = 3/2\ R = 12.5$ J/mol · K

For all monatomic gases, This is in good agreement with experimental results for monatomic gases.

In a constant-pressure process, $\Delta U = q + W$ and $C_{P,m} - C_{V,m} = R$

- This also applies to any ideal gas
- $C_{p,m} = 5/2\ R = 20.8$ J/mol · K

Table 5.2 Sample Values of Molar Specific Heats



Molar Specific Heats of Various Gases

	Molar Specific Heat (J/mol · K)[a]			
Gas	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a] All values except that for water were obtained at 300 K.

We can also define the ratio of molar specific heats.

The ratio of these molar specific heats is a dimensionless quantity γ (Greek letter gamma):

$$\gamma = \frac{C_P}{C_V} \tag{5.9}$$

Theoretical values of $C_{V,m}$, $C_{P,m}$, and γ are in excellent agreement for monatomic gases. But they are in serious disagreement with the values for more complex molecules. Not surprising since the analysis was for monatomic gases

The internal energy of more complex gases must include contributions from the rotational and vibrational motions of the molecules. In the cases of solids and liquids heated at constant pressure, very little work is done, since the thermal expansion is small, and $C_{P,m}$ and $C_{V,m}$ are approximately equal.

Measurements of internal energy and enthalpy changes

We can use calorimetry to measure the heat produced or absorbed by a reaction, and can identify q with a change in internal energy (a constant-volume process) or a change of enthalpy (a constant-pressure process).

Experimental determination of heat evolved or released during chemical reactions is done using a calorimeter by measuring the temperature changes produced. If the calorimeter was isolated from the surroundings, the heat evolved in the reaction will be reflected in a rise in temperature of the system. The amount of heat evolved during the reaction can be determined from knowledge of how much energy is required to raise the temperature of a substance.

Constant volume calorimetry

To measure a change in internal energy we should use a fixed volume calorimeter (such as the bomb calorimeter) and monitor the energy released ($q < 0$) or supplied ($q > 0$) as heat by measuring the corresponding change in temperature.

In the calorimeter, the total heat capacity is $C_{total} = C_{water} + C_{caloremeter}$. For a constant volume process, we can write the following expression for the heat capacity.

$$C_V = \frac{q_V}{\Delta T} = \frac{\Delta U}{\Delta T} \qquad (5.10)$$

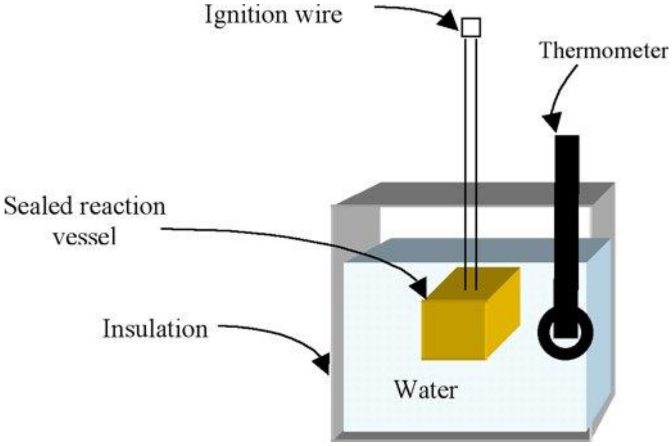


Figure 5.5 Constant volume calorimeter assembly with pressure regulatory valve. Reaction takes place in bomb immersed in water. Reaction is triggered using ignition wires.

From the first law of thermodynamics we recall

$\Delta U = q + w = q - P\,\Delta V$

If the reaction is performed in a closed container called a bomb calorimeter then the volume remains constant and $\Delta V = 0$.

Hence the first law reduces to

$\Delta U = q_V = C_V\,\Delta T$

Electric heating for a measured time: $q = IVt$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = \Delta U + \Delta nRT, \qquad (5.11)$$

where Δn = *no. of moles of gaseous products* - *no. of moles of gaseous reactants* for the reaction of one mole of the substance of interest.

Example 5.2

Calculate the amount of heat required to raise the temperature of 9.25 L of water from 22.0 to 29.4 ^{0}C given that the specific heat of water is 4.18 J g^{-1} ^{0}C^{-1}.

Solution

From equation (5.8)

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

Solving for the quantity of heat transferred q = mass x change in temperature x specific heat of water.

$q = 9.25 \times 10^3$ g x (29.4 - 22.0) ^{0}C x 4.18 J g $^{-1}$ ^{0}C $^{-1}$
= 286.3 kJ

Constant pressure calorimeter

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change at constant pressure: isobaric calorimeter.

A thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature. For a combustion reaction an adiabatic flame calorimeter may be used to measure ΔT when a given amount of substance burns in a supply of oxygen. Another route: to measure ΔU using a bomb calorimeter, and then convert ΔU to ΔH. Because solids and liquids have small molar volumes, for them pV_m is so small that the molar enthalpy and molar internal energy are almost identical: $H_m = U_m + pV_m \approx U_m$ If a process involves only solids or liquids, the values of ΔU and ΔH are almost identical. But this is not the case when gases are produced or consumed in the reaction.

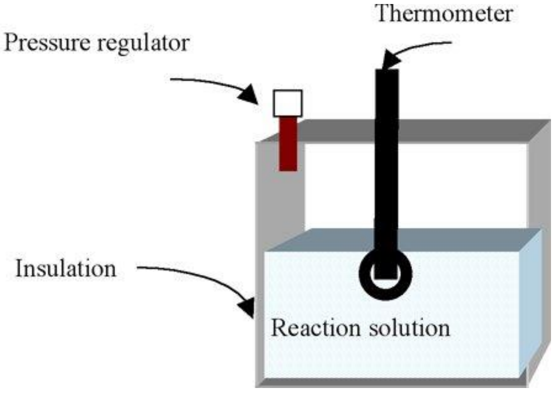


Figure 5.6 Energy changes during: (a) an exothermic reaction and (b) an endothermic reaction between the system and surroundings.

For a constant pressure process, we can write the following expression for the heat capacity.

$$C_P = \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T} \qquad (5.12)$$

Example 5.3

Water is heated under p = 1 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s, 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

Solution

$\Delta H = q_p = \mathrm{IV}t$

ΔH_m = 0.50 A x12 V x300 s / (0.798/18.02) mol

$\Delta H_\mathrm{m} = +41\ \mathrm{kJ\ mol^{-1}}$ $\quad H_2O(l) \rightarrow H_2O(g) \quad \Delta n_\mathrm{g} = +1$ mol

$\Delta U_\mathrm{m} = \Delta H_\mathrm{m} - RT = +38\ \mathrm{kJ\ mol^{-1}}$

Practice problem 5.2

A sample of carbon, 3.0 g, was burned to carbon dioxide in a copper calorimeter. The mass of the calorimeter was 1.5 kg and the mass of water in the calorimeter was 2 kg. The initial temperature was 20 ^{0}C and the final temperature was 31 ^{0}C.

Calculate the heat liberated for the combustion of 1 g of carbon. The specific heat capacity or copper and water are 0.389 J g^{-1} ^{0}C^{-1} and 4.18 J g^{-1} ^{0}C^{-1}.

(a) 3.2 x 10^4 J (b) 9.3 x 10^4 J

(c) 6.4 x 10^4 J (d) 9.2 x 10^4 J

Temperature dependence of reaction enthalpy

The heat capacity at constant pressure is expressed in the equation

$$C_P = \frac{dq_P}{dT} = \frac{dH}{dT} \qquad (5.13)$$

Not all reactions take place at 298 K, so we must examine how the tabulated thermochemical data can be adapted for use under different conditions. We have seen before that the heat capacity at constant pressure is related to temperature by

$$\Delta H = C_P \, dT \qquad (5.14)$$

If a substance is heated from an initial temperature T_1 to a temperature T_2, the enthalpy change from $H(T_1)$ to $H(T_2)$ is according to the equation.

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_P dT \qquad (5.15)$$

It is assumed that no phase transition occurred between the two temperatures of interests T_1 and T_2.

Practice problem 5.3

Prove that, $C_{p,m} - C_{V,m} = R$ for the ideal gas?

Hint: $\Delta H_m - \Delta U_m = R\Delta T$ divided by ΔT. we get $C_{p,m} - C_{V,m} = R$

Standard enthalpy changes

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, ΔH^o , the change in enthalpy for a process in which the initial and final substances are in their standard states. The **standard state** of a substance at a specified temperature is its pure form at 1 bar.

Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition**. The standard enthalpy of vaporization, $\Delta_{vap}H^o$, is one example.

$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_{vap}H^o$ (373 K) =+40.66 kJ mol^{-1}

Example 5.4

Find the enrgy needed to vaporate 1 L of water if you know that the standard enthalpy of vaporization of water is 40.66 kJ mol^{-1} and the density of water is 1g/mL.

Solution

$$d_{H_2O} = \frac{m_{H_2O}}{V_{H_2O}}$$

$$m_{H_2O} = d_{H_2O} \times V_{H_2O}$$

$$m_{H_2O} = (1\ g/ml) \times (1000\ ml)$$

$$m_{H_2O} = 1000\ g$$

$$n_{H_2O} = \frac{m_{H_2O}}{Mw_{H_2O}}$$

$$n_{H_2O} = \frac{1000g}{(2 \times 1+16)}$$

$$n_{H_2O} = 55.56\ mol$$

$$1\ mol\ (H_2O) \longrightarrow 40.6\ kJ$$

$$55.56\ mol \longrightarrow \Delta H_V$$

$$\Delta H_V = \frac{40.6\ kJ \times 55.56\ mol}{1\ mol}$$

$$\Delta H_V = 2255.74\ kJ$$

Enthalpies of chemical change

Enthalpy changes accompanying chemical reactions:

$CH_2{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g) \quad \Delta H = -137\ kJ$

This equation is called **thermochemical equation**.

During hydrogenation of ethane, the enthalpy of the system decreases by 137 kJ – if the reaction takes place at constant pressure, 137 kJ of heat is released into the surroundings when 1 mol $CH_2{=}CH_2$ combines with 1 mol H_2 at 25ºC.

If we write ΔH^o, we mean the change of enthalpy that occurs when the reactants in their standard states change into products in their standard states:

Pure, unmixed reactants → pure, separated products (in their standard states)

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) \qquad \Delta H^o = -572$ kJ

When 2 mole H_2 as pure hydrogen gas at 1 bar combines with 1 mole O_2 as pure oxygen gas at 1 bar to form 2 mole H_2O as pure liquid water at 1 bar, the initial and final temperature being 25ºC, the enthalpy of the system decreases by 572 kJ and (at constant p). 572 kJ of heat is released into the surroundings.

A thermochemical equation is a balanced reaction equation accompanied with the enthalpy change associated with it.

The heat evolved or absorbed during a chemical reaction is the enthalpy change. In chemistry we normally do our experiments at standard conditions of temperature and pressure (STP). So, the results from the measurements are usually at STP.

The standard reaction enthalpy,

$$\Delta_r H^o = \sum_{Products} v\ \ H_m^o - \sum_{Reactants} v\ \ H_m^o \tag{5.16}$$

Combustion – the complete reaction of a compound with oxygen (completeoxidation):

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \qquad \Delta H^o = -890$ kJ

The standard enthalpy of combustion, $\Delta_c H^o$ – the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is present. $\Delta_c H^o$ – a molar quantity.

Standard enthalpies of formation

The **standard enthalpy of formation**, $\Delta_f H^o$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The **reference state** of an element is its most stable state at the specified temperature and 1 bar. The value of $\Delta_r H^o$ for the overall reaction is the sum of these 'unforming' and forming enthalpies. The enthalpy of an unforming step is the negative of the enthalpy of formation.

Consider the reaction

$n_A A + n_B B \rightarrow n_C C + n_D D$

The standard enthalpy of reaction is calculated as:

ΔH = *Sum of enthalpies of products* - *Sum of enthalpies of reactants*

Mathematically written a

$$\Delta_r H^o=(n_C\ \Delta_f H^o{}_c+n_D \Delta_f H^o{}_D)-(n_A\ \Delta_f H^o{}_A+n_B \Delta_f H^o{}_B)$$

$$\Delta_r H^o = \sum_{Products} v\ \Delta_f H^o - \sum_{Reactants} v\ \Delta_f H^o \qquad (5.17)$$

The standard enthalpy of formation, $\Delta_f H^o$, for the pure elements ($Cu(s)$, $N_2(g)$, $Fe(s)$, $Na(s)$, $Cl_2(g)$, $Hg(L)$) is equals to zero at any temperature.

Example 5.5

Find $\Delta(PV)$ and ΔU for the reaction of

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ at 298.15 K. Use $\Delta_f H^o\ (H_2O(l))= -285.83\ \text{kJ mol}^{-1}$

Solution

Since the single product, H_2O, is liquid, $\Delta n(g) = -3.000$ mol

$\Delta(PV) = \Delta n(g)RT = (-3)(8.3145\ \text{JK}-1\ \text{mol}-1)(298.15\ \text{K})$

$= -7437\ \text{J mol}^{-1} = -7.437\ \text{kJ mol}^{-1}$

$\Delta H = 2\Delta_f H^o (H_2O) - 0 - 0 = -571.660 \text{ kJ mol}^{-1}$

$\Delta U = -571.660 \text{ kJ mol}^{-1} - (-7.437 \text{ kJ mol}^{-1}) = -564.223 \text{ kJ mol}^{-1}$

Example 5.6

The standard reaction enthalpy of $2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$ is calculated as follows:

$\Delta_r H^o = \{ \Delta_f H^o (H_2O_2,l) + 4\ \Delta_f H^o (N_2,g)\} - \{2\ \Delta_f H^o (HN_3,l) + 2\ \Delta_f H^o (NO,g)\}$

$= \{-187.78 + 4(0)\} \text{ kJ mol}^{-1} - \{2(264.0) + 2(90.25)\} \text{ kJ mol}^{-1}$

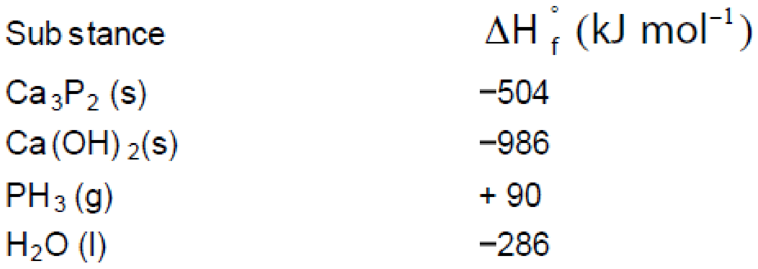
$= -896.3 \text{ kJ mol}^{-1}$

Example 5.7

Phosphine gas may be prepared using by the following reaction.

$Ca_3P_2 (s) + 6H_2O (l) \rightarrow 3Ca(OH)_2(s) + 2PH_3 (g)$

Use the standard enthalpies of formation given below to calculate the standard enthalpy change for the above reaction.



Substance	ΔH°_f (kJ mol^{-1})
Ca_3P_2 (s)	−504
$Ca(OH)_2$(s)	−986
PH_3 (g)	+ 90
H_2O (l)	−286

Solution

The enthalpy change for the reaction is given by the following relationship.

