

What is Matter

Matter is anything that has mass, and occupy space. Matter makes up everything in the universe: water, soil, clothes, animals, trees, human beings etc. One way to describe matter is to study its properties. Such properties should be measurable without affecting the identity of the matter. That type of property is called a physical property. For example, you can describe a human being according to his height, color of his hair or eyes, weight, gender, race, etc. In chemistry, typical physical properties include: shape, weight, color, melting point, boiling point, freezing point, volume, length etc.

State of Matter

There are three states of matter: solid, liquid and gas.

Solid: A solid have mass, volume and shape. For example, a stone has mass, volume and shape. In a solid, the atoms or molecules to that solid are held together by strong forces such that its constituents are arranged in a certain way that defines its shapes and form. Solids form may be crystalline or amorphous. Atoms of solids are also arranged in a way such that they cannot move about but can only vibrate slowly in a fixed position.

Liquid: Liquids have volume but no definite shape. It assumes the shape of the container in which the liquid occupies. Its atoms or molecules are not rigidly held like in the solid. They move randomly apart but are still close to each other to maintain a definite volume. Example include, water, soda etc

Gases: A gas does not have a definite shape or volume. Its atoms or molecules are widely apart and move randomly at high speed often colliding with each other. Gases take the shape and volume of its container. Examples include Hydrogen, air, helium etc.

A Perfect Gas

Gas atoms or molecules moves randomly at high speed and its average speed increases with increase in temperature. Atoms or molecules of a perfect gas are so much apart that they are not affected by intermolecular forces. The only thing that happens to them is collision with the walls of its container

The State of Gases: The state of a pure gas include: its volume **V**, amount of substance (number of moles) **n**, pressure **p** and its temperature **T**. To describe any gas, any three of its physical properties is sufficient. The fourth property is automatically fixed. Therefore, any substance is described by the **equation of state** that relates all the four variables.

The equation of state has the form: $p=f(T,V,n)$ which implies that if we know T,V, and n, then we can know p. For a gas the equation of state is described as $P = nRT/V$

- **Pressure:** Pressure is the amount of force divided by the area over which it is applied. Pressure increases if the force applied is increased. The converse is also true. The pressure of a gas is derived from the collision of its atoms or molecules with the walls of its container. This collision is constant and it produces a steady or constant pressure for the gas. The SI unit of pressure is the *pascal* (Pa). **The SI unit of force is the Newton (N) = 1kgm/s^2**

Pascal = 1 Newton of force per meter squared (1 Nm^2) = $1\text{ kg m}^{-1}\text{s}^{-2}$

Other Units of pressure include:

bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa or 760 mmHg
torr	1 Torr	$(101.325/760) = 133.32\text{ Pa}$
milli meter of mercury	1 mmHg	133.32 Pa
pounds per square inch	1 psi	0.894757 kPa

- **Example.** A substance has a mass of 1.0 kg and it exerts a pin point force on an area with size $1.0 \times 10^{-2}\text{mm}^2$ on the surface of the earth. (Hint: force is mass x force of gravity, $g = 9.8\text{ m/s}^2$). Calculate the pressure exerted the substance

Mechanical Equilibrium: If 2 gasses of unequal pressure occupy the same container but separated by a wall, both gases exert their respective pressure on the wall. The value of the higher pressure decreases with time while the lower pressure increases. At a certain time, the pressure on both side of the wall will become the same. This state is called the state of mechanical equilibrium.

How to measure Pressure: Pressure is measured with a barometer. A barometer is a column of mercury in mechanical equilibrium with the atmosphere. The pressure at the base of the column is in equilibrium with the atmosphere, then the height of the column is proportional to the atmospheric pressure. Nowadays we use electronic pressure gauge such as Bayard-Alpert pressure gauge, capacitance manometer, or semiconductor traducers.

Example: Derive the equation for the pressure at the base of the column of a liquid of mass density ρ and height h on the surface of the earth?

Answer: $P = F/A$

Density = m/V hence mass = ρV

If the area of the column is A and its height h , $V = Ah$ then mass $m = \rho Ah$

$F = mg = \rho Ahg$ therefore $P = F/A = \rho Ahg/A = \rho hg$

Temperature: When 2 substances are in contact with each other through a diathermic boundary, heat energy may flow from one with higher temperature to the one at lower temperature. After some time, a thermal equilibrium will be established between the two substances. Temperature is the parameter that dictates the direction of the flow of heat energy through a thermally conducting material.

There are two types of boundary when describing heat flow between two substances, viz,

1. Diathermic boundary: occur if a change of state occurs when two thermally conducting substances at different temperature comes into contact with each other.
2. Adiabatic boundary: when no heat exchange occurs when two thermally conducting substances are brought in contact with each other. This is called insulation.

Zeroth Law of thermodynamics: If A is in thermal equilibrium with B and B is also in thermal equilibrium with C, then A and C are in thermal equilibrium with each other.

Thermometers: Temperature is measured relative to changes in length of a column of liquid when in contact with substances of different temperature. The first thermometer was made by Celsius who measured the change in length of a column of mercury to Freezing (melting) ice and boiling water. The interval at these two sets points was divided into 100 parts to form the Centigrade thermometer. The Freezing (melting) point, which is the lower point was set to Zero (0) and the highest point, which is the boiling point was set at hundred (100). Each interval is called a degree centigrade ($^{\circ}C$). The Fahrenheit thermometer was similarly developed with the lowest point set at 32° and the highest point at 212° .

If different materials are used to make the thermometer, different temperature values are obtained for the same set point. This indicates that the nature of the materials affects the values of temperatures at the same set point. Therefore, a physical property that is independent of the identity of the material is needed to be used to develop a perfect or universal thermometer. The pressure of a gas is independent of the identity of a gas, hence it can be used to develop a **perfect gas thermometer or temperature scale (pgt)**. PGT is identical to the commonly used **thermodynamic temperature scale** based on degree Kelvin (absolute).