$\Delta_r H^o$ = Sum of enthalpies of products - Sum of enthalpies of reactants

$\Delta_r H^o = [3 \text{ x } (-986) + (3 \text{ x } 90)] - [(-504) + 6 \text{ x } (-286)]$

$= (-3048 + 270 + 504 + 1716) \text{ kJ}$

$= 558 \text{ kJ}$

Example 5.8

Calculate the standard enthalpy of the reaction

$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O(L)$

If you know that

$\Delta H_f^\circ(CH_4(g)) = -74.9$ kJ

$\Delta H_f^\circ(O_2(g)) = 0$

$\Delta H_f^\circ(CO_2(g)) = -393.5$ kJ

$\Delta H_f^\circ(H_2O(L)) = -285.8$ kJ

Solution

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(L)$$

$$\Delta H^\circ = \underbrace{\sum n_P(\Delta H_f^\circ)_P}_{\text{products}} - \underbrace{\sum n_R(\Delta H_f^\circ)_R}_{\text{Reactants}}$$

$$\Delta H^\circ = \left[\Delta H_f^\circ(CO_2) + 2\Delta H_f^\circ(H_2O)\right] - \left[\Delta H_f^\circ\ CH_4 + 2\Delta H_f^\circ(O_2)\right]$$

$$\Delta H^\circ = [(-393.5) + 2(-285.8)] - [(-74.9) + 2(0)]$$

$$\Delta H^\circ = -890.2 \text{ kJ}$$

Practice problem 5.4

The enthalpy change for the combustion of 1 mole of pentane to carbon dioxide and water is -3526 kJ. Calculate the standard enthalpy of formation of pentane given the following standard enthalpies of formation:

CO_2 (g) $\Delta_f H^o = -393$kJ mol^{-1}

H_20 (l) $\Delta_f H^o = -286$kJ mol^{-1}

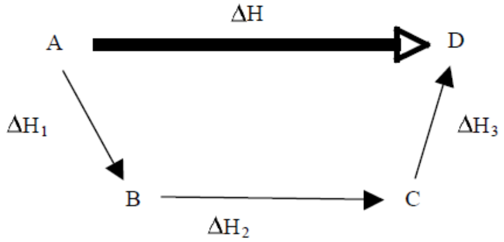
(a) -160 kJ
(b) 155.2 kJ
(c) -155.2 kJ
(d) - 77.6 kJ

Hess's law

Hess's law states that when a reaction takes place to form products, the change in enthalpy is the same regardless of whether it is in a single step or involves several stages. For example, in the hypothetical reaction below, the overall enthalpy change is given by

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 \qquad (5.19)$$

The significance of the law is that it enables calculation of enthalpies for reactions that maybe difficult or two dangerous for us to perform in the laboratory. Many thermochemical data can be found in Tables for use in calculations for various chemical reactions.



One restriction of Hess's law is that all the enthalpies must be measured at the same temperature and pressure. All enthalpy changes measured under these conditions are referred to as standard enthalpy changes denoted by ΔH^0. The reactant and products must be in their standard states. The standard state of a pure substance being the form (gas, liquid or solid) in which a substance is most stable at 1 atm pressure and a specified temperature.

Example 5.9

$2C\ (graphite) + H_2\ (g) \rightarrow C_2H_2\ (g)\ \Delta H = ?$

If you know that

a- $C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H = -393.5\ kJ$

b- $H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O(L) \qquad \Delta H = -285.9\ kJ$

c- $2C_2H_2\ (g) + 5O_2\ (g) \rightarrow 4CO_2\ (g) + 2H_2O(L)\ \Delta H = -2598.8\ kJ$

Solution

a- $2C\ (graphite) + 2O_2\ (g) \rightarrow 2CO_2\ (g) \qquad \Delta H = -787kJ$

b- $H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O(L) \qquad \Delta H = -285.9\ kJ$

c- $2CO_2\ (g) + H_2O(L) \rightarrow C_2H_2\ (g) + 5/2O_2\ (g) \quad \Delta H = +1299.4kJ$

$2C\ (graphite) + H_2\ (g) \rightarrow C_2H_2\ (g) \qquad \Delta H = +226.5\ kJ$

Practice problem 5.5

C (graphite) + $2H_2$ (g) → CH_4 (g) ΔH =?

If you know that

a- C (graphite) +O_2 (g) → CO_2 (g) ΔH = - 393.5 kJ

b- H_2 (g) + 1/2 O_2 (g) → H_2O(L) ΔH = - 285.9 kJ

c- CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (L) ΔH = - 890 kJ

(a) - 75.3 kJ

(b) + 75.3 kJ

(c) -150.6 kJ

(d) +150.6 kJ

Practice problem 5.6

Given the following thermochemical equations

BCl_3 (g) + $3H_2O$ (l) → H_3BO_3 (g) + 3HCl (g) ΔH□ = - 112.5 kJ

B_2H_6 (g) + $6H_2O$ (g) → $2H_3BO_3$ (s) + $6H_2$ (g) ΔH□ = + 493.4 kJ

H_2 (g) + Cl_2 (g) →   2HCl (g) ΔH□ = - 184.6 kJ

Calculate the value of ΔH□ for the reaction

B_2H_6 (g) + $6Cl_2$ (g) → $2BCl_3$ (g) + 6HCl (g)

(a) 492.2 kJ

(b) 389.2 kJ

(c) 3892 kJ

(d) -389.2 kJ

Chapter 6

by Dr. Hasan Maridi

Second law of thermodynamics
Entropy and Spontaneity in Chemical Change

Spontaneous processes

Some things happen and some things don't.

- A ball rolls down a hill but never spontaneously rolls back up a hill.
- Steel rusts spontaneously if exposed to air and moisture. The iron oxide in rust never spontaneously changes back to iron metal and oxygen gas.
- A gas fills its container uniformly. It never spontaneously collects at one end of the container.
- Heat flow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.
- Wood burns spontaneously in an exothermic reaction to form CO_2 and H_2O, but wood is never formed when CO_2 and H_2O are heated together.
- Ink mixes with water.
- At temperatures below 0°C water spontaneously freezes and at temperatures above 0°C ice spontaneously melts.

For chemical systems, when heat is released from the system to the surroundings during a chemical reaction, the energy of the system decreases. The system energy changes from a higher state to a lower one. The analogue of the previous examples leads to the proposition that exothermic processes have a tendency to proceed spontaneously. Exothermic processes are generally spontaneous. Several endothermic processes are spontaneous. Typical examples include:

- the melting of ice in which heat is absorbed and the energy of the system increases
- evaporation of water from a surface is also endothermic
- and so is the expansion of carbon dioxide into a vacuum. Conclusion – the enthalpy change alone is not sufficient to determine whether a change is spontaneous or not.

A **spontaneous process** is a process that occurs without external intervention. A **non-spontaneous process** is process that requires external action to start. A reaction that does occur under the given set of conditions is called a spontaneous reaction. If a reaction does not occur under specified conditions, it is said to be non-spontaneous.

Spontaneity and disorder

All the examples that we have considered for spontaneous processes are characterised by a change to a more disordered state. In other words, there is an increase in the degree of randomness. In addition, there is no change in energy involved in the process.

Mixing of two gases

Two ideal gases are confined to two chambers separated by a valve as shown in the diagram below.

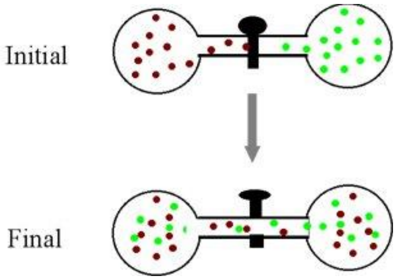


Figure 6.1 Illustration of the mixing of two gases. Gases spontaneously migrate to opposite chambers once the valve is opened.

When the tap is opened, the gases migrate into opposite chambers and mix. Mixing continues until the partial pressures in each chamber are uniform. One characteristic of an ideal gas is that the internal energy depends only on temperature. When the two gases mix at constant temperature, the change in internal energy (ΔU) is equal the change in enthalpy (ΔH), which is equal to zero (i.e. $\Delta U = \Delta H = 0$). Thus, it can be concluded that enthalpy change is not the driving force for the spontaneous mixing of the gases.

Consider a similar experiment to the one above in which the gas is confined one chamber (A) separated from a chamber (B) that has been evacuated.

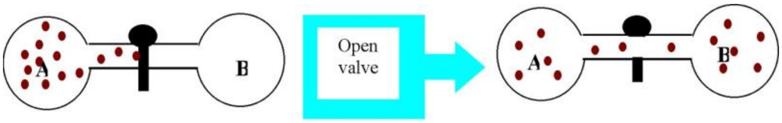


Figure 6.2 Illustration of free expansion of a gas into a vacuum. Molecules spontaneous migrate to the chamber with a vacuum.

Upon opening the tap, gas molecules move from the left chamber (A) to the right chamber (B) resulting in an increase in disorder as each molecule has a larger volume to travel around

- no work is performed on the system or the surroundings
- heat is neither evolved nor absorbed in the process
- the process is spontaneous and irreversible.

There is evidently no change in energy. The process therefore is not spontaneous to minimize energy but is driven by the tendency to increase disorder. In both cases, the degree of randomness increases and the manner in which energy is distributed among the gas molecules changes. The driving force is the tendency of the molecules to achieve a maximum state of disorder.

Entropy

The thermodynamic function that measures the degree of disorder of the system is called **entropy**, ***S***. In mixing of the two gases in the example above, entropy of the system increases so that ΔS is greater than zero. The more disordered the state, the larger its entropy.

Entropy has a unit of J/K.

Entropy is a function that depends only on the initial and final state of the system. The change in entropy accompanying a processing can be written as

$\Delta S = S_{final} - S_{initial}$ (6.1)

The value of S is positive if the degree of disorder increases, and is negative if disorder decreases. The reactions in the following example help illustrate this point.

Example 6.1

H_2 (g) + O_2 (g) → H_2O (l) entropy decreases since the liquid state is more ordered than the gaseous state.

$2NH_4NO_3$ (s) → $2N_2$ (g) + $4H_2O$ (g) + O_2 (g) entropy increases since the reaction yields a large amount of gas.

Example 6.2

Make qualitative predictions of entropy changes in the following processes.

(a) Reaction of sulphur dioxide with oxygen to form sulphur trioxide. $2SO_2$ (g) + O_2 (g) → $2SO_3$ (g)

(b) Vaporisation of one mole of water H_2O (l) → H_2O (g)

Solution

(a) The number of moles of gaseous products is smaller than that of the reactants. Three moles of reactants giving 2 moles of products. Entropy decreases.

(b) Molecules in the vapour phase have greater freedom of movement. Entropy increases.

Practice problem 6.1

Suggest if there is an increase or decrease in entropy for the reaction shown below.

$CuSO_4(s) \xrightarrow{H_2O} Cu^{2+}(aq) + SO_4^{2-}(aq)$

Entropy measures the spontaneous dispersal of energy :How much energy is spread out in a process, or how widely spread out it becomes – at a specific temperature.

Mathematically we can define entropy change as energy dispersed/temperature.

$\Delta S = q_{rev} / T$ (6.2)

Since ΔS is independent of the path taken. We assume that the process proceeds via a reversible process so that the changes in heat are independent of the path taken, $q = q_{rev}$.

The use of entropy as the sole criteria for predicting spontaneous processes is somewhat problematic. One classical example is the freezing of water spontaneously at - 10 ^{0}C. Ice is a more ordered state and yet the process occurs spontaneously. This apparent difficult is overcome by considering the change in entropy for both the system and the surroundings. The combined change of the system and surroundings entropy is called the entropy change of the universe expressed mathematically by

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \qquad (6.3)$$

Second law of thermodynamics

For a spontaneous (irreversible process), that produces an increase in entropy, in both the system and surroundings, the universe gains in entropy. We can therefore write that

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0 \qquad (6.4)$$

This is the mathematical representation of the ***second law of thermodynamics***, which states that all spontaneous processes produce an increase in entropy of the universe.

This helps us explain the spontaneous freezing of water despite a having a negative entropy. In freezing heat is absorbed from the surroundings, the entropy change in the surroundings is therefore positive. In this case, the entropy increase in the surroundings is higher than the decrease in entropy of the system. Thus, the total entropy of the universe is positive when water freezes.

The First Law uses the internal energy to identify permissible changes; the Second Law uses the entropy to identify the spontaneous changes among those permissible changes.

Entropy and reversible processes

In chemistry you have met a number of reactions that are reversible reactions. A common example is the reaction of hydrogen and nitrogen to give ammonia.

$H_2 (g) + N_2 (g) \rightarrow NH_3 (g)$

The reaction can go in both directions to give either ammonia (forward) or hydrogen and nitrogen in the reverse direction. Another example of a reversible process is the phase transition of ice to liquid water. However, for ice to melt in a thermodynamic sense we would need to apply a minute amount of heat so that only a small amount of ice melts. If a small amount of heat was then withdrawn, the water would change back into ice. In a perfect reversible phase change of ice to water, the surroundings return to their initial state without affecting the rest of the universe. The entropy change in the system is given by

$\Delta S = \Delta H_{rev}/T \qquad (6.5)$

where $\Delta H_{rev} = q_{rev}$

Example 6.3

Calculate the entropy change when one mole of water is converted into water vapour at 100 ^{o}C. The heat of vaporisation is 40.6 kJ mol^{-1}

Solution

For a process occurring at constant temperature, the change in entropy, ΔS, is equal to the heat absorbed divided by temperature. At constant pressure q = ΔH. Thus

$\Delta S = \Delta H_{vap}/T = 40.6 \times 10^3 \text{ J} / 373\text{K} = 108.8 \text{ J K}^{-1}$

Practice problem 6.2

The entropy change for the vaporisation of mercury is 86.5 J K^{-1}mol^{-1} at standard pressure. Calculate the boiling point if the enthalpy of vaporisation is 54.5 kJ mol^{-1}.

(a) 6250 K (b) 650 K
(c) 0.630 K (d) 630 K

Effect of temperature and volume

The entropy of a system increases with increasing temperature. The number of ways in which energy is able to distribute also increases as temperature increases. When the temperature is low, approaching absolute zero, the kinetic energy of the random motion of the molecules is small. The number of ways to distribute energy is fewer and hence low entropy. Consider for example molecules in a solid. Molecules are at fixed locations within the lattice structure. These molecules have vibrational motion about their location. When the solid absorbs energy in form of heat, the vibrations of the molecules increases and the molecules are no longer found at a fixed point. The number of ways to spreading energy has increased.

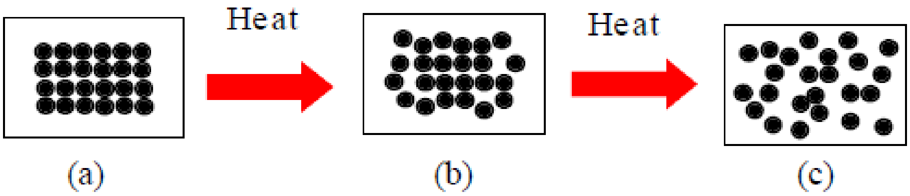


Figure 6.3 Illustration of the molecules locations in the three states.

In Figure 6.3: (a) Many substances a t very low temperature form highly ordered structures (crystals). There are fewer ways to distribute energy. (b) As temperature increases, molecules have greater motion and no longer found in fixed locations. Molecules move more freely with greater ways to distribute energy. (c) With still more heat added, molecules acquires more mobility, molecules are randomly distributed and have many ways to distribute energy.

Variation of entropy with temperature

The fact that entropy is influenced by temperature was highlighted qualitatively in the sections above. A quantitative analysis can be done by evaluating equation (2). For a system changing form an initial state with temperature (T_i) to a final temperature (T_f), the total entropy change for the process is found by integrating equation (2).

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

For a constant pressure process, the heat change dq can be related to the heat capacity C_P, $dq = C_P dT$

So that

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_P dT}{T} \qquad (6.6)$$

Similarly, for a process taking place at constant volume the heat capacity (C_V) can be used in the expression

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_V dT}{T} \qquad (6.7)$$

The overall entropy change between a temperature T_1 and T_2 is found by integrating and finding the solutions for the constant pressure and volume processes as shown below.

Expression for constant pressure process

$$S(T_2) = S(T_1) + C_P \ln (T_2 / T_1) \qquad (6.8)$$

Expression for constant volume process

$$S(T_2) = S(T_1) + C_V \ln (T_2 / T_1) \qquad (6.9)$$

These equations enable us to calculate the entropy change by measuring the heat capacity at different temperatures and evaluating the integrals. The change in entropy is calculated as a difference in entropy between the temperatures of interest and absolute zero temperature, T = 0.

Example 6.4

What is the change in entropy if a sample of solid magnesium is heated from 27 ^{o}C to 227 ^{o}C at 1 atm pressure? The specific heat capacity in region 0 – 600 ^{0}C varies according to the expression

$C_p = 26.0 + 5.46 \times 10^{-2}\ T - 28.6 \times 10^{4}\ T^{-2}$

Solution

The change in entropy in the temperature range 300 - 500 K can be calculated by applying equation (6).

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p\, dT}{T}$$

Making necessary substitutions,

$$\Delta S = \int_{300_1}^{500_2} \frac{26.0}{T} dT + \int_{300}^{500} 5.46 \times 10^{-3} dT - \int_{300}^{500} 28.6 \times 10^{4} \frac{dT}{T^3}\ \mathrm{J\ K^{-1}}$$

$$= 26.0 \ln [T]_{300}^{500} - 5.46 \times 10^{-3} \times [T]_{300}^{500} + \frac{28.6 \times 10^{4}}{2} \left[\frac{1}{T^2}\right]_{300}^{500}\ \mathrm{J\ K^{-1}}$$

$$= 26.0 \ln \frac{500}{300} + 5.46 \times 10^{-3} \times 200 + 14.3 \times 10^{4} \left[\frac{1}{500^2} - \frac{1}{300^2}\right]\ \mathrm{J\ K^{-1}}$$

Practice problem 4.3

What is the change in entropy when 1 mole of water at 0 °C is heated to form steam at 110°C at atmospheric pressure. The specific heat is 4.18 J K^{-1} g^{-1} and the enthalpy of vaporisation is 2257 J g^{-1}

(a) 5.8 (b) 140

(c) 132.1 (d) 8.3

Standard Entropies

Standard entropies are measured at 298 K and 1 atm with units of JK^{-1}. Using tabulated standard enthalpy values entropy changes for chemical reaction may be calculated as the difference between the sum of entropies of the products and the reactants.

$$\Delta S^o = \sum S^o \textit{(products)} - \sum S^o \textit{(reactants)} \qquad (6.10)$$

Effect of volume

An increase in the volume of a gas results in increased entropy. There are a greater number of possible states to gas molecules due to the larger space. Let us examine the expansion of an ideal gas confined in a piston.

For an ideal gas that expands at constant temperature the expression for the change in entropy is

$$\Delta S = \frac{1}{T}\int dq$$

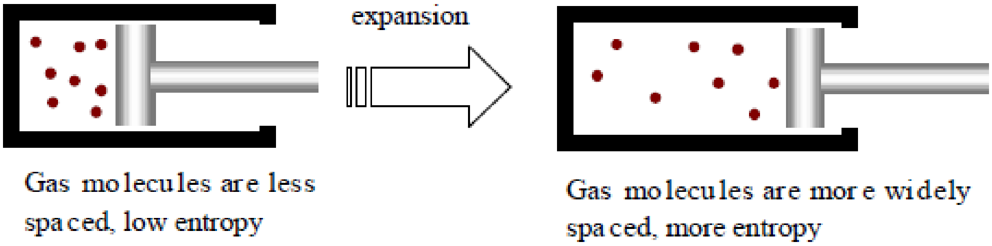


Figure 6.5 Gas molecules have greater space when the piston moves outwards.

We know from chapter 4 that for an *isothermal reversible process*

$$q_{rev} = -w = nRT\int_{Vi}^{Vf}\frac{dV}{V} = nRT\ \ln\frac{V_2}{V_1}$$

therefore the change in entropy can be expressed as

$\Delta S = nR\ ln(V_2 / V_1)$ (6.11)

The equation can be transformed to relate to pressure using the volume-pressure inverse relationship.

$\Delta S = nR\ ln(P_1 / P_2)$ (6.12)

Absolute entropies and the third law of thermodynamics

At $T = 0$, all energy of thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because $S = 0$ if there is only one way of arranging the molecules and only one microstate is accessible (the ground state).

As temperature is reduced, entropy is also reduced and reaches a minimum at absolute zero. This leads us to the statement of **the third law of thermodynamics**, which states that *at absolute zero the entropy of a perfect crystalline substance is zero.*

Third-law entropies

Entropies reported on the basis that $S(0) = 0$ are called **Third-law entropies** (and often just ‘entropies’). When the substance is in its standard state at the temperature T, the **standard (Third-Law) entropy** is denoted $S^\ominus(T)$.

The **standard reaction entropy**, $\Delta_r S^\ominus$, is defined, like the standard reaction enthalpy, as the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature:

$$\Delta_r S^{\ominus} = \sum_{\text{Products}} \nu S_m^{\ominus} - \sum_{\text{Reactants}} \nu S_m^{\ominus} \qquad (6.13)$$

In this expression, each term is weighted by the appropriate stoichiometric coefficient v.
Standard reaction entropies are likely to be positive if there is a net formation of gas in a reaction, and are likely to be negative if there is a net consumption of gas.

Example
To calculate the standard reaction entropy of
$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ at 25°C,
we use the data in Table 2.7 of the *Data Section* to write

$$\begin{aligned}\Delta_r S^{\ominus} &= S_m^{\ominus}(H_2O, l) - \{S_m^{\ominus}(H_2, g) + \tfrac{1}{2}S_m^{\ominus}(O_2, g)\}\\ &= 69.9\ \text{J K}^{-1}\ \text{mol}^{-1} - \{130.7 + \tfrac{1}{2}(205.0)\}\ \text{J K}^{-1}\ \text{mol}^{-1}\\ &= -163.4\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

Entropy on a Microscopic Scale

We can treat entropy from a microscopic viewpoint through statistical analysis of molecular motions. A connection between entropy and the number of microstates (W) for a given macrostate is

$$S = k_B \ln W \qquad (6.14)$$

The more microstates that correspond to a given macrostate, the greater the entropy of that macrostate. This shows that entropy is a measure of disorder.

Example 6.5 Entropy of Molecule

One molecule in a two-sided container has a 1-in-2 chance of being on the left side. Two molecules have a 1-in-4 chance of being on the left side at the same time. Three molecules have a 1-in-8 chance of being on the left side at the same time.

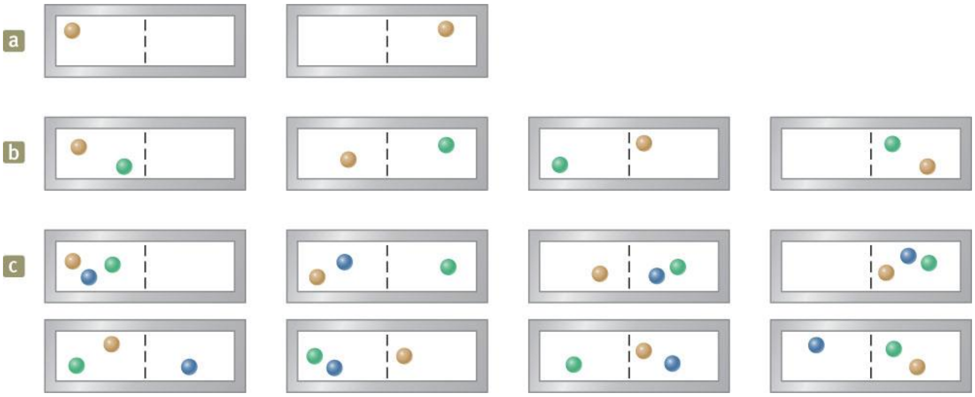


Figure 6.6 (a) One molecule in a container has a 1-in-2 chance of being on the left side. (b) Two molecules have a 1-in-4 chance of being on the left side at the same time. (c) Three molecules have a 1-in-8 chance of being on the left side at the same time.

Consider 100 molecules in the container. The probability of separating 50 fast molecules on one side and 50 slow molecules on the other side is $(½)^{100}$. If we have one mole of gas, this is found to be extremely improbable.

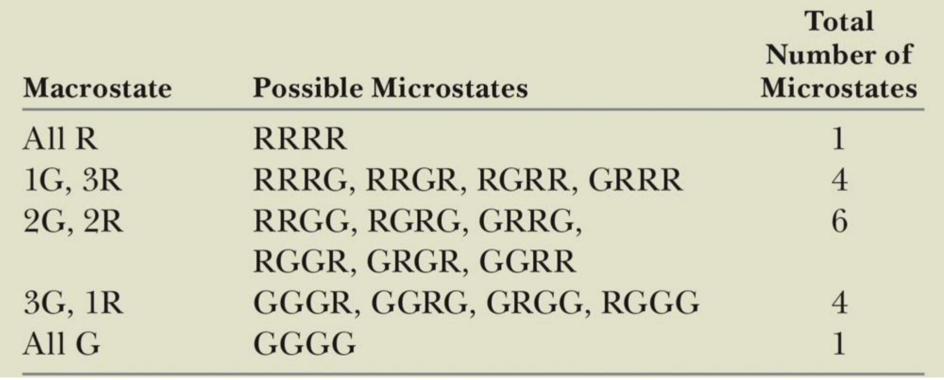
Example 6.6 Marble

Suppose you have a bag with 50 red marbles and 50 green marbles.

You draw a marble, record its color, return it to the bag, and draw another. Continue until four marbles have been drawn. What are possible macrostates and what are their probabilities?

The most likely, and most disordered, macrosate corresponds to the largest number of microstates. The least likely, and most ordered, macrosate corresponds to the smallest number of microstates.

Table 6.3 Possible Results of Drawing Four Marbles from a Bag



Macrostate	Possible Microstates	Total Number of Microstates
All R	RRRR	1
1G, 3R	RRRG, RRGR, RGRR, GRRR	4
2G, 2R	RRGG, RGRG, GRRG, RGGR, GRGR, GGRR	6
3G, 1R	GGGR, GGRG, GRGG, RGGG	4
All G	GGGG	1

Gibbs free energy

What factors ultimately determine that a reaction proceeds spontaneously? Spontaneous reactions are often exothermic (negative enthalpy, $\Delta H < 0$) and are accompanied by an increase in entropy (increase in disorder, $\Delta S > 0$). Both enthalpy and entropy appear to influence whether a reaction occurs spontaneously or not. Furthermore, spontaneous reactions are those where the final state (pro- ducts) tend to be of lower energy than the initial state (reactants). Another factor for consideration in predicting if a chemical reaction or process is spontaneous is temperature. Some reactions are spontaneous only at high temperature and not at low temperature. Why?

We define a new function that reflects the balance between enthalpy, entropy and temperature, known as Gibbs free energy (G or simply Gibbs function).

$$G = H - TS \qquad (6.15)$$

The expression reflects the stored energy (H), inherent disorder (S) at a given temperature (T in Kelvin). Since all the parameters in the equation are state functions so is G. The change in Gibbs energy is

$\Delta G = \Delta H - T\Delta S$ (6.16)

at constant temperature. The change of free energy (energy available to do work) depends primarily on the magnitudes of ΔH and $T\Delta S$ (enthalpy and entropy terms).

Consider the reaction: $A + B \rightarrow C + D$

The reaction will behave in three ways depending on the value of ΔG.

$\Delta G < 0$ Reaction proceeds to give products *C*, *D*

$\Delta G = 0$ This represents an equilibrium condition in which the rates for the forward reactions is equal to that of the reverse reaction

$\Delta G > 0$ The reverse process is favoured to produce *A*, *B*

In general we can conclude that the direction of spontaneous change in either the forward or reverse is that which leads to a decrease in free energy. In summary if:

$\Delta G < 0$ Reaction is spontaneous in the forward direction.

$\Delta G = 0$ Reaction is at equilibrium.

$\Delta G > 0$ Reaction is spontaneous in reverse direction.

Example 6.5

In the sublimation of iodine crystals at 25 ^{0}C and atmospheric pressure, the process is accompanied by an enthalpy change of 39.3 kJ mol^{-1} and an entropy change of 86.1 J K^{-1}. At what temperature will iodine crystals (solid) be in equilibrium with its vapour (gaseous iodine)?

The change in Gibb's free energy (ΔG) is related to the change in enthalpy (ΔH) and entropy (ΔS) by $\Delta G = \Delta H - T\Delta S$

At equilibrium ΔG = 0 and T in the equation therefore the equilibrium tempera- ture T_{eq}. Thus, $0 = \Delta H - T_{eq}\,\Delta S$

Solving for T_{eq}

$T_{eq} = \Delta H / \Delta S = 39.3\text{x}10^3 / 86.1 = 454$ K

Practice problem 6.4

Determine the melting point of sodium chloride (table salt) if 30.3 kJ is required to melt the crystals and that the process involves an increase in entropy of 28.2 J K $^{-1}$ mol $^{-1}$.

(a) 1.071 (b) 1070 (c) 1000 (d) 1075

Standard free energy, ΔG^o

Gibbs function consists of two thermodynamic state functions, which can be used to calculate standard free energies. For a chemical reaction, the standard free energy of change (ΔG^o) is related to the formation of the products from the reactants. The standard being defined as before for ΔH^o and ΔS^o.

Properties of Gibbs function are very much similar to those of ΔH^o that is

- ΔG^o is zero for free energies of formation of elements in their standard state.
- ΔG^o changes sign when the process is reversed but with the same magnitude.
- For a process comprising several steps, the total free energy change is the sum of the ΔG^o *s* associated with each individual steps.

The free energy change for a chemical reaction can be calculated if the standard free energies of formation of the reactants and products are known.

$$\Delta G^o = \sum a \, \Delta G^o_f \text{ (products)} - \sum b \, \Delta G^o_f \text{ (reactants)} \quad (6.17)$$

Example

To calculate the standard Gibbs energy of the reaction

$CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$ at 25° C, we write

$$\begin{aligned}\Delta_r G^{\ominus} &= \Delta_f G^{\ominus}(CO_2, g) - \{\Delta_f G^{\ominus}(CO, g) + \tfrac{1}{2}\Delta_f G^{\ominus}(O_2, g)\} \\ &= -394.4 \text{ kJ mol}^{-1} - \{(-137.2) + \tfrac{1}{2}(0)\} \text{ kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1}\end{aligned}$$

Chapter 7 *by Dr. Hasan Maridi*

Heat Engines

Review

First Law of Thermodynamics

- 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.
- The first law makes no distinction between processes that occur spontaneously and those that do not.
- Only certain types of energy-conversion and energy-transfer processes actually take place in nature.