Conversion Factor

It is possible to convert from one temperature scale to the other. The conversion expressions are shown below

$$^{\circ}\text{C} = 5/9(^{\circ}\text{F}-32)$$

$$^{\circ}\text{F} = 9/5^{\circ}\text{C} + 32$$

$$\text{K} = ^{\circ}\text{C} + 273.15$$

Gas Laws

The common gas laws include:

Boyles law: Pressure is inversely related to volume when n and T are constant.

$$PV = \text{constant (n, T are constant)}$$

Charles Law: Volume is directly related to Temperature when n and P are constant

$$V = kT, \text{ when n and P are constant (k is a constant of the relationship) or}$$

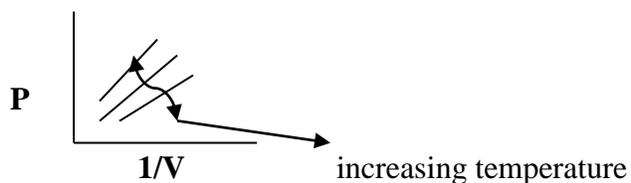
Pressure is directly related to Temperature when n and V are constant

$$P = kT \text{ when n and V are constant}$$

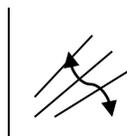
Avogadro: Equal volume of gases at constant temperature and pressure contain the same amount of molecules: $V = k \times n$ at constant P and T $\Rightarrow V/n = k$ (constant)

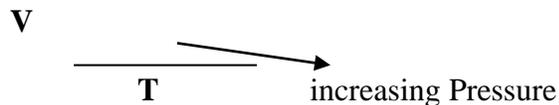
All the three laws are limiting laws i.e. they are true within a certain limit.

Isotherm: If a graph of Boyles law is plotted (P vs. V or P vs. 1/V) at constant temperature, a hyperbolic or a straight line is obtained. These lines are called **isotherms (curve at a fixed temp)**

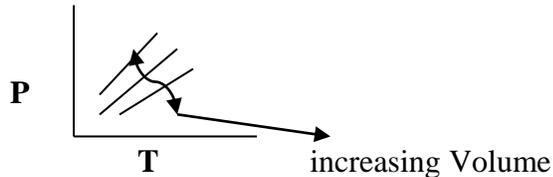


Isobar: Charles law is also plotted ($V=kT$) at constant pressure, the curve obtained is called an **isobar**





Isochores: If Charles law is plotted as $P = kT$, at constant volume, the curve is called **isochores**



All lines extrapolate to zero when $V, T, P = 0$

Perfect Gas Law

The three gas laws expressed above is combined together to form the perfect gas laws indicated below

$$PV = nRT \quad \text{where } R \text{ is the gas constant}$$

$$PV/T = nR = \text{constant.}$$

Values of R (Gas Constant)

$$8.31447 \quad \text{K}^{-1} \text{ mol}^{-1}$$

$$8.29574 \times 10^{-2} \quad \text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

2/14/12 Kinetic Theory of Gases

Empirical or Qualitative Model: Molecular Approach

Boyles Law: This law can be explained at the molecular level by assuming that the gas pressure is very low and the molecules are very far apart that they do not exert any influence on each other. Therefore, if the pressure of the gas is compressed to half its volume, then twice the number of molecules will hit its walls than before it was compressed. This indicates that the average force exerted on its walls will be doubled. The converse is also true. The final result shows that pressure and volume are inversely related to each other, hence, $PV = \text{constant}$.

Charles Law: The average speed of the molecules of a gas increases if its temperature is increased. Increase in the average speed increases the frequency of collision and the force exerted on its walls and hence the pressure increases.

Quantitative Model

The qualitative explanation of gas laws can be quantitatively explained by the Kinetic theory of gases. The Kinetic theory of gases is based on the following assumptions:

1. Gas consists of extremely small molecules with mass m that moves in random motion.
2. The molecules are separated by great distances, hence occupies a small fraction of the total gas volume.
3. There are no intermolecular forces between the molecules.
4. The molecules interact only briefly by infrequent and elastic collision with each other and to the walls of its container
5. Sizes of gas molecules are very negligible such that their diameter is very small compared to the average distances travelled between collisions.
6. The only contribution to the energy of the gas is from the kinetic energy of its molecules

An elastic collision is one that its total translational energy is conserved. That is, the momentum (mv , m = mass of molecule and v = its velocity) before collision is the same after collision. No energy is lost. Therefore the change in momentum after each collision is $2mv$.

The equation of the kinetic theory is obtained by totaling the forces exerted by the gas molecules on the wall of its container of volume V . The total force divided by the area over which is exerted gives the pressure P of the gas.

In molecular collision, the force of collision depends on (1) frequency of collision which is determined by the speed of its molecules (the faster the speed, the more frequent is the collision) and (2) the average translational kinetic energy, e_k , of the gas molecules.

$$e_k = \frac{1}{2} mv^2, \text{ (m mass of gas molecule and v its speed)}$$

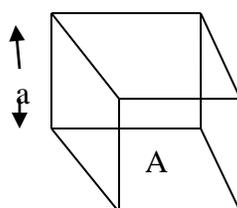
Deviation of the Ideal Gas Equation From the Kinetic Theory

We shall attempt to obtain the pressure of a gas from its molecular quantities such as mass and velocity of the molecules. As we know, Pressure is force per unit area and the force exerted by a molecule of mass m moving with acceleration a at a given instant is by Newton's second law $F = ma$. The instantaneous acceleration is v/t where v is the velocity of the molecule. Thus the force of impact is

$$F = ma = mv/t \quad (1)$$

mv is the momentum of the molecule. We can define force as the time rate of change of momentum. To obtain the pressure, we must calculate the change of momentum for each collision. If we multiply this change in momentum by the total number of collision with the container wall occurring in a given time interval t , we shall have the total force on the wall. Dividing this total force by the area of the wall upon which this force is acting will give the total pressure of the gas. Let us consider a cubic container (figure 1) containing a total number of molecules, N . The edge of the cube is of length a . The velocity v of a molecule can be resolved into its components v_x, v_y , and v_z which are the velocities parallel to the three mutually perpendicular axes. By Pythagorean theorem the magnitude of the velocity is

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad (2)$$



To calculate the number of collisions occurring at surface A of the cube, we may consider a molecule starting from surface A moving in the x-direction with velocity v_x to the opposite surface. It travels back to the surface A with the same velocity but in opposite direction. In travelling back and forth to surface A, the molecule would have strike the surface every $2a$ cm of path length. The frequency of collision at surface A will be

$$\text{Number of collision per unit time per molecule at face A} = \frac{\text{distance travelled per unit time}}{\text{distance between collisions}} = \frac{v_x}{2a} \quad (3)$$

Since the collisions are assume to be elastic and the walls of the container are rigid, the velocity of the molecule will not change after rebounding from the wall. Only its direction will change. The molecule travels in the positive direction will a $+v_x$ velocity and after collision will have a $-v_x$ velocity. The change in momentum per collision per molecule at surface A = $mv_x - (-mv_x) = 2mv_x$ (4).