The Second Law of Thermodynamics

- Establishes which processes do and which do not occur
- Some processes can occur in either direction according to the first law.
- They are observed to occur only in one direction.
- 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.

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.

A heat engine carries some working substance through a cyclical process.

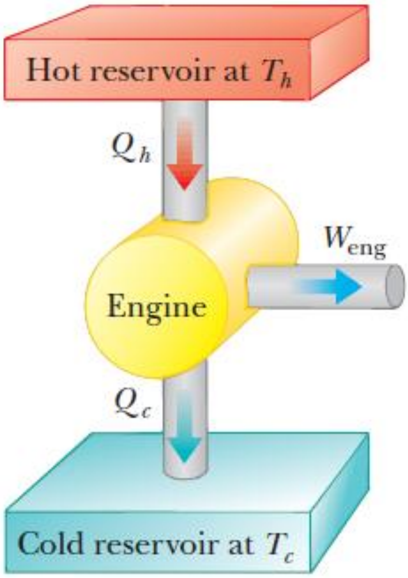


Figure 7.1 Schematic representation of a heat engine. The engine does work W_{eng}. The arrow at the top represents energy $Q_h > 0$ entering the engine. At the bottom, $Q_c < 0$ represents energy leaving the engine.

The working substance absorbs energy by heat from a high temperature energy reservoir (Q_h). Work is done by the engine (W_{eng}). Energy is expelled as heat to a lower temperature reservoir (Q_c). Since it is a cyclical process, $\Delta U = 0$, i.e. its initial and final internal energies are the same. Therefore,

$$W_{eng} = Q_{net} = |Q_h| - |Q_c| \qquad (7.1)$$

The net work done by a heat engine equals the net energy transferred to it.

Thermal Efficiency of a Heat Engine

Thermal efficiency (e or η) is defined as the ratio of the net work done by the engine during one cycle to the energy input at the higher temperature.

$$e \equiv \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} \qquad (7.2)$$

We can think of the efficiency as the ratio of what you gain to what you give. 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 $e = 100\%$, Q_C must be 0

Second Law: 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.

- W_{eng} can never be equal to $|Q_h|$. Means that Q_c cannot equal 0
- Some energy $|Q_c|$ must be expelled to the environment. Means that e cannot equal 100%

Perfect Heat Engine

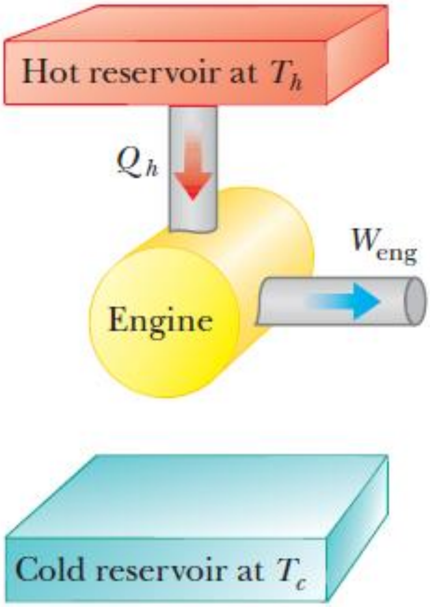
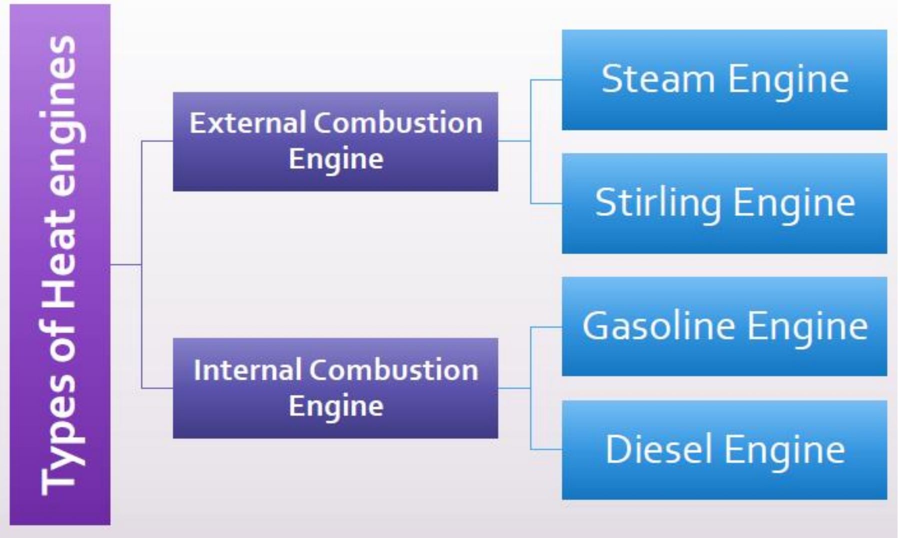


Figure 7.2 Schematic diagram of a heat engine that takes in energy from a hot reservoir and does an equivalent amount of work. It is impossible to construct such a perfect engine.

No energy is expelled to the cold reservoir. It takes in some amount of energy and does an equal amount of work. *i.e.* $e = 100\%$. It is impossible to construct such an engine.



Example 7.1

An engine transfers 2.00×10^3 J of energy from a hot reservoir during a cycle and transfers 1.50×10^3 J as exhaust to a cold reservoir.

(A) Find the efficiency of the engine.

This example involves evaluation of quantities from the equations introduced in this section, so we categorize it as a substitution problem.

$$e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{1.50 \times 10^3\ \mathrm{J}}{2.00 \times 10^3\ \mathrm{J}} = 0.250, \text{ or } 25.0\%$$

(B) How much work does this engine do in one cycle?

$$\begin{aligned} W_{\text{eng}} &= |Q_h| - |Q_c| = 2.00 \times 10^3\ \mathrm{J} - 1.50 \times 10^3\ \mathrm{J} \\ &= 5.0 \times 10^2\ \mathrm{J} \end{aligned}$$

Problems 7.1

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?

Problems 7.2

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.

Problems 7.3

A particular heat engine has a mechanical power output of 5.00 kW and an efficiency of 25.0%. The engine expels 8.00×103 J of exhaust energy in each cycle. Find (a) the energy taken in during each cycle and (b) the time interval for each cycle.

Heat Pumps and Refrigerators

All heat engines have:

- Working substance
- High-temperature reservoir
- Low-temperature reservoir
- Cyclical engine

Heat engines can run in reverse.

- This is not a natural direction of energy transfer.
- Must put some energy into a device to do this
- Devices that do this are called heat pumps or refrigerators

Examples

- A refrigerator is a common type of heat pump.
- An air conditioner is another example of a heat pump.

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.

Heat Pump Process

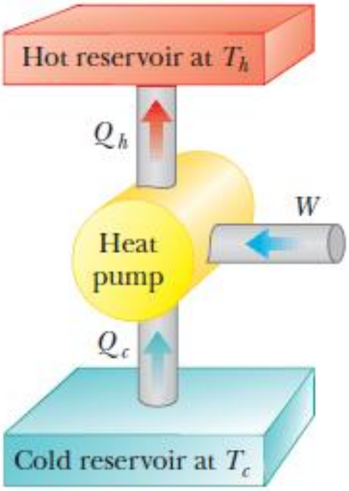


Figure 7.3 Schematic diagram of a heat pump, which takes in energy $Q_c > 0$ from a cold reservoir and expels energy $Q_h < 0$ to a hot reservoir. Work W is done *on* the heat pump. A refrigerator works the same way.

Energy is extracted from the cold reservoir, $|Q_C|$. Energy is transferred to the hot reservoir $|Q_h|$, work must be done *on* the engine, W.

Second Law – 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 Pump

The so called *heat pump* It takes energy from the cold reservoir and expels an equal amount of energy to the hot reservoir. No work is done.

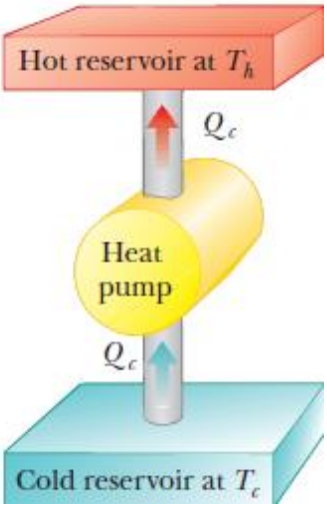


Figure 7.4 Schematic diagram of an impossible heat pump or refrigerator, that is, one that takes in energy from a cold reservoir and expels an equivalent amount of energy to a hot reservoir without the input of energy by work.

Figure 7.5 The coils on the back of a refrigerator transfer energy by heat to the air. Due to the input of energy by work, this amount of energy must be greater than the amount of energy removed from the contents of the refrigerator.

Coefficient of Performance

The effectiveness of a heat pump is described by a number called the **coefficient of performance** (COP). It is similar to thermal efficiency for a heat engine.

It is the ratio of what you gain (energy transferred to or from a reservoir) to what you give (work input).

In **cooling mode**, you "gain" energy removed from a cold temperature reservoir.

$$\text{COP} = \frac{\textit{energy transferred at low temp}}{\textit{work done on the pump}} = \frac{|Q_c|}{W} \qquad (7.3)$$

A good refrigerator should have a high COP. Typical values are 5 or 6.

In **heading mode**, the COP is the ratio of the heat transferred in to the work required.

$$\text{COP} = \frac{\textit{energy transferred at high temp}}{\textit{work done by heat pump}} = \frac{|Q_h|}{W} \qquad (7.4)$$

Q_h is typically higher than W. Values of COP are generally about 4 for outside temperature about 25° F.

The use of heat pumps that extract energy from the air is most satisfactory in moderate climates.

Example 7.2

If the coefficient of performance of a refrigerator is 5 find the ratio of the heat rejected to the work done on the refrigerant.

Reversible and Irreversible Processes

A reversible process is one in which every point along some path is an equilibrium state. And one for which the system can be returned to its initial state along the same path.

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 that convert mechanical energy to internal energy present. No friction or turbulence, for example

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

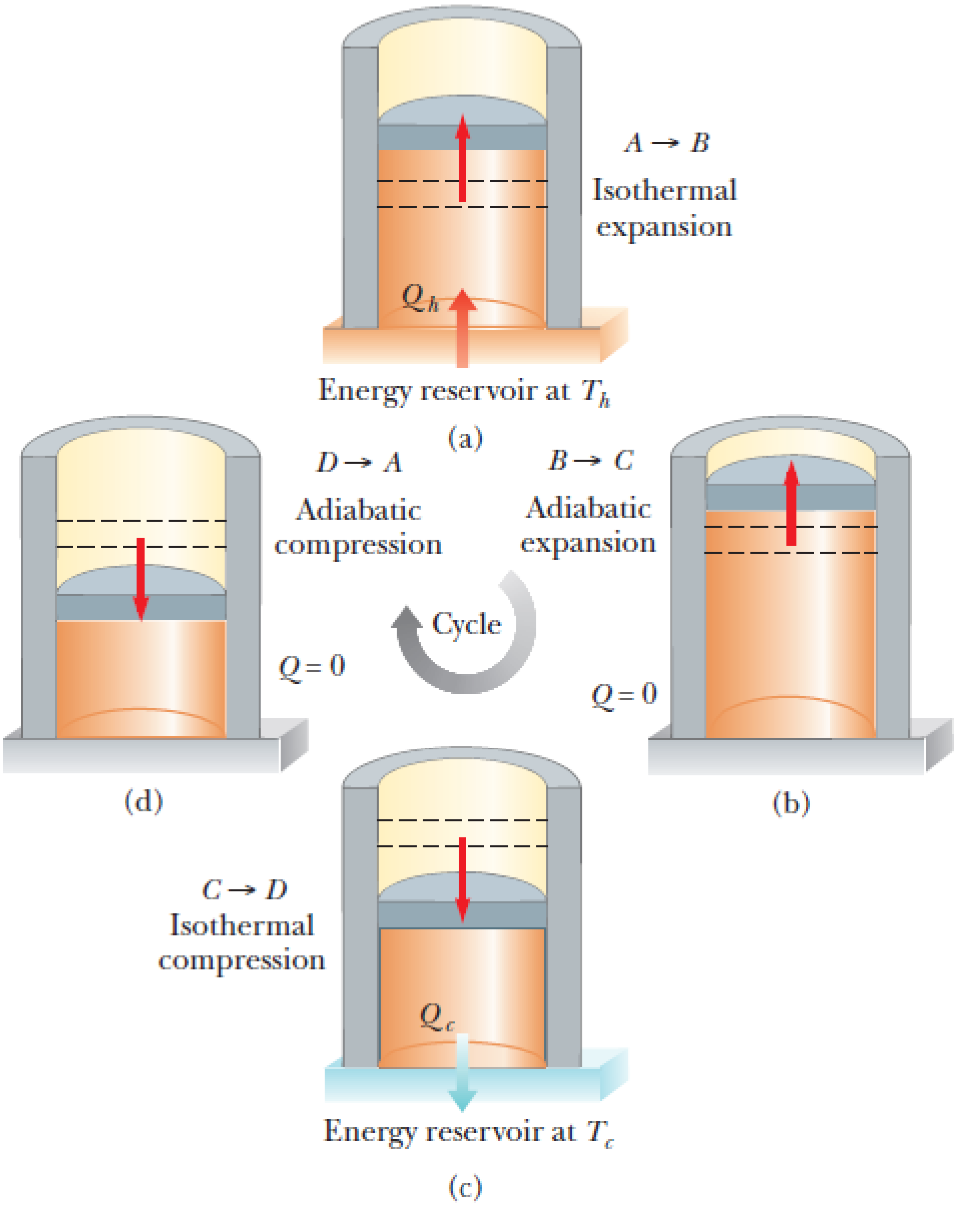


Figure 7.6 The Carnot cycle. (a) In process $A \rightarrow B$, the gas expands isothermally while in contact with a reservoir at T_h. (b) In process $B \rightarrow C$, the gas expands adiabatically ($Q = 0$). (c) In process $C \rightarrow D$, the gas is compressed isothermally while in contact with a reservoir at $T_c < T_h$. (d) In process $D \rightarrow A$, the gas is compressed adiabatically. The arrows on the piston indicate the direction.

Carnot Engine

Carnot Engine is a theoretical engine developed by Sadi Carnot, 1796 – 1832, French engineer, which is the first one show quantitative relationship between work and heat. He reviewed industrial, political and economic importance of the steam engine. He gave a definition of work.

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.

Carnot's Theorem

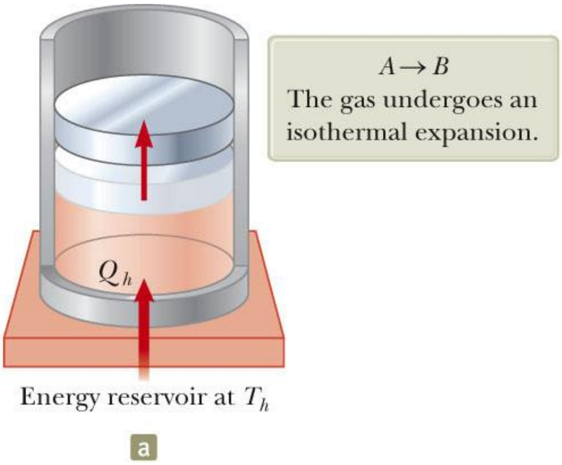
No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs. All real engines are less efficient than a Carnot engine because they do not operate through a reversible cycle.

The efficiency of a real engine is further reduced by friction, energy losses through conduction, etc.

Carnot Cycle

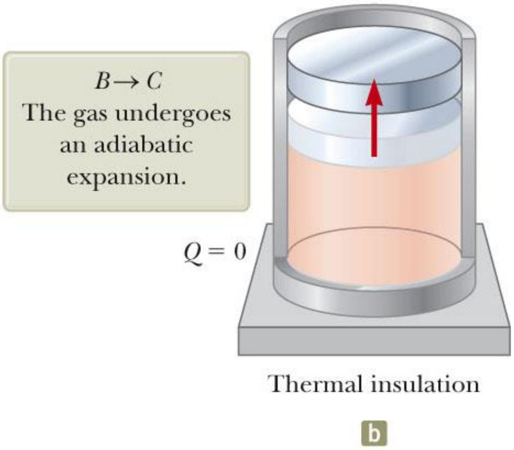
Look figure 7.6.

Carnot Cycle, *A* to *B*



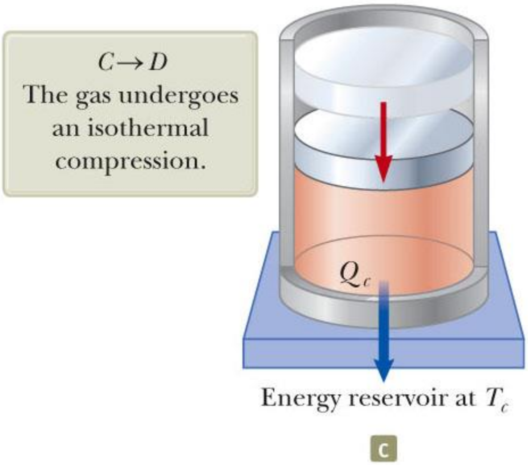
$A \rightarrow B$ is an isothermal expansion.
The gas is placed in contact with the high temperature reservoir, T_h.
The gas absorbs heat $|Q_h|$.
The gas does work W_{AB} in raising the piston.

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_c.
The gas does work W_{BC}.

Carnot Cycle, *C* to *D*



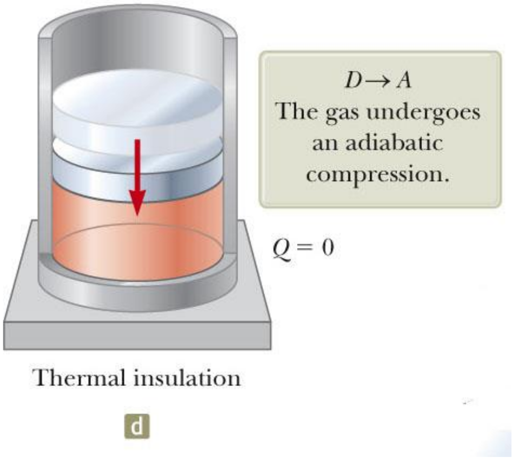
The gas is placed in thermal contact with the cold temperature reservoir.

$C \rightarrow D$ is an isothermal compression.

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_c to T_h.

The work done on the gas is W_{DA}.

Carnot Cycle, *PV* Diagram

The work done by the engine is shown by the area enclosed by the curve, W_{eng}.

The net work is equal to $|Q_h| - |Q_c|$.

$\Delta U = 0$ for the entire cycle.

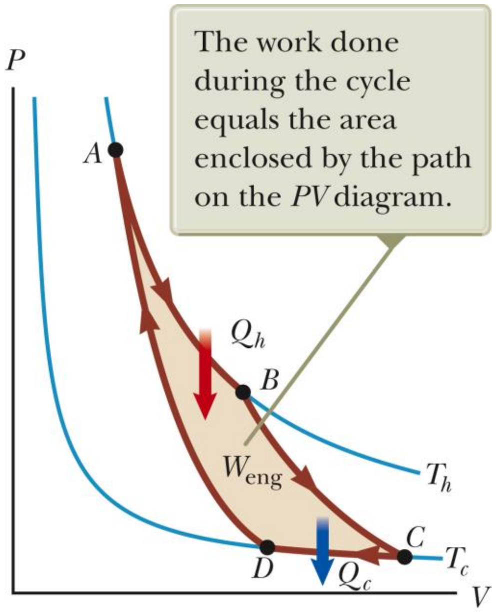


Figure 7.7 *PV* diagram for the Carnot cycle. The net work done W_{eng} equals the net energy transferred into the Carnot engine in one cycle, $|Q_h| - |Q_c|$. As with any cycle, the work done during the cycle is the area enclosed by the path on the *PV* diagram. Notice that $\Delta U = 0$ for the cycle.

Efficiency of a Carnot Engine

Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs.

$$e = \frac{W_{eng}}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h} \qquad (7.5)$$

Temperatures must be in Kelvins

All Carnot engines operating between the same two temperatures will have the same efficiency.

- Efficiency is 0 if $T_h = T_c$
- Efficiency is 100% only if $T_c = 0$ K but Such reservoirs are not available because 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.

Carnot Heat Pump COPs

In heating mode:

$$COP_C = \frac{|Q_h|}{W} = \frac{T_h}{T_h - T_c} \qquad (7.6)$$

In cooling mode:

$$COP_C = \frac{|Q_c|}{W} = \frac{T_c}{T_h - T_c} \qquad (7.7)$$

In practice, the COP is limited to values below 10.

Example 7.4 The Steam Engine

A steam engine has a boiler that operates at 500 K. The energy from the burning fuel changes water to steam, and this steam then drives a piston. The cold reservoir's temperature is that of the outside air, approximately 300 K. What is the maximum thermal efficiency of this steam engine?

$$e_C = 1 - \frac{T_c}{T_h} = 1 - \frac{300\text{ K}}{500\text{ K}} = 0.400 \qquad \text{or} \qquad 40.0\%$$

Example 7.5 The Carnot Efficiency

The highest theoretical efficiency of a certain engine is 30.0%. If this engine uses the atmosphere, which has a temperature of 300 K, as its cold reservoir, what is the temperature of its hot reservoir?

$$e_C = 1 - \frac{T_c}{T_h}$$

$$T_h = \frac{T_c}{1 - e_C} = \frac{300\text{ K}}{1 - 0.300} = 429\text{ K}$$

The Conventional Gasoline Engine

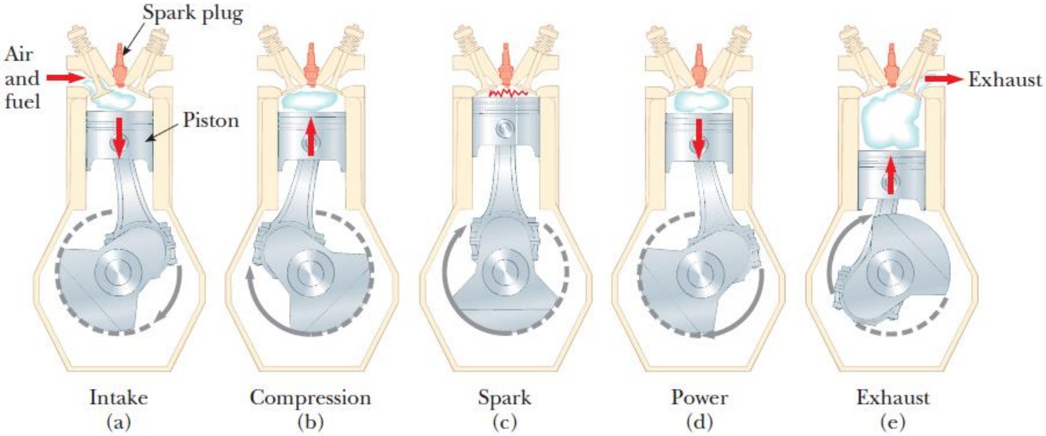


Figure 7.8 The four-stroke cycle of a conventional gasoline engine. The arrows on the piston indicate the direction of its motion during each process. (a) In the intake stroke, air and fuel enter the cylinder. (b) The intake valve is then closed, and the air–fuel mixture is compressed by the piston. (c) The mixture is ignited by the spark plug, with the result that the temperature of the mixture increases at essentially constant volume. (d) In the power stroke, the gas expands against the piston. (e) Finally, the residual gases are expelled and the cycle repeats.

In a gasoline engine, six processes occur during each cycle.
For a given cycle, the piston moves up and down twice.
This represents a four-stroke cycle.
The processes in the cycle can be approximated by the Otto cycle.

Otto Cycle

The PV diagram of an Otto cycle is shown at right.
The Otto cycle approximates the processes occurring in an internal combustion engine.

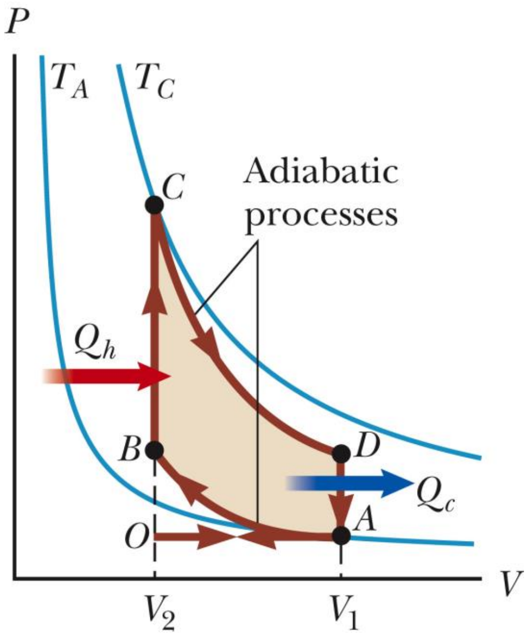


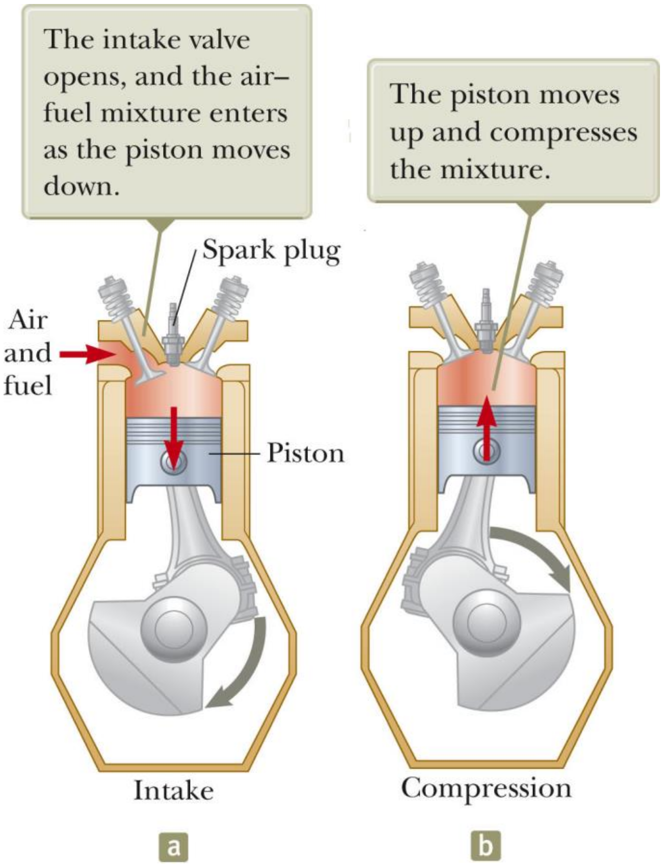
Figure 7.9 *PV* diagram for the Otto cycle, which approximately represents the processes occurring in an internal combustion engine.

Gasoline Engine – Intake Stroke

During the intake stroke, the piston moves downward.
A gaseous mixture of air and fuel is drawn into the cylinder.
Energy enters the system by matter transfer as potential energy in the fuel.
The volume increases from V_2 to V_1.
$O \rightarrow A$ in the Otto cycle PV diagram.

Gasoline Engine – Compression Stroke

The piston moves upward.
The air-fuel mixture is compressed adiabatically.
The volume changes from V_1 to V_2.
The temperature increases.
The work done on the gas is positive and equal to the negative area under the curve.
$A \rightarrow B$ in the Otto cycle PV diagram.



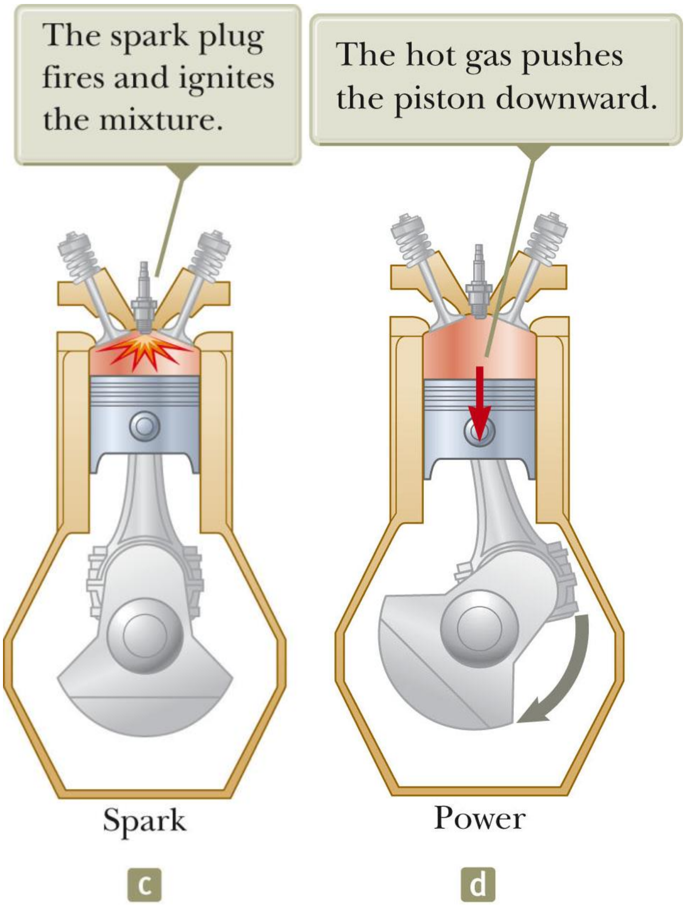
Gasoline Engine – Spark

Combustion occurs when the spark plug fires.
This is not one of the strokes of the engine.
It occurs very quickly while the piston is at its highest position.
The combustion represents a rapid energy transformation from potential energy to internal energy.
The temperature changes from T_B to T_C but the volume remains approximately the same.
$B \rightarrow C$ in the Otto cycle PV diagram.

Gasoline Engine – Power Stroke

In the power stroke, the gas expands adiabatically.
Volume changes from V_2 to V_1
The temperature drops from T_c to T_D.
Work is done by the gas .The work is equal to the area under the curve.