The product of equations 3 and 4 will now give the change in momentum per unit time i.e.

$$\text{Number of collisions per unit time per molecule at face A} \times \text{change in momentum per collision per molecule at face A} = \text{change in momentum per time per molecule at face A}$$

$$\frac{v_x}{2a} \times 2mv_x = mv_x^2/a \quad (5)$$

Since there are a large number of molecules moving randomly in the box, one must use the average velocity for the molecules which will be for a molecule moving in the x direction $\overline{v_x}$. Then the total average change in momentum for N molecules will be

$$\text{Total average change in momentum per unit time for } N \text{ molecules} = Nm\overline{v_x^2}/a \quad (6)$$

This quantity is the total average force. Then the total pressure at face A due to N molecules is equal

$$P = Nm\overline{v_x^2}/a(a^2) = N\overline{mv_x^2}/V \quad (7)$$

Where $V = a^3$ the volume of the cube. Because the direction of the molecules are similar, the average values of the square of the components in the three perpendicular direction are equal

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \quad (8)$$

If we put equation 8 in 7 we will have $PV = Nm\overline{v^2}/3 \quad (10)$

Since the velocity depends on temperature, the mean square velocity will also depend of temperature and will be constant for a given temperature. For a fixed number of molecules of a given gas at constant temperature the RHS of equation 10 will be constant, thus equation 10 will become $PV = \text{constant}$ for a constant mass and temperature which is Boyles law.

If we multiply the RHS of equation 10 by $2/2$ we will have

$$PV = \frac{2N}{3} \overline{\left(\frac{1}{2}mv^2\right)} \quad (11)$$

3

Since $\frac{1}{2}m\overline{v^2}$ is the average translational energy of the molecules, then the quantity $\frac{1}{2}Nm\overline{v^2}$ will be equal to the average translational kinetic energy E_k of all molecules in the gas. Then

$$PV = \frac{2}{3} E_k \quad (12)$$

If N is the same as Avogadro's number, then $Nm = M$ the molecular weight and V becomes the volume of one mole of a gas, the molar volume. Under this condition then

$$(E_k)_T = Nm\overline{v^2} = \frac{1}{2} M\overline{v^2} \quad (13)$$

Where $(E_k)_T$ is the total kinetic energy per mole of molecules of the gas. If we compare equation 12 with the ideal gas equation, then

$$\frac{2}{3}E_k = RT \quad \text{per mole} \quad (14)$$

Equation 14 means that average translational kinetic energy of a gas depends only on its absolute temperature and independent of its pressure/ volume or type of gas. Thus a small

molecule such as hydrogen will at the same temperature the same kinetic energy as a heavy molecule like ethane. The for two molecules of molecular weights M_1 and M_2 respectively at the same temperature will have $(E_k)_{M_1} = (E_k)_{M_2}$

Therefore, from equation 14, then $\frac{1}{2} M_1 \overline{v_1^2} = \frac{1}{2} M_2 \overline{v_2^2}$ (15)

If we define the quantity called root mean square velocity, v_{rms} , as $v_{rms} = (\overline{v^2})^{1/2}$ (16)

Then we can put equation 16 in 15 to have

$$\frac{1}{2} M_1 (v_{rms})_1 = \frac{1}{2} M_2 (v_{rms})_2 \quad (17) \text{ then}$$

$$(v_{rms})_1 / (v_{rms})_2 = \sqrt{M_2 / M_1} \quad (18)$$

Equation 18 is the same as Graham's law of Diffusion which says that gases diffuse the rate inversely proportional to the square root of their respective densities.

We can use equation 10 to prove Avogadro's hypothesis. If consider two gases of mass M_1 and M_2 at the same temperature and pressure and volume, then

$$N_1 m_1 \overline{v_1^2} / 3 = N_2 m_2 \overline{v_2^2} / 3 \quad (19)$$

Since their temperatures are the same, equation 14 requires that their translational energy be equal, therefore equation 19 becomes $N_1 = N_2$ (20) saying that in equal volumes at the same temperature and pressure are equal.

New Temperature Definition

Temperature T is the Kelvin Temperature which is directly proportional to the translational energy of a gas. This means that changes in temperature at the molecular level is due to changes in molecular motion. That is, heat transfer involves the motion of molecules of the hotter body slowing down by colliding with the molecules of the colder body until the temperature of the two bodies equalizes. That is, there is a transfer of translation energy that results into slowing down of molecule of gases. When $T = 0$, the absolute temperature, all motion seizes.

Avogadro's Law: For 2 different gases A and B

$$P_A = \frac{2}{3} n_A / V_A (\overline{e_k})_A \quad \text{and} \quad P_B = \frac{2}{3} n_B / V_B (\overline{e_k})_B$$

If T is constant for the two gases, then $\overline{e_k}$ will be the same and if the pressures are the same, then, $n_A / V_A = n_B / V_B$. By Avogadro's law, if equal volumes are compared then $n_A = n_B$

SATP AND STP

The perfect gas equation can be used to calculate the properties of a gas under a variety of conditions such as Standard ambient temperature and pressure (SATP) or Standard Temperature and pressure (STP). SATP is defined as 298.15 K and 1 bar (10^5 Pa). At this condition, the molar volume of a gas $V_m = V/n = 24.789 \text{ dm}^3\text{mol}^{-1}$. The same molar volume can be calculated for STP at 0°C and 1 atm. to give $22.414 \text{ dm}^3\text{mol}^{-1}$.

Real Gases

Real gases do not obey exactly the perfect gas law because their molecules interact with each other. They deviate due to forces of attraction and repulsion. Deviation also occurs at high pressure and low temperatures, especially when gases are about to condense to a liquid. Repulsive forces are significant when gas molecules are very near each other. For example, when the pressures are high, the volume is smaller; hence the molecules are nearer each other. Attractive and intermolecular forces work at fairly longer distances than those of repulsive forces. Low temperature reduces the average speed of molecules; hence they are at a higher probability to interact with each other.

Compression Factor: How far can you compress a gas?

The compression factor (Z) of a gas is the ratio of its molar volume, $V_n = V/n$ to that of the perfect gas, V_m at the same pressure and temperature.

$$Z = V_n / V_m$$

Molar volume of a perfect gas, $V_m = RT/P$,

Then, $Z = V_n P/RT$ and $PV_n = RTZ$,

$Z = 1$ for a perfect gas. Deviation of Z from 1 is a measure of departure from a perfect behavior. At low pressure, $Z = 1$ and gases behave like a perfect gas. When pressures are high, $Z > 1$ and their molar volume is greater than that of a perfect gas, hence repulsive forces are dominant. At intermediate pressures, $Z < 1$, showing that, attractive forces reduce the molar volume compared to that of a perfect gas.