$C \rightarrow D$ in the Otto cycle PV diagram.



Gasoline Engine – Valve Opens

This is process $D \rightarrow A$ in the Otto cycle PV diagram

An exhaust valve opens as the piston reaches its bottom position.

The pressure drops suddenly.

The volume is approximately constant. So no work is done.

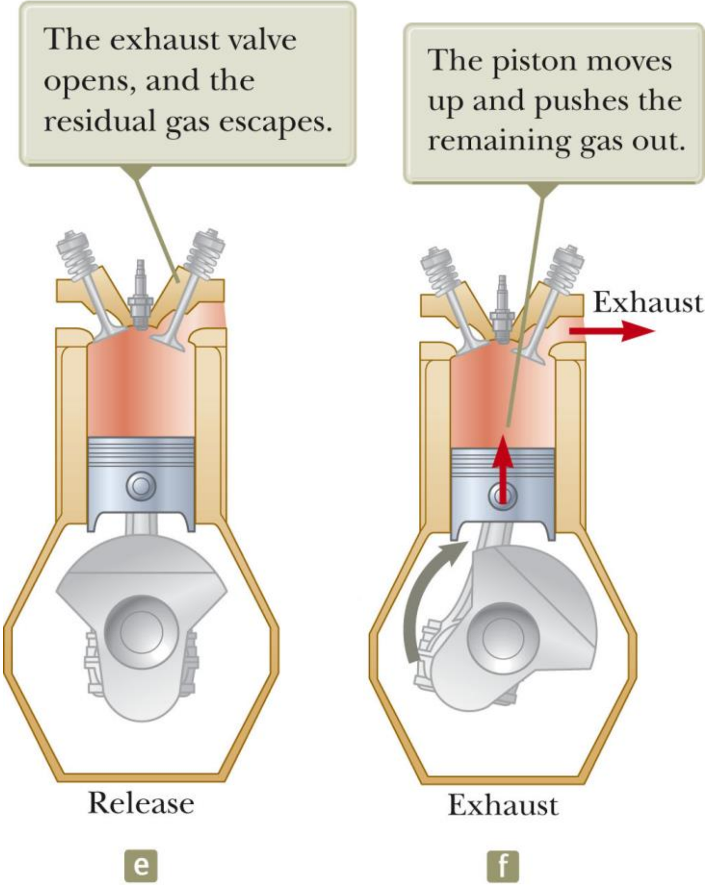
Energy is expelled from the interior of the cylinder. It continues to be expelled during the next process.

Gasoline Engine – Exhaust Stroke

In the exhaust stroke, the piston moves upward while the exhaust valve remains open.

Residual gases are expelled to the atmosphere

The volume decreases from V_1 to V_2.
$A \rightarrow O$ in the Otto cycle PV diagram
The cycle then repeats.



The exhaust valve opens, and the residual gas escapes.

The piston moves up and pushes the remaining gas out.

Otto Cycle Efficiency

If the air-fuel mixture is assumed to be an ideal gas, then the efficiency of the Otto cycle is

$$e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

γ is the ratio of the molar specific heats.
V_1 / V_2 is called the compression ratio.
Typical values:

- Compression ratio of 8
- $\gamma = 1.4$
- e = 56%

Efficiencies of real engines are 15% to 20%, mainly due to friction, energy transfer by conduction, incomplete combustion of the air-fuel mixture

Diesel Engines

Operate on a cycle similar to the Otto cycle without a spark plug.
The compression ratio is much greater and so the cylinder temperature at the end of the compression stroke is much higher.
Fuel is injected and the temperature is high enough for the mixture to ignite without the spark plug.
Diesel engines are more efficient than gasoline engines.

Chapter 8

by Dr. Hasan Maridi

Chemical Equilibrium

Chemical Equilibrium

Heat is energy flowing from a high temperature object to a low temperature object. When the two objects are at the same temperature, there is no net flow of energy or heat. That is why a covered cup of coffee will not be colder than or warmer than the room temperature after it has been in there for a few hours. This phenomenon is known as **equilibrium**. In this example, we deal with the flow of energy.

Equilibria happen in phase transitions. For example, if the temperature in a system containing a mixture of ice and water is uniformly 273.15 K, the net amount of ice formed and the melt will be zero. The amount of liquid water will also remain constant, if no vapour escape from the system. In this case, three phases, ice (solid) water (liquid), and vapour (gas) are in equilibrium with one another. Similarly, equilibrium can also be established between the vapour phase and the liquid at a particular temperature. Equilibrium conditions also exist between solid phases and vapour phases. These are **phase equilibria.**

In Stoichiometry calculations, chemical reactions may not be as complete as we have assumed. For example, the following reactions are far short of completion.

$2\ NO_2 \rightleftharpoons N_2O_4$
$3\ H_2 + N_2 \leftrightharpoons 2\ NH_3$
$H_2O + CO \rightleftharpoons H_2 + CO_2$
Let us consider only the first reaction in this case. At room temperature, it is impossible to have pure NO_2 or N_2O_4. However, in a sealed tube (closed system), the ratio $[N_2O_4]/ [NO_2]^2$ is a constant. This phenomenon is known as **chemical equilibrium**.

Reversible chemical reactions

Heat transfer, vapourization, melting, and other phase changes are physical changes. These changes are reversible and you have already experienced them. Many chemical reactions are also reversible. For example

$N_2O_4 \rightleftharpoons 2\ NO_2$
$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$

The Law of Mass Action

Such a law of nature is called the law of mass action or mass action law. The law of mass action is universal, applicable under any circumstance. However, for reactions that are complete, the result may not be very useful. We introduce the mass action law by using a general chemical reaction equation in which reactants A and B react to give product C and D.

$a\ A + b\ B \dashrightarrow c\ C + d\ D$
where a, b, c, d are the coefficients for a balanced chemical equation.
When equilibrium is establish, rate forward = rate reverse
$K_f\ [A]^a\ [B]^b = K_b[C]^c\ [D]^d$
Then
$K_f\ /\ K_b = [C]^c\ [D]^d / [A]^a\ [B]^b$

The **mass action law** states that if the system is at equilibrium at a given temperature, then the following ratio is a constant.

$$\frac{[C]^c\ [D]^d}{[A]^a [B]^b} = K_{eq} \equiv K_c \qquad (8.1)$$

The **equilibrium constant, K_c or K_{eq},** is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.
The square brackets "[ ]" around the chemical species represent their

concentrations. This is the **ideal law of chemical equilibrium** or **law of mass action**.

The equilibrium concentrations of reactants and products may vary, but the value for K_c remains the same. Equilibrium can be approached from either direction.

The units for *K* depend upon the units used for concentrations. If M is used for all concentrations, *K* has units of $M^{c+d-(a+b)}$.

Equilibrium systems are dynamic (in constant chemical change) and reversible (chemical change can be approached from either direction).

Meaning of K_c ,Which is favored, Reactant or Product?

If the K_c value is large ($K_c >> 1$), the equilibrium lies to the right and the reaction mixture contains mostly products.

If the K_c value is small ($K_c <<1$), the equilibrium lies to the left and the reaction mixture contains mostly reactants.

If the K_c value is close to 1 ($0.10 < K_c < 10$), the mixture contains appreciable amounts of both reactants and products.

The reaction quotient Q

If the system is not at equilibrium, the ratio is different from the equilibrium constant. In such cases, the ratio is called a **reaction quotient** which is designated as ***Q***.

$$\frac{[\mathrm{C}]^c\ [\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = Q \qquad (8.2)$$

A system not at equilibrium tend to become equilibrium, and the changes will cause changes in *Q* that its value approaches the equilibrium constant, *K*

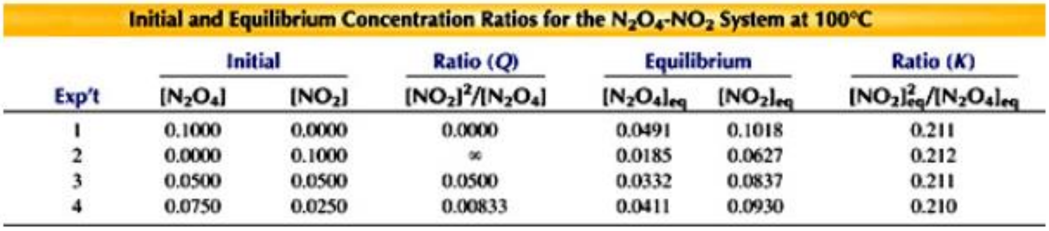
Predicting the direction of reaction

If Q > K, the reaction will go to the left. The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.

If Q < K, the reaction will go to the right. The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.
If Q = K, the reaction mixture is already at equilibrium, so no shift occurs.

The reaction: $N_2O_4 \rightleftharpoons 2\ NO_2$

The reaction coordinate diagram shows how the concentration of N_2O_4 and NO_2 changes as the reaction approaches equilibrium. This is also reflected in Q. As the reaction proceeds to the right, N_2O_4 to NO_2, the Q value increases, N_2O_4 becomes smaller and NO_2 becomes larger. The reaction finally reaches equilibrium at teq, at which time the concentration of N_2O_4 and NO_2 remains constant. Equilibrium is reached and the reaction quotient becomes equal to the equilibrium constant. $Q = K_c$.



Initial and Equilibrium Concentration Ratios for the N_2O_4-NO_2 System at 100°C

	Initial		Ratio (*Q*)	Equilibrium		Ratio (*K*)
Exp't	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$	$[N_2O_4]_{eq}$	$[NO_2]_{eq}$	$[NO_2]^2_{eq}/[N_2O_4]_{eq}$
1	0.1000	0.0000	0.0000	0.0491	0.1018	0.211
2	0.0000	0.1000	∞	0.0185	0.0627	0.212
3	0.0500	0.0500	0.0500	0.0332	0.0837	0.211
4	0.0750	0.0250	0.00833	0.0411	0.0930	0.210

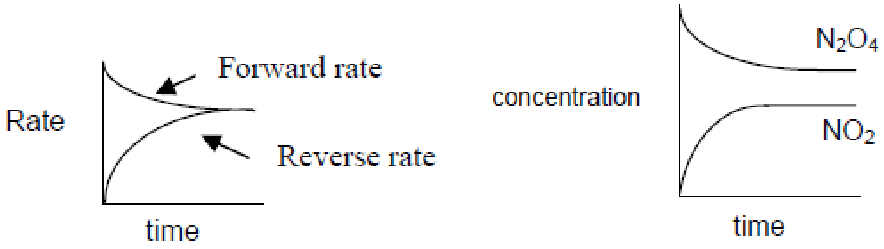


Figure 8.1 Concentration changes of N_2O_4 and NO_2 and rate change of the reaction.

Homogeneous equilibria: reactants and products exist in a single phase.
For the gas phase reaction:
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity, K_c, is:
$K_c = [NO_2]/[N_2O_4]$

Gas Phase Expressions can also be expressed by K_p

The K_p expression is written using equilibrium partial pressures of reactants and products.

$$\frac{[P_C]^c\,[P_D]^d}{[P_A]^a[P_B]^b} = K_p \qquad (8.3)$$

For the reaction given above, the K_p expression is:

$$K_p = \frac{P_{NO_2}{}^2}{P_{N_2O_4}}$$

Since pressure and molarity are related by the Ideal Gas Law, the following equation relates K_p and K_c:

$$K_p = K_c(RT)^{\Delta n} \qquad (8.4)$$

where R = 0.0821 L atm / K mol; T = temperature in Kelvin
Δn = moles of gaseous products - moles of gaseous reactants.
Note that $K_c = K_p$ when the number of gas molecules are the same on both sides.

Example 8.1
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Where the concentrations at equilibrium are:
$[NH_3] = 3.1\times10^{-2}$ M
$[N_2] = 8.5\times10^{-2}$ M
$[H_2] = 3.1\times10^{-3}$ M
What is the value of equilibrium constant K?

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.1\times10^{-2})^2}{(8.5\times10^{-1})(3.1\times10^{-3})^3} = 3.8\times10^4$$

Example 8.2

$[NH_3] = 3.1\times10^{-2}$ M

$[N_2] = 8.5\times10^{-2}$ M

$[H_2] = 3.1\times10^{-3}$ M

$2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$

Just the reverse of the previous example, What is the value of K'?

$$K' = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K} = 2.6\times10^{-5}$$

Practice problem 8.1

Consider the following equilibrium, at 480 °C:

$2Cl_2(g) + 2H_2O\,(g) \leftrightarrow 4\,HCl(g) + O_2\,(g) \quad K_p = 0.0752$

i. What is the value of K_p for:
$4\,HCl(g) + O_2\,(g) \rightleftharpoons 2Cl_2(g) + 2H_2O\,(g)$

ii. What is the value of K_p:
$Cl_2(g) + H2O\,(g) \rightleftharpoons 2HCl(g) + 1/2\,O_2\,(g)$

iii. What is the value of K_c:
$2Cl_2(g) + 2H_2O\,(g) \rightleftharpoons 4HCl(g) + O_2\,(g)$

Heterogeneous equilibria

In Heterogeneous equilibria, reactants and products are present in more than one phase.

Example 8.3

$CaCO3(s) \rightleftharpoons CaO(s) + CO_2(g)$

You would think that the equilibrium constant would be

$$K' = \frac{[CO_2][CaO]}{[CaCO_3]}$$

But heterogenous equilibrium does not depend on the amounts of pure solid or liquids present. Therefore

$K = [CO_2]$

Free energy and equilibrium constant

The free energy of the reaction is zero at equilibrium, $\Delta G = 0$ and $\Delta G^o = 0$ for the standard state. The condition of equilibrium is attained when two opposing processes are occurring at equal rates. It is often desirable to describe equilibrium under non-standard conditions. The change in free energy under a variety of conditions is calculated in relation to its standard value.

$$\Delta G = \Delta G^{o} + RTlnQ \qquad (8.5)$$

For a reaction of the general type
$aA + bB + ... \rightarrow \ cC + dD + ...$

$$Q = \frac{[\mathrm{C}]^{c}\,[\mathrm{D}]^{d}}{[\mathrm{A}]^{a}[\mathrm{B}]^{b}} \qquad (8.6)$$

Where Q is the reactions quotient calculated for a reaction under non-standard conditions. At equilibrium $Q_C = K_C$, $Q_P = \mathrm{K_P}$ and $Q = K_{eq}$. For the condition where $\Delta G = 0$, equation (8.5) becomes
$0 = \Delta G^{o} + RTlnQ,$ so that,
$\Delta G^{o} = - RTln(K_{eq})$ (8.7)

Equation (8.3) relates the standard free energies and to measurable quantities T and the equilibrium composition.

All chemical reactions comprise a forward and a reverse reaction to varying extents. The system is always seeking a minimum in energy. Therefore, the direction of spontaneous change is one that decreases Gibbs function from either direction as shown in Figure 8.2. The graph depicts the change in free energy for a hypothetical reaction. The free energy is observed to be decreasing both from the left and right. A minimum is reached at some point which corresponds to the equilibrium point. The plot shows that the standard free energy is the difference between the standard molar free energies of formation of the reactants and products.