Mixtures of Gases

The atmosphere is the largest mixture of gases that exist. Its composition is fairly constant but varies from locality to locality. Its pressure and temperature also varies according to altitude and local condition. The total pressure of any mixture of gases is the sum of the pressure exerted by its individual component (partial pressure). This is called **Dalton's law of partial pressure**

$$P = p_1 + p_2 + p_3 + \dots$$

Distribution of Molecular Velocities

In molecular collisions, there is distribution of speeds and energies from high to low. This is so because, the velocities of the individual molecule are constantly changing because of collisions with themselves or the walls of the containers. The motion of the molecules of the gas becomes random. There is a need to find the averages of these speeds to calculate their average translational energy, e_k .

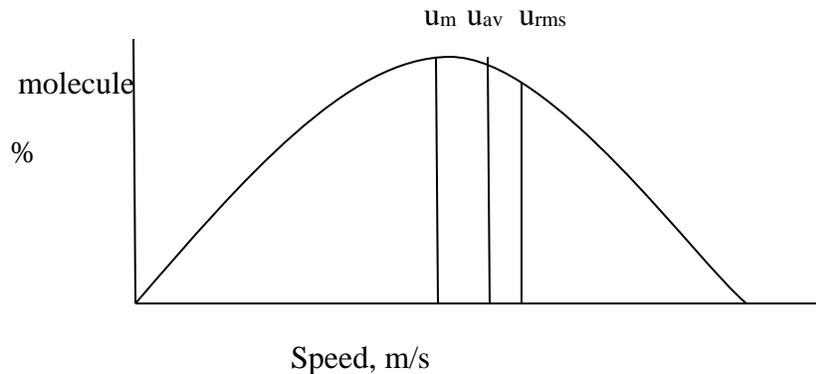


Figure 1. Distribution of Molecular Speeds – Hydrogen at 0°C

Figure 1 shows a typical distribution of energies for Hydrogen at 0°C. This called Maxwell-Boltzmann distribution molecular distribution of velocities. The area under the curve for an two velocities v_1 and v_2 gives the total number of molecules having velocities between these values. There are three types of speeds shown in the figure: u_m = most probable or modal speed; which is the speed of molecule having velocities near the maximum or the velocities possessed the greatest number of molecules; u_{av} = average speed (u = average speed of a molecule); u_{rms} = root mean square speed ($\sqrt{u^2}$ = square root of the averages of the square of all molecules in the sample or the speed of a molecule possessing the average kinetic energy)

$$\text{Average kinetic energy } \bar{e}_k = \frac{1}{2} m \bar{u}^2 = \frac{1}{2} m (\sqrt{u^2})^2 = \frac{1}{2} m (u_{rms})^2 = \frac{3}{2} (R/N_A)T \quad (1)$$

$$\text{Remember that } \frac{2}{3}e_k = RT \text{ therefore } e_k = \frac{3}{2}RT \text{ per mole} = \frac{1}{2} m(u_{rms})^2 \quad (2)$$

Therefore, $u_{rms} = \sqrt{3RT/mN_a}$ ($M = mN_A$ = molar mass of 1 mole of a gas, N_A = Avogadro's number)

$$u_{rms} = \sqrt{3RT/M} \quad (3)$$

In general, $u_m = 0.816u_{rms}$ and $u_{av} = 0.921u_{rms}$ when $R = 8.314 \text{ J/mol K}$ or $8.314 \text{ kgm}^2/\text{s mol K}$

Assignment

1. Calculate the modal (u_m), average (u_{av}) and the root mean square (u_{rms}) of ten automobiles on a highway traveling at the following speed 40 42 45 48 50 50 55 57 58 60 mi/h.

Speed, u (mi/h)	Speed ² , u ²
40	1600
42	1764
45	2025
48	2304
50	2500
50	2500
55	3025
57	3249
58	3364
60	3600
Sum = 505 mi/h	Sum = 25,931
Average Speed $u_{av} = 505/10 = 50.5$ mi/h	Average Square of speed = $25931/10 = 2593.1$
Most probable speed $u_m = 50$ (highest frequency)	$U_{rms} = \sqrt{2593.1} = 50.9$

2. Calculate the u_{rms} of Hydrogen molecule, H₂ at 50 °C?

$$U_{rms} = \sqrt{3 \times 8.314 \text{ kgm}^2\text{s}^{-2}\text{mol}^{-1}\text{K}^{-1} \times 323 \text{ K} / 2.06 \times 10^{-3} \text{ kg/mol}} = 2.00 \times 10^3 \text{ m/s}$$

$$\text{Molecular weight of hydrogen molecule} = 2.06 \text{ g/mol} = 2.06 \times 10^{-3} \text{ kg/mol}$$

The mathematical expression that relates the number of molecules, n_i , having an energy E_i at a given temperature is the Boltzmann distribution law

$$n_i = C e^{-E_i/kT} \quad (4)$$

where C is a constant of proportionality and k = the Boltzmann constant, the gas constant per molecule

$$\text{the Boltzmann constant} = \frac{R}{N} = \frac{8.315 \times 10^7 \text{ erg/mole } ^\circ\text{K}}{6.02 \times 10^{23} \text{ molecules/mol}} = 1.381 \times 10^{-6} \text{ erg/molecule } ^\circ\text{K} \quad (5)$$

C is the total number of molecules, n_T in the gas then,

$$n_i = n_T e^{-E_i/kT} \quad (6)$$

Equation 6 means that $n_i/n_T = e^{-E_i/kT}$ (7) i.e. the exponential is the fraction of molecules with an energy E_i greater than the average energy of the molecules in whole system.

[Example](#)

2/21/12 Law of Thermodynamics

Concepts

Any scientific law is an attempt to describe one aspect of nature and there are limited in applicability. Scientific laws can be rejected or modified with time if need findings surfaces.

The law of thermodynamics deals with interchanges among different forms of energy. It deals with the relationship between heat and other forms of energy

First Law of Thermodynamics

The first law of thermodynamics says that energy is conserved. It can be transferred between the system and the surroundings, but the total energy of the system and the surroundings is constant.

Thermodynamics applies to everything from black holes so massive that light cannot escape from it to little neutrino particles. It can answer questions like 'How do we calculate the work done when a muscle contracts or stretches? How much heat can be generated when 1g of sugar is digested?

Energy Conversion and Conservation

Experiments have shown that energy can be converted from one form to the other but the total amount of energy used in the process remains the same. For a example, a piece of brick sitting on the window sledge of a fifth story building possesses gravitational energy or potential energy. When falling to the sidewalk, the potential energy is converted to Kinetic energy, heat energy due to friction. When it hit the sidewalk, light energy is produced and other forms of energy like energy that breaks the brick into pieces, sound energy, etc are produced. The first law says that the sum of this energy remains the same.

Systems and Surroundings

In order to discuss inter-conversion of energy, it good to define some terms

System: A specific part of the universe under focus e.g. the earth, sun, moon, liver etc

Surroundings: Everything else apart from the system.

Boundaries: demarcation between the system and the surroundings

Isolate system: a system that does not exchange anything with its surroundings. It is difficult to find or construct such a system in nature. The closest to an isolated system is a thermally insulated flask that exchanges little or no heat with its surroundings for a short period of time.

Closed System: Does not exchange matter with its surroundings but allow energy exchanges across its boundaries. An example is a chemical reaction performed in a closed flask.

Open System: Exchanges both matter and heat with its surroundings. Example includes the fertilization of egg. Oxygen goes in during the process of fertilization and CO₂ comes out. Heat is also exchanged with the environment. Another example is water in a beaker. The boundaries are glass water and glass air. Water may evaporate into the air and air may dissolve into the water. Heat may flow in either direction depending on which one is warmer. Another example is adding a catalyst to a beaker containing hydrogen peroxide. The reaction produces water and Oxygen gas.. Oxygen escapes to the surround while heat is released during the reaction

Reversible Process: If the external pressure is infinitesimally different from the pressure of the system, the system is said to be reversible. A slight change in pressure will reverse a process of expansion to compression and vice versa

Irreversible Process: if the pressure difference between the surrounding and the system is significant, then the process is irreversible.

Energy Exchanges

In thermodynamics, we are interested in change of energy not the absolute value of energy for a system. It is convenient to divide energy exchanges between a system and its surroundings into different types e.g. heat, work, sound, light etc, Two most common types of energy exchange is heat and work.

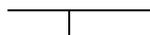
Work: The system can do work on the surrounding or vice versa. Work is defined as

$$\text{Work} = \text{force} \times \text{distance}$$

For purpose of discussion, work is positive if the surrounding is doing work on a system and vice versa.

Examples of Work

If a spring of length x_0 is suspended on a cross bar and a weight is added on the other end of the spring. The spring will extend over a certain distance x is the elastic limit is not exceeded





To calculate the work of extending the spring, the weight is considered an external force f_1 and the spring force opposing it as f_{sp} . Both forces are equal but opposite.

By Hooks law $f_{sp} = -k(x-x_0)$ and $f_1 = k(x-x_0)$

(where x_0 is the length of the spring when no force is acting on it)

The work done $w = \int f_1 dx$

If the spring extends from x_1 to x_2

$$\begin{aligned}
 W &= \int f_1 d(x-x_0) \\
 &= \int k(x-x_0) d(x-x_0) \\
 &= \frac{1}{2} k[(x_2-x_0)^2 - (x_1-x_0)^2] \\
 &= \frac{k[(x_2-x_1)(x_1+x_2 - x_0)]}{2}
 \end{aligned}$$

II Calculate the work PV done when a system expands from 1.0 L to 2.0 L against an external pressure of 10 atm

$$\text{Ans: } w = -P(V_2 - V_1) = n(2-1) = 10 \text{ Latm} = 10 \text{ Latm} \times 101.3 \text{ J/Latm} = 1013 \text{ J}$$

Assignment

Calculate the PV work done in joules when a sphere of water 1.0 μm ($1\mu\text{m} = 10^{-6}\text{m}$) in diameter freezes to ice at 0°C and 1 atm pressure (Density of ice is 0.915 g/cm^3)

Ans: We need to calculate the volume of water and then use the density of ice and liquid water to calculate the volume of ice

$$\text{Volume of sphere of water} = \frac{1}{6} \pi D^3 = \frac{3.14}{6} \times (10^{-6}\text{m})^3 = 5.237 \times 10^{-19}\text{m}^3$$

$$\text{Volume of sphere of ice} = 5.237 \times 10^{-19} \times (1/0.915) \text{ m}^3 = 5.723 \times 10^{-19} \text{ m}^3$$

$$W = -P(V_2 - V_1) = -(1 \text{ atm})(5.723 - 5.237) \times 10^{-19} \text{ m}^3 = -0.486 \text{ atmm}^3 = -0.486 \times 1.013 \times 10^5 \text{ atmm}^3 \times \text{J/m}^3 \text{ atm} = -4.92 \times 10^{-15} \text{ J}$$

Work in a gravitational field

$$W = mg(h_2 - h_1) \quad \text{if } m \text{ is in kg, } h \text{ in meters and } g = 9.807 \text{ m/s}^2 \text{ then } w = \text{Joules}$$

Work in and Electrical Field

$W = EIt$ E in volts = potential difference or electromotive force, I = current and t = time the time

Heat

When two bodies at two different temperatures are in contact with each other, heat exchange occurs and the hotter body loses heat to the colder body. Heat transfer occurs between the two bodies. The temperature of the two bodies will be equal after some time. For convenience, heat flow into the system is positive and negative if it flows out of the system

For a closed system, transfer of a small quantity of heat dq will result into a change dT in its temperature. Ratio dq/dT is called the Heat capacity of the system, C

$$dq/dT = C$$

For a change in temperature from T_2 to T_1 ,

$$q = \int C dT = C(T_2 - T_1)$$

C is different for different materials and varies with temperature for a given material. Heat capacity increases with increase in the amount of material.

$$Q = mC(T_2 - T_1) \quad m = \text{mass of material}$$

Example:

Calculate the heat in joules, necessary to change the temperature of 100.0 g of liquid water by 50°C at constant pressure.? The heat capacity of water at constant pressure is 1.0 cal/g deg and is nearly independent of temperature.

$$\text{Ans: } q = mC(T_2 - T_1) = 100.0 \text{ g} \times (1.0 \text{ cal/g deg})(50^\circ\text{C})(4.184 \text{ J/cal}) = 20.9 \text{ kJ}$$

First Law

The first says that heat is conserved in a system. Hence if heat and work are the only energy exchanged that occur in a closed system, then, the change in energy of the system is

$$\Delta E = q+w \quad (1)$$

ΔE = change in energy of the system

q is positive if the system absorb heat (heat in) and negative if the system loses heat (heat out).

w is positive if work is done on the system (work in) and negative if work is done by the system (work out)

Example

A gas does 243 J of work while expanding. During the expansion, the gas absorbed 225 J of heat from the surrounding. What is the change in energy for the system?

Ans. Heat is absorbed by the system, hence it is positive. $\Delta E = q+w = 225+ (-243) = -18 \text{ J}$

If the system is an open one or other types of energy exchanges apart from heat and work is done between the system and the surroundings, then additional terms can be added to the equation (1).