The equilibrium constant for a reaction can be calculated by solving equation (8.7).

$$K = e^{\frac{-\Delta G^{O}}{RT}} \qquad (8.9)$$

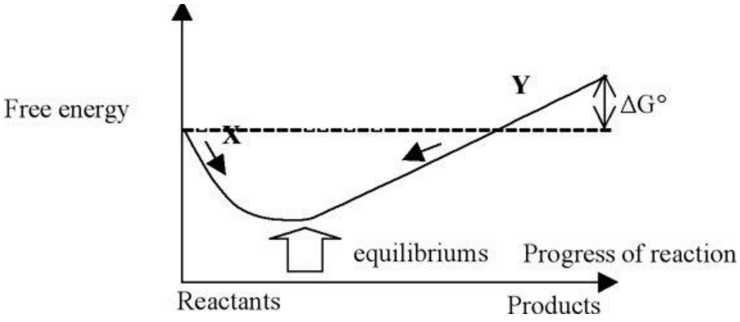


Figure 8.2 Plot showing free energy against extent of reaction. Shows free energy, equilibrium position and direction of spontaneous change.

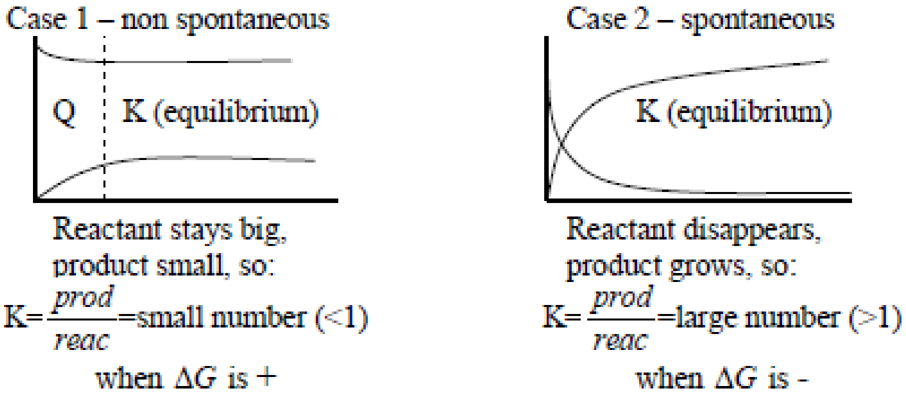


Figure 8.3 Plot showing the spontaneous and non-spontaneous process conditions.

Example 8.4

The reaction of hydrogen and iodine to form hydrogen iodide at 763 K has a standard free energy of formation – 12.1kJ mol $^{-1}$.

$H_2 (g) + I_2 (g) \rightarrow 2 HI (g)$

What is the equilibrium constant for the reaction?

Solution

At equilibrium the standard free energy of formation is given by

$\Delta G^o = - RT \ln K_{eq}$ equation

In this example $\Delta G^o = -12.1$ kJ mol $^{-1}$, R = 8.314 J K^{-1} mol^{-1}, and T = 763 K. Hence,

$$\ln K = -\frac{2 \times (-12.1 \times 10^3 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 763 \text{ K}}$$

ln K = 3.81

Taking the antilog K = 45

Practice problem 8.2

Dinitrogen tetroxide is a common rocket fuel, which at 25 ^{0}C dissociates into nitrogen dioxide forming an equilibrium between the two gases. The equilibrium mixture depends on the temperature of the mixture. What is the change in Gibbs free energy if the quantities of the two gases present in a 1 L container are 11.5 g N_2O_4 and 2.54 g NO_2. The standard Gibbs free energy for the reaction is + 4853 J.

Chapter 9 *by Dr. Hasan Maridi*
Equilibrium electrochemistry

Equilibrium electrochemistry

The principles of thermodynamics can be applied to solutions of electrolytes. For that we need to take into account activity coefficients: they differ significantly from 1 on account of the strong ionic interactions in electrolyte solutions. These coefficients are best treated as empirical quantities, but it is possible to estimate them in very dilute solutions. This chapter describes thermodynamic properties of reactions in electrochemical cells, in which, as the reaction proceeds, it drives electrons through an external circuit. Thermodynamic arguments can be used to derive an expression for the electric potential of such cells and the potential can be related to their composition. Two major topics: (1) the definition and tabulation of standard potentials; (2) the use of these standard potentials to predict the equilibrium constants and other thermodynamic properties of chemical reactions.

Electrochemical cells

An electrochemical cell consists of two electronic conductors (metal or graphite) dipping into an electrolyte (an ionic conductor), which may be a solution, a liquid, or a solid. The electronic conductor and its surrounding electrolyte – **electrode**. The physical structure containing them – **an electrode compartment**. The two electrodes may share the same compartment (left). If the electrolytes are different, then the two compartments may be joined by **a salt bridge** – and electrolyte solution that completes the electrical circuit by permitting ions to move between the compartments (right). Alternatively, the two solutions may be in direct physical contact (through a porous membrane) and form **a liquid junction**.

There are two types of electrochemical cells: **galvanic** (ones that spontaneously produce electrical energy) and **electrolytic** (ones that consume electrical energy).

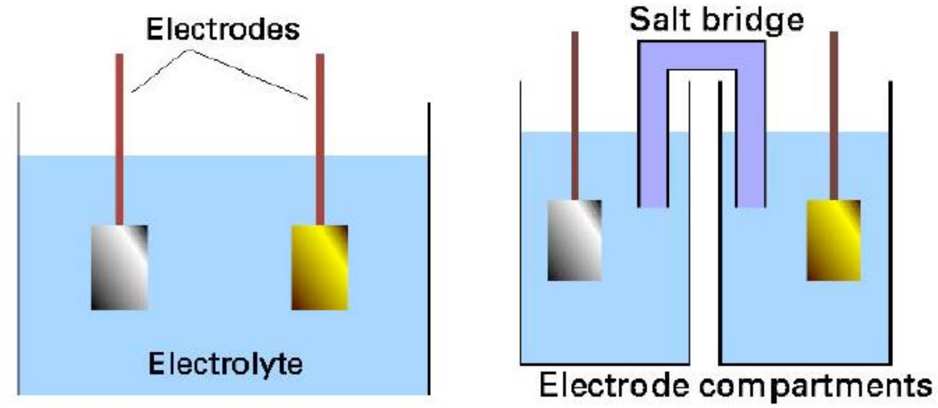


Figure 9.1 An electrochemical cells.

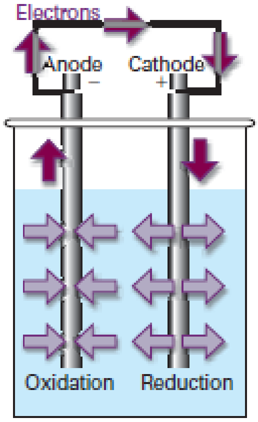


Figure 9.2 When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in the anode and collected from the cathode, and so there is a net flow of current. Note that the + sign of the cathode can be interpreted as indicating the electrode at which electrons enter the cell, and the sign of the anode is where the electrons leave the cell.

Half-reactions and electrodes

Oxidation is the removal of electrons from a species, a **reduction** is the addition of electrons to a species, and a **redox reaction** is a reaction in which there is a transfer of electrons from one species to another. In general we write a couple as Ox/Red and the corresponding reduction half-reaction as

$Ox + e^- \rightarrow Red$

For example:
$Cu(s) + Zn^{+2} \rightarrow Cu^{+2} + Zn(s)$
$Cu(s) \rightarrow Cu^{+2} + 2e^-$ (oxidation)
$Zn^{+2} + 2e^- \rightarrow Zn(s)$ (reduction)

Electrochemical cells consist of two electrodes: an **anode** (the electrode at which the oxidation reaction occurs) and a **cathode** (the electrode at which the reduction reaction occurs).

A Zn electrode dipping in $Zn^{2+}(aq)$ solution, connected to a Cu electrode dipping in $Cu^{2+}(aq)$ solution.
The two electrodes are connected by an electrical conductor, which permits the flow of electrons from one electrode to the other.
The two solutions are connected by a porus partition or a "salt bridge," which permits the flow of ions.
The electrode processes consist of **oxidation** (loss of electrons) at one electrode and **reduction** (gain of electrons) at the other:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The electrode at which oxidation takes place is called the **anode**. The electrode at which reduction takes place is called the **cathode**.
In electrochemical cells, the anode is negatively charged because electrons are given to the electrode by the species undergoing oxidation. The cathode is positively charged because electrons are removed from it by the species undergoing reduction.
So, when an electrochemical cell is written as indicated above, the electron-flow in the external circuit is from the electrode on the left to the electrode on the right.

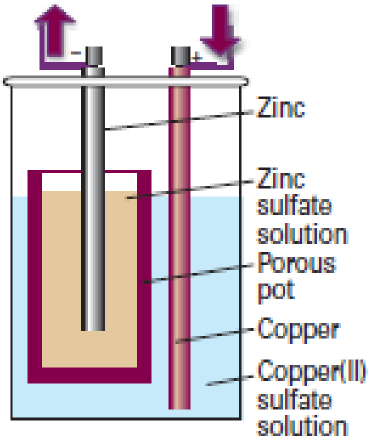


Figure 9.3 In the Daniell cell. The copper electrode is the cathode and the zinc electrode is the anode. Electrons leave the cell from the zinc electrode and enter it again through the copper electrode.

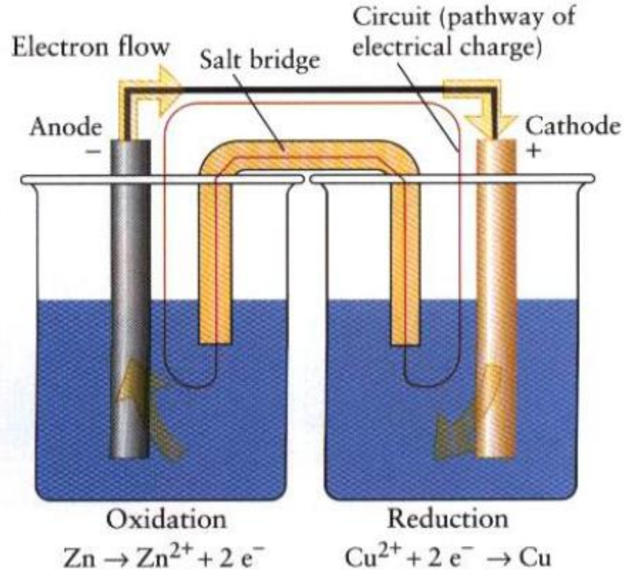


Figure 9.4 The salt bridge, essentially an inverted U-tube full of concentrated salt solution in a jelly, has two opposing liquid junction potentials that almost cancel.

Varieties of cells

The simplest type of cell has a single electrolyte common to both electrodes (as in Fig. 6.1). In some cases it is necessary to immerse the electrodes in different electrolytes, as in the 'Daniell cell' in which the redox couple at one electrode is Cu^{2+}/Cu and at the other is Zn^{2+}/Zn (Fig. 6.3).

In a cell with two different electrolyte solutions in contact, as in the Daniell cell, there is an additional source of potential difference across the interface of the two electrolytes. The contribution of the liquid junction to the potential can be reduced by joining the electrolyte compartments through a salt bridge (Fig. 9.4).

The cell reaction

The current produced by a galvanic cell arises from the spontaneous reaction taking place inside it. **The cell reaction** – the reaction in the cell written on the assumption that the right-hand electrode is the cathode and the reduction is taking place in the right-hand compartment. We'll see later how to predict if the right-hand electrode is in fact the cathode; if it is, then the cell reaction is spontaneous as written. If the left-hand electrode turns out to be the cathode, then the reverse of the cell reaction is spontaneous.

Conventions and notations

There are a few conventions and notations used for short-hand representation of electrochemical cells.

An electrochemical cell is viewed as the combination of two "half-cells." Each half-cell consists of an electrode, which may participate in the cell reaction, and chemicals in contact with that electrode.

Vertical lines are used to indicate important phase boundaries across which half-cell reactions take place. Often, the electrolyte concentration is also shown.

When two half-cells are combined to make an electrochemical cell, the half-cell in which oxidation takes place is written on the left-hand side and the half-cell in which reduction takes place is written on the right.

The electrodes are written on the "outside" with the electrolytes in-between.

A double vertical line is drawn between the two electrolytes to indicate a physical separation, either by a porus membrane or a salt-bridge.

Example 9.1
In the standard Daniel cell:
$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$
Or:
$Zn(s)|Zn^{2+}(1\ m)||Cu^{2+}(1\ m)|Cu(s)$
Or:

$$\underbrace{Zn(s)\ |Zn^{2+}(aq\ ,\ 1M)}_{\text{zinc electrode - anode}}\quad \underbrace{||}_{\text{salt bridge}}\quad \underbrace{Cu^{2+}(aq\ ,\ 1\ M)\ |Cu(s)}_{\text{copper electrode - cathode}}$$

Left-hand electrode: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$
Right-hand electrode: $Cu^{2+}(aq) + 2e– \rightarrow Cu(s)$
Overall cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The cell potential

A galvanic cell does electrical work as the reaction drives electrons through an external circuit. The work done by a given transfer of electrons depends on **the cell potential** – the potential difference between the two electrodes (measured in volts, $1\ V = 1\ J\ C^{-1}$). Large cell potential – large amount of electrical work can be done by given number of electrons traveling between the electrodes.
The maximum electrical work that a system (the cell) can do is given by ΔG. For a spontaneous process at constant temperature and pressure $w_{e,max} = \Delta G$

The force that drives this reaction is, of course, the decrease in free energy, ΔG.
The force that drives the reaction is manifested in the form of the **electromotive force** (**emf**) or cell voltage, denoted as ***E***, which can be measured using a Wheatstone bridge, under conditions in which no current is drawn from the cell.
If the concentrations of the ions are maintained at 1 mol kg^{-1} (or 1 *m*), the cell is called the **standard Daniel cell** and the cell emf is called the **standard cell emf**, denoted as $\boldsymbol{E}°$.

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} \qquad (9.1)$$

where $E^0_{cathode}$ and E^0_{anode} are the standard reduction potential.

To identify which the electrode is cathode and wich is anode, we can use this rule:

$$E^0_{\text{cathode}} > E^0_{\text{anode}} \qquad (9.2)$$

The fact that the spontaneous cell reaction leads to the oxidation of Zn(*s*) to Zn^{2+}(*aq*) and the reduction of Cu^{2+}(*aq*) to Cu(*s*) indicates that the tendency for Cu^{2+}(*aq*) ions to accept electrons (to get reduced) is greater than that for Zn^{2+}(*aq*) ions. In the terminology of electrochemistry, we say that Cu^{2+}(*aq*) has a greater **reduction potential** than Zn^{2+}(*aq*).

Standard Electrode Potentials

The difference in the reduction potentials of the two electrodes chosen to make up the cell determines the total cell emf.

A scale of reduction potentials is needed to quantitatively assign the reduction potentials of various electrodes used to make up electrochemical cells.

Since there is no way to measure the reduction potential of a single electrode, the hydrogen electrode is chosen as the ultimate standard.

The Hydrogen electrode operating at 25°C and 1 bar pressure is assigned a reduction potential of 0.0 V. If we were to construct a cell using a $Cu(s)|Cu^{2+}(1\ m)$ electrode and the standard hydrogen electrode [Pt, H_2(1 bar, 25°C)|H^+(1 *m*)], the electrode reactions would be

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

The measured emf of such a cell would be 0.3419 V. Therefore, we say that the standard reduction potential of the $Cu(s)|Cu^{2+}(1\ m)$ electrode is +0.3419 V.