If the system does not exchange matter or heat with the system, then the system is an isolated system and

$$\Delta E = 0$$

State of a System

Pressure, Volume and Temperature are variables that describe the state of a system.

The units of pressure we are going to use = atm, torr (mm Hg), Pascal (Nm^2)

$T = \text{Kelvin} = ^\circ\text{C} + 273.15$, and Volume = L or $\text{cm}^3 = \text{mL}$

If we consider a closed system containing water (on earth, and assume gravity has no effect on it, then, PVT can be used to describe the property of the system). PVT can be used to describe other properties of the system such as, density, refractive index, surface tension etc. All these properties including PVT are called *variables of state (VOS)*.

The state of a system can be described in many ways such as the **Initial or final state of a system. VOS depend only on the state of the system and not how the system arrive at the state.** Once a few VOS is used to describe a system, other variables are automatically determined.

In a closed system with adiabatic or insulated wall (negligible heat exchange with the surrounding, $q \sim 0$), the change of state of the system depends only on the amount of work, w , done on the system and not the type of work done or how the work was done. Also, if both heat and work exchanges were done on the system, the changes of state of the system depends only on the sum of the heat and work ($q+w$) and not on how or the type of heat and work done on the system.

The only function of the state that changes when $q=0$ and work, w , is done or when q and w are both applied to a system is the Energy, E of the system. This is stated by the first law of thermodynamics, $\Delta E = q + w$. Hence, ΔE is a **function of the state** and is described as the **internal energy of the system**. If one teaspoon of sugar is converted to CO_2 and H_2O either by burning in a reaction vessel or metabolized by the cells of the body, as long as the initial and final states of the conversion are the same, the change in energy will be the same. That is, the process of getting from the initial to the final states does not affect the net change in energy.

A corollary (result) of the statement is that if a system undergoes a complex process and returns to its initial state, then the change in E is zero. That is for a cyclic system, the change in energy is zero

Since q and w depends on the way one state changes to another, then q and w are not state functions.

Sometimes, a new VOS may be defined by combining some other variable of states. For example, enthalpy, $H = E + PV$

Classes of Variables Of State

There are two classes of VOS, Intensive and Extensive.

Intensive: They are variables that do not change if the system is subdivided. For example, if 100g of water at a uniform temperature is divided into two parts, the temperature will not change. Hence, T is an intensive property. Another example is Pressure

Extensive: If the value of a variable changes when the system is subdivided, then, such a variable is described as extensive e.g dividing the volume of a system, change in mass of a system, E , C and H .

However, an extensive property can become an intensive property if it is expressed as per unit amount. For example, energy can be expressed as energy/mol or energy per gram etc.

Change In Internal Energy For A Chemical Reaction

A chemical reaction can be expressed as



A and B are called reactants and represent a thermodynamic state, E_1 . C and D are called products and represent another state, E_2 . A change in internal energy, $\Delta E = E_2 - E_1$.

By the first law of thermodynamics, ΔE is also $\Delta E = q + w$.

Therefore, to measure ΔE , we need to measure q and w . The values of q and w depends on how the reaction is carried out (is the reaction carried out in a closed or open system)

If the reaction is carried out in a bomb calorimeter, the system is what is in the calorimeter. It implies that the volume of the system is constant, hence the system cannot do work or have work done on it ($w=0$). Therefore, the change in energy is only due to heat changes at constant volume, $\Delta E = q_v$ (heat change at constant volume)

Enthalpy

If a reaction is done in an open vessel, both pressure, P , and Volume, V will affect the change in energy of that reaction. However, the pressure is constant in this case (atmospheric pressure, 1 atm.) while the volume changes. The heat of reaction at constant pressure is designated as q_p .

If the only work done in this system is pressure-volume work, then $w = P\Delta V$, then the change in energy

$$\Delta E = q_p + P\Delta V$$

$q_p = \Delta E - P\Delta V$ (if the work is done on the system at constant pressure) , and

$q_p = \Delta E + P\Delta V$ (if the system does the work at constant pressure)

Enthalpy, H , is defined as heat effect that accompanies a change in the system at constant pressure, hence,

$$\Delta H = q_p = \Delta E + P\Delta V$$

Reactions Involving Only Liquids and Solids

In a reaction where only liquids and solids are involved, the volume is literarily constant. Hence,

$\Delta H = \Delta E$ since $P\Delta V = 0$ (V is constant)

Reactions Involving Gases

6th Week

Thermochemistry

Energy transfer can occur as heat (q) or in several other forms collectively known as work (w). Energy transfers (q,w) affect the total amount of energy within a system (its internal energy). Internal energy is independent of where the energy comes from which may include heat, chemical bonds, intermolecular forces of attraction or repulsion, KE etc.

Work = Force x distance = any form of energy transfer that can be expressed thro' lifting or lowering of weights

Unit = 1 joule = kg/m²s²

Heat: is the energy transferred d/t change in temperature. It flows from a warm body to a colder body. At molecular level, molecules of the warmer body lose KE to the molecules of the colder body, hence the avg. translation energy of the warmer body is lowered while that of the colder body is raised and its temperature increases. The final result is a transfer of heat from the warmer body to the colder body until equilibrium is reached.

It is noteworthy to know that a body contains energy not heat. Heat flows as a result of energy transfer between boundaries of a system and its surroundings. The quantity of heat needed to change the temperature of a body depends on how much change in temperature is delivered, quantity of the substance, and the identity of the substance (type of molecule).

The amount of heat is called the specific heat capacity or heat capacity (SHC). It is the amount of heat needed to raise the temperature of 1g of a body by 1^oC. For water SH = 4.184 J/g^oC = 1 calorie.

Molar heat capacity is the amount of heat needed to raise the T of 1 mole of a substance by 1^oC

In general $Q = mc\Delta T$ Q= quantity of heat, m = mass of body, c= SH, ΔT = change in temperature.

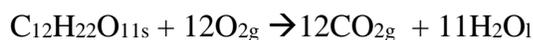
Law of Conservation of Energy

The total energy of a system remains unchanged i.e. energy lost = energy gained

$$Q_{\text{lost}} + q_{\text{gained}} = 0$$

Heat of Reaction.

Sugar (sucrose) can be transformed into carbon dioxide and water in two different ways (1) metabolism by living cells (2) combustion in a reaction vessel such as a bomb calorimeter. The net result is a change in internal energy or conversion of one form of energy to another



The calorific value of sucrose metabolism or combustion can be summarized as

- The difference in the internal energy between the products and the reactants
- The quantity of heat energy transferred between the reactants (system) and its surroundings
- This quantity of heat is called the **Heat of Reaction** = q_{reac}

Calorimetry

In the laboratory, we use a calorimeter to measure the heat of a reaction. A typical calorimeter is the Bomb Calorimeter.

The system in a bomb calorimeter = sugar/ $\text{CO}_2 + \text{H}_2\text{O}$

Surrounding = bomb, thermometer, stirrer, water, electrical wire

Heat evolved during combustion is transferred to water (q_w) and the other item of the surrounding (q_{cal})

By the law of conservation of matter

$$q_{\text{reac}} + q_w + q_{\text{cal}} = 0 \text{ so,}$$

$$q_{\text{reac}} = -(q_w + q_{\text{cal}}) = -(m_w C_w \Delta T + C_{\text{cal}} \Delta T)$$

Example

The burning of 1.010 g of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in a bomb calorimeter causes the water temperature to rise from 24.92 – 28.33 °C. The calorimeter contains 980.0 g of water and the heat capacity of the calorimeter is 785 J/°C. (a) What is the heat of combustion of sucrose expressed in KJ/mole $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (b) Verify the claim of sugar manufacturers that one teaspoon of sugar (4.8g) contain only 18 cal.

Answer

$$\begin{aligned} \text{a) } q_{\text{reac}} &= -(q_w + q_{\text{cal}}) = -(m_w C_w \Delta T + C_{\text{cal}} \Delta T) \\ &= -(980.0 \text{ g} \times 4.184 \text{ J/}^\circ\text{C} \times (28.33 - 24.92)^\circ\text{C} + 785 \text{ J/}^\circ\text{C} \times (28.33 - 24.92)) \\ &= 1.67 \times 10^4 \text{ J} - \text{the amount of heat that raises the temp of 1.010 g of water} \end{aligned}$$

For 1g of water

$$q_{\text{reac}} = 1.67 \times 10^4 / 1.010 \text{ J} = 1.65 \times 10^4 \text{ J} = 16.5 \text{ KJ/g}$$

1 mole of sucrose = 342 g/mole

$$q_{\text{reac}} \text{ for one mole of sucrose} = 342 \text{ g/mole} \times 16.5 \text{ J/g} = 5.64 \times 10^3 \text{ KJ/mole}$$

$$\text{b) } 18 \text{ cal} = 18 \times 4.184 \text{ J/}^\circ\text{C} = 75.312 \text{ J/}^\circ\text{C} = 1 \text{ teaspoon} = 4.8 \text{ g} - \text{ manufacturer}$$

$$\text{Hence 1 g of sugar will} = 75.312 / 4.8 \text{ J/}^\circ\text{C} = 15.69 \text{ J/g}^\circ\text{C}$$

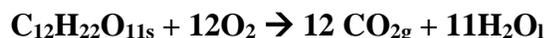
From a) 1g of sucrose will give $1.65 \times 10^4 \text{ J}$ – which implies that the manufacturer's claim is false.

Enthalpy and Enthalpy Changes

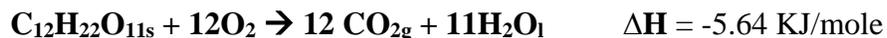
In the bomb Calorimetry experiment with burning of sucrose, the heat of reaction is the change in internal energy between the product and the reactant, ΔE . The volume of the bomb is constant, hence ΔE_v . The heat of reaction of metabolizing sucrose in the human cell is not at constant volume, but the heat of reaction is the same as the one obtained with the bomb calorimeter. If the reaction is carried out in a beaker exposed to the atmosphere, ΔE , will be ΔE_p at constant pressure and is the same as ΔE_v .

In many reactions carried out under atmospheric condition involves some P-V work. In this case, the change in (internal energy) heat of reaction involves heat transfer and P-V work. This heat of reaction is defined as the **Enthalpy change, ΔH** .

Representing ΔH in a Chemical Reaction

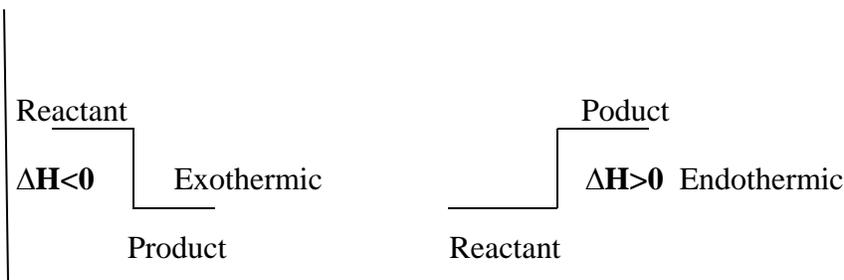


Combustion of sucrose is represented in equation above, For one mole of sucrose, we calculated the heat of reaction as -5.64 KJ/mole, in the example above. The equation can be then be written as



Exothermic and Endothermic Reaction

The negative sign in the above example implies that the enthalpy of the product is lower than that of the reactants. This decrease in ΔH . appears as energy lost in to the surrounding. This type of reaction called Exothermic. The converse is called Endothermic. Both can be represented diagrammatically as



Example: A 1.50 g sample of NH_4NO_3 is added to 35.0 g of water in a Styrofoam cup and stirred until it totally dissolves. The temperature of the solution drops from 22.7°C to 19.4°C . (a) is the process exothermic or endothermic (b) what is the heat of solution of NH_4NO_3 in water represented as $\text{KJ/mol NH}_4\text{NO}_3$?

Answer: (a) the reaction is endothermic- drop in temperature

(b) $q_{\text{NH}_4\text{NO}_3} + q_{\text{water}} = 0$

$$q_{\text{NH}_4\text{NO}_3} = -q_{\text{water}} = -(35 \times 4.184 \text{ J/g}^\circ\text{C} \times (19.4 - 22.7)^\circ\text{C}) = 4.8 \times 10^2 \text{ J}$$

This is the amount of heat lost by water to dissolve 1.5 g of sample.

So, for 1 mole of sample, $\Delta H = 4.8 \times 10^2 \text{ J} / 1.5 \text{ g} \times 1000 \text{ g} = \underline{25.6 \text{ KJ}}$

Relationships Including ΔH

ΔH : is an extensive property i.e. change in the ΔH directly proportional to the amount of substance involved in the process of change. If we double the amount of substances, the change in ΔH will be doubled.

ΔH : change in sign when a process is reversed.

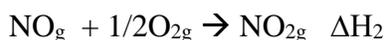
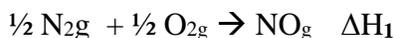
In the process of sucrose combustion, if one add CO_2 to H_2O to form sucrose, the sign of ΔH will change to +ve.

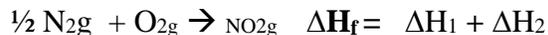
Hess Law of Constant Heat of Summation

If a process be considered to occur in stages or steps (either actual or hypothetical), the enthalpy change for the overall process can be obtained by summing the enthalpy change for the individual steps

Example: $\frac{1}{2} \text{N}_2\text{g} + \frac{1}{2} \text{O}_2\text{g} \rightarrow \text{NO}_2\text{g}$ $\Delta H = ?$

The combustion of N to NO_2 can take the following steps;





Standard Enthalpies of Formation

There are no absolute values of ΔE or ΔH . We only measure changes in their values. Elevation of mountains, hills, and land is measured relative to the sea level and is assigned a value of zero. We can do the same to the Enthalpy by assigning the value of zero to the enthalpy of the elements in their most stable form at 1 atm, Pressure, and specific temperature T. This condition is called standard state.

Enthalpies of compounds can then be measured relative to this arbitrary value of zero. The difference in the enthalpy of a compound in the standard state and those of its elements in their standard state is called the standard molar enthalpy of formation, ΔH_f^0 .

Example

Determine the enthalpy of formation of $\text{C}_2\text{H}_6\text{g}$ for the following reaction



Answer:



The aim is to synthesize $\text{C}_2\text{H}_6\text{g}$. so we can reverse equation 1 to form $\text{C}_2\text{H}_6\text{g}$



To obtain proper number of moles of each reactant and product, we can multiply eqns. 2 and 3 by 3 and 4 respectively;



Assignment

Determine the enthalpy change for the combustion of 1 mole of C_2H_6g with all reactants and product in their standard state.



Given that $\Delta H_f(C_2H_6g) = -84.68 \text{ KJ/mol}$, $\Delta H_f(CO_2g) = -393.4 \text{ KJ/mol}$, $\Delta H_f(H_2O_l) = -285.85 \text{ KJ/mol}$

Answer



$$\Delta H_1 = \sum \Delta H_{\text{product}} - \sum \Delta H_{\text{reactant}}$$

$$= ((2x\Delta H_f(CO_{2g}) + 3x\Delta H_f(H_2O_l)) - \Delta H_f(C_2H_6g))$$

$$= ((2x(-393.4) + 3x(-285.85)) - (-84.68)) \text{ KJ/mol}$$

$$= (-1644.5 + 84.68) = -1559.67 \text{ KJ/mol}$$

Assignment 2.

The heats of combustion per mole of sucrose, fructose, glucose and water are -1349.6, -675.6, 673.0 and -285.85 KJ respectively. Use this data to calculate the $\Delta H_{\text{reaction}}$ for the following reaction



Sucrose fructose glucose

Answer

$$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{product}} - \sum \Delta H_{\text{reactant}}$$

$$= (-675.6 + (-673.0)) - (-1349.6 + (-285.85)) \text{ KJ/mol}$$

$$= (-1348.6 + 1635.45) = 286.85 \text{ KJ/mol}$$

27/3/2012

Relationship Between H and E

In a chemical reaction that involves only liquids and solids, there is little or no change in volume, hence $\Delta H = \Delta E$ are equal to each other since $P\Delta V = 0$.

But when gases are involved, there is a great change in volume and PV work will be done

Consider the equation: $C_{10}H_{8s} + 12O_{2g} \rightarrow 10CO_{2g} + 4H_2O_l$ (1) $\Delta E = -5151.9KJ/mol$

If we consider T and P to be constant and CO_2 and O_2 as ideal gases,

$V_{CO_2} = n_{CO_2}RT/P$ and $V_{O_2} = n_{O_2}RT/P$ (2)

$\Delta V = V_{CO_2} - V_{O_2} = (n_{CO_2} - n_{O_2})RT/P = \Delta n_g RT/P$ (3) where $\Delta n_g = \#$ of moles of product - # mole of reactant

$$\Delta H = \Delta E + P\Delta V = \Delta E + P\Delta n_g RT/P = \Delta E + \Delta n_g RT \quad (4)$$

Eqn 4 is often used at 25°C. If H and E units are in KJ/mol, then $R = 8.314 \times 10^{-3} \text{KJ/molK}$

$$RT = 8.314 \times 10^{-3} \text{KJ/molK} \times 298 \text{K} = 2.48 \text{KJ/mol}$$

Hence equation (4) $\Delta H = \Delta E + 2.48\Delta n_g$ (5)

Assignment. Use equation (1) and (5) to calculate ΔH for the combustion of $C_{10}H_{18}$

Answer: $\Delta H = [-5151.9 + 2.48(-2)] \text{KJ/mol} = -5156.9 \text{KJ/mol}$

Second Law of Thermodynamics

Spontaneous Change (Natural Process): is one that happens without contribution from external stimuli. The spontaneous change will continue until equilibrium is reached and the net change will stop. Example of a mechanical spontaneous process is the whining down of a clock. The whining needs external input and hence is non-spontaneous, but the whining down is spontaneous and continues until it is exhausted. An example of a spontaneous chemical reaction is that of the element Fe exposed to the atmosphere. It starts to rust and continues to do so until all the iron is consumed. The reverse is possible but is non spontaneous.

In both examples given, we can conclude that:

- (1) Spontaneous processes have a reversible non spontaneous process
- (2) Both spontaneous and non spontaneous processes are possible but only the spontaneous process is natural. Non spontaneous process needs external influence.
- (3) It is possible to predict the direction of spontaneous change: Determine the Criterion for spontaneous change.

There are both endothermic and exothermic reactions that are spontaneous. Hence, a parameter that will reach a minimum when a chemical reaction has reached an equilibrium is desired as a criterion for spontaneous process.

If we look at the physical process of a ball falling down the hill, change in **potential energy** down the hill is a parameter that drives the spontaneous change. Similarly, a change in **chemical potential** can be said to drive the spontaneous process that occur during a chemical reaction. This chemical potential is assumed to have a minimum value in between formation of the product from the reactant. At this point, the reaction is at

equilibrium and the direction of spontaneous process is towards this equilibrium. The reaction coefficient Q will be equal to the equilibrium constant.

Second Law of Thermodynamics

However, the concept of energy in the first law does not account for the observation that natural processes have a preferred direction of progress. For example, spontaneously, heat always flows to regions of lower temperature, never to regions of higher temperature without external work being performed on the system. The first law is completely symmetrical with respect to the initial and final states of an evolving system. The key concept for the explanation of this phenomenon through the second law of thermodynamics is the definition of a new physical property, the

Entropy.

A change in the entropy (S) of a system is the infinitesimal transfer of heat (Q) to a closed system driving