The fact that Cu^{2+} ions undergo spontaneous reduction indicates that the tendency for Cu^{2+}(*aq*) ions to accept electrons (to get reduced) is greater than that for H^+ ions.

In contrast, in the cell

$Zn(s)|Zn^{2+}(1\ m)||H^+(aq)|H_2(1\ \text{bar}, 25°C),Pt$

the cell reactions will be

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$,

$2H^+(aq) + 2e^- \rightarrow H_2(g)$,

and the measured cell emf will be –0.7618 V. In this case, it is clear that the tendency for H+ ions to accept electrons is greater than for the $Zn^{2+}(aq)$ ions.

Therefore, the reactions and electrode potentials in the cell

$Zn(s)|Zn^{2+}(1\ m)||Cu^{2+}(1\ m)|Cu(s)$

will be

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$, $E° = +0.7618$ V

$Cu^{2+}(aq) + 2e^{-}(aq) \rightarrow Cu(s)$, $E° = +0.3419$ V

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. $E° = +1.1037$ V

Other Standard Electrodes

A hydrogen electrode is difficult to set up and is not portable. Therefore, other standard electrodes have been adopted.

The $Ag|AgCl(s)|Cl^{-}(1\ m)$ electrode:

This electrode consists of a silver wire in contact with solid AgCl which, in turn, is in contact with 1 *m* KCl solution. The reduction potential of this electrode is measured by constructing the cell $Pt, H_2(1\ \text{bar}, 25°C)|H^{+}(1\ m)||Cl^{-}(1\ m)|AgCl(s)|Ag(s)$ in which the following reactions take place:

Anode: $\frac{1}{2}H_2(g) \rightarrow H^{+}(aq) + e^{-}$; $E° = 0.0000$ V

Cathode: $AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$. $E° = 0.22233$ V

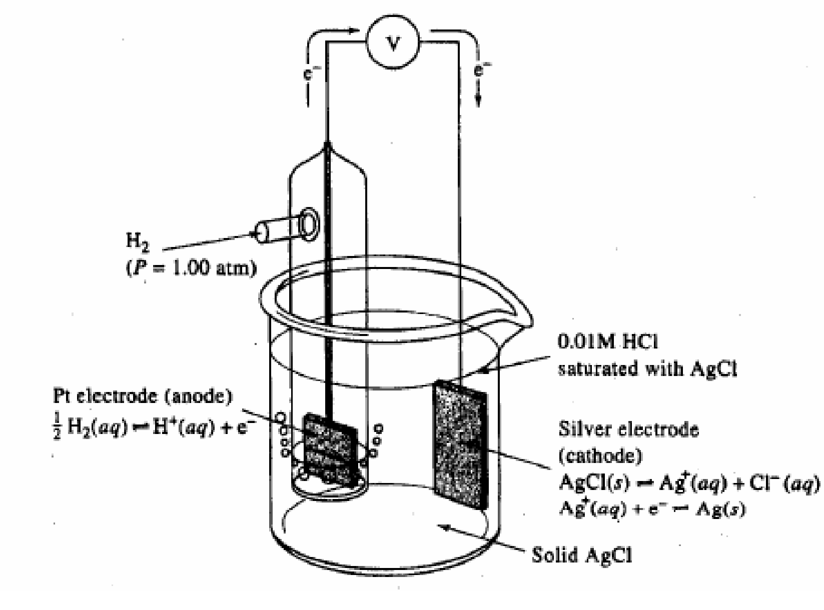


Figure 9.4 A galvanic cell without a liquid junction.

The Standard Calomel electrode

The half-cell is Hg(*l*)|Hg_2Cl_2(*s*)|Cl^-(1 *m*). Calomel is the common name for the mercury (II) chloride used in this electrode. The electrode develops a half-cell reduction potential of 0.3337 V.
If saturated potassium chloride solution used (rather than 1 *m*), the half-cell potential is 0.2412 V, and the electrode is called the saturated calomel electrode.
Another very common reference electrode is the glass electrode, which is essentially a thin-walled glass bulb filled with 0.1 *m* HCl, in concact with a AgCl(*s*)|Ag electrode. The glass membrane is permeable to H^+ ions and, therefore, the glass electrode is commonly used for pH determinations

The Thermodynamics of Electrochemical Cells

The relationship between the standard cell emf $E°$ and the standard Gibbs free
energy $\Delta G°$ is

$$\Delta G° = -nFE° \qquad (9.3)$$

where the superscript on G and E denotes the standard concentrations (strictly speaking, activities) of the electrolytes in the cell. F is Faraday constant = eN_A = 96,500 C mol^{-1} and n is the number of electrons transferred in cell reaction.
Under non-standard concentrations, we use the relationship

$$\Delta G = \Delta G^o + RT \ln Q \qquad (9.4)$$

where Q is the reaction quotient for the cell reaction. So, for a cell reaction
aA + bB → cC + dD
in which n electrons are involved, we write

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (9.5)$$

and

$\Delta G = \Delta G^{o} + RT \ln Q$

or, in terms of cell emf's,

$-nFE = -nFE^{o} + RT \ln Q$

This is easily simplified to give

$$E = E^{o} - \frac{RT}{nF} \ln Q \qquad (9.6)$$

This is called **the Nernst equation**, and is one of the most important equations in electrochemistry. The Nernst equation is the basis for many practical applications of electrochemical principles.

At equilibrium,
K=Q
W=0
$\Delta G=0$
$E_{cell}=0$
Then,

$$K = e^{\frac{-\Delta G^{o}}{RT}} = e^{\frac{nFE^{o}}{RT}} \qquad (9.7)$$

Example 9.2 Calculating K and ΔG^0 from E^0_{cell}

Lead can displace silver from solution. As a consequence, silver is a valuable by product in the industrial extraction of lead from its ore. Calculate K and ΔG^0 at 25^0C for this reaction.

Solution

Break the reaction into half-reactions, find the E^0 for each half-reaction
and then the E^0_{cell}.

$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $E^0 = -0.13V$
$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ $E^0 = 0.13V$
$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^0 = 0.80V$

$E^0_{cell} = 0.80-(-0.13) = 0.93$ V

$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$ $E^0 = -0.13V$
2x [$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$ $E^0 = 0.80V$]

$\Delta G^0 = -nFE^0_{cell} = -(2)(96.5\ kJ/mol\ V)(0.93V) = -1.8x10^2\ kJ$

$$K = e^{\frac{-\Delta G^o}{RT}} = e^{\frac{nFE^o}{RT}}$$

$K = 2.6x10^{31}$

Example 9.3 Using the Nernst equation to calculate E_{cell}

In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$[Zn^{2+}] = 0.010M$ $[H^+] = 2.5M$ $P_{H2} = 0.30atm$

Calculate E_{cell} at 25^{0}C.

Solution

Find E^0_{cell} and Q in order to use the Nernst equation

$2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$ $E^0 = 0.00V$
$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ $E^0 = -0.76V$
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $E^0 = +0.76V$

We have $E^0_H > E^0_{Zn}$

We Know that $E^0_{cathode} > E^0_{anode}$, then, H is cathode where the reduction is occur and Zn is anode where the oxidation.

$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_H - E^0_{Zn} = 0.0\ V - (-0.76\ V) = 0.76\ V$

In the reaction contains gases, we can be write the partial pressures of gases instead of their concentrations

$Q = P_{H2} \times [Zn^{2+}] / [H^+]^2 = (0.30)(0.010) / (2.5)^2 = 4.8x10^{-4}$

$$E = E^o - \frac{RT}{nF} \ln Q$$

$E_{cell} = E^0_{cell} - 0.0592V \log Q / n = 0.86V$

Example 9.4

A voltaic cell consisting of a Cu/Cu^{2+} half-cell and an Ag/Ag^+ half-cell under the following conditions:

$[Cu^{2+}] = 0.01M$, $[Ag^+] = 0.005M$, $E^0_{Cu} = 0.34$ V, $E^0_{Ag} = 0.8$ V

(a) Which is the cathode and which is anode

(b) Write the two half-reactions and the overall reaction,

(c) Determine the standard cell potential E^0 for the reaction

(d) Find the reaction quotient Q

(e) Calculate the total cell potential E_{cell} at 25^0C.

Solution

(a) We use the rule $E^0_{cathode} > E^0_{anode}$

where $E^0_{cathode}$ and E^0_{anode} are the standard reduction potential.

$E^0_{Ag} > E^0_{cu}$

then Ag is cathode and Cu is anode.

(b) Break the reaction into half-reactions,

$$Cu(s) \xrightarrow{\text{oxidation}} Cu^{2+}(aq) + 2\bar{e}$$

$$2Ag^+(aq) + 2\bar{e} \xrightarrow{\text{reduction}} 2Ag(s)$$

$$Cu(s) + 2Ag^+(aq) \xrightarrow{\text{overall reaction}} Cu^{2+}(aq) + 2Ag(s)$$

(c) the E^0 for the reaction

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = E^0_{Ag} - E^0_{Cu} = 0.8V - 0.34V = 0.46\ V$$

(d) To find Q

$$Cu(s) + 2Ag^+(aq) \xrightarrow{\text{overall reaction}} Cu^{2+}(aq) + 2Ag(s)$$

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$Q = \frac{(0.01)}{(0.005)^2}$$

(e) The cell potential is

$$E_{cell} = E^o{}_{cell} - \frac{RT}{nF}\ln Q$$

$$E_{cell} = 0.46 - \frac{8.314\ J\ mol^{-1}\ K^{-1}\ \times 298\ K}{2 \times 96500}\ln\left(\frac{0.01}{(0.005)^2}\right)$$

$$E_{cell} = 0.38\ V$$

Appendix A. Key Concepts (Glossary)

Absolute temperature scale. This refers to a temperature scale that uses the absolute zero of temperature as the lowest temperature.

Absolute zero. The lowest temperature theoretically attainable. It is the temperature at which the kinetic energy of atoms and molecules is minimal.

Adiabatic boundary. A boundary that does not permit energy transfer as heat.

Avogadro’s law. At constant pressure and temperature, the volume of a gas is directly proportional to the number of moles of the gas present.

Bomb calorimeter. A calorimeter in which there is no net loss of heat from the calorimeter to the surroundings. It is used to measure the heat of a combustion reaction. The measured heat of reaction at constant volume, $q_v = \Delta U$.

Boyle’s law. The volume of a fixed mass of a gas maintained at constant temperature is inversely proportional to the gas pressure.

Calorimeter. A device for measuring the heat transfer.

Charles’s law. The volume of a fixed amount of gas maintained at constant pressure is directly proportional to the absolute temperature.

Closed system. A system with a boundary through which matter cannot be transferred.

Dalton’s law. The total pressure of a mixture of gases is just a sum of the pressures that each gas would exert if it were present alone.

Diffusion. The spreading of a substance (usually a gas) into a region where it is not originally present due to the random motion of the molecules.

Dipoles. A pair of separated opposite charges. The dipole moment (□) is the product of the positive charge and the distance separating the charges.

Endothermic process. A process that absorbs energy as heat from its surroundings.

Energy. The capacity to do work.

Enthalpy (*H*). A thermodynamic quantity used to describe heat changes taking place at constant pressure, $H = U + PV$.

Enthalpy change. The heat (under certain familiar conditions) involved in a process; symbolized ΔH. At constant pressure, $\Delta H = \Delta U + P\Delta V$.

Entropy (*S*). A direct measure of the degree of disorder or randomness of a system.

Equilibrium. A condition in which an infinitesimal change in a variable in the opposite direction results in opposite change in the state. In chemical reactions, it represents the situation in which the reactants and products are producing each other at the same rate.

Exothermic process. A process that releases energy as heat.

Free energy (*G*). The energy available to do useful work. Defined by $G = H – T\Delta S$. Changes in free energy are useful in indicating the conditions under which a reaction will occur.

First law of thermodynamics. Energy can be converted from one form to another but can not be created or destroyed.

Gibbs Free Energy. See free energy.

Heat capacity. The quantity of heat required to change the temperature of a substance by one degree usually expressed as J ^{0}C $^{-1}$ or cal ^{0}C $^{-1}$.

Heat of reaction. The energy change accompanying a chemical reaction.

Heat. The transfer of energy as a result of a temperature difference.

Hess's law. The law that states that the enthalpy change for an overall or net process is the sum of enthalpy changes for the individual steps in the process.

Ideal gas. A hypothetical gas whose pressure-volume-temperature behaviour can be accounted for by the ideal gas equation.

Ideal gas constant (*R*). The numerical constant appearing in the ideal gas equation. The constant has a value of 0.0821 L atm mol^{-1} K^{-1} or 8.314 J K^{-1} mol^{-1}. An ideal gas (perfect gas) is a hypothetical gas that obeys the ideal gas equation.

Ideal gas equation. An equation expressing the relationship between pressure, volume, temperature, and amount of gas. Mathematically stated as $PV = nRT$, where n is the number of moles, P is the pressure of gas and V the volume of gas.

Internal energy. Total energy of the system; symbolized by E. The sum of all the kinetic energies and potential energies of the particles within the system.

Isobaric calorimeter. A calorimeter for the studying processes at constant pressure.

Isolated system. A system with a boundary through which neither matter nor energy can be transferred.

Kelvin (temperature). The SI base unit of temperature. The Kelvin temperature is an absolute temperature. The lowest attainable temperature is 0 K = – 273.15 ^{0}C. It is related to the Celsius temperature through the expression $T\,(K) = T(^0\mathrm{C}) + 273.15$.

Kinetic-molecular theory of gases. The treatment of gas behaviour in terms of random motion of molecules. It is a model used for describing gas behaviour based on a set of assumptions.

Open system. A system with a boundary through which both matter and energy can be exchanged with the surroundings.

Potential energy. The energy due to the position or arrangement. Associated with forces of attraction and repulsion.

Pressure-volume work. The work associated with the expansion or compression of gases.

Root-mean-square-velocity. The square root of the average of the squares of speeds of all molecules in a sample.

Specific heat. The quantity of heat required to change the temperature of one gram of substance by one degree Celsius.

Standard conditions of temperature and pressure. Refers to conditions at a temperature of exactly 273.15 K (^{0}C) and a pressure of 101325 Pa (1 atm or 760 mmHg).

Standard enthalpy of formation. The heat change involved when 1 mol of the substance is made from its elements in their standard state; symbolized

Standard enthalpy of reaction. The enthalpy change when a reaction is carried out under standard states conditions.

Standard enthalpy. The change in enthalpy for a process in which the initial and final substances are in their standard state, symbolized ΔH.

Standard temperature and pressure (STP). At 273 K (^{0}C) and 101325 Pa (1 atm).

State function. Property that depends only on the current state of the system and is independent of how that state has been prepared. A function that depends only on the initial and final states of the system.

Surroundings. The part of the world outside the system where we make our measurements.

System. Part of the world in which we have specific interest.

van der Waals equation. An equation used to describe the P, V, and T of a non- ideal gas.

van der Waals forces. A term used to describe the dipole-dipole, dipole-induced dipole and dispersion forces

Work. The transfer of energy by motion against an opposing force.

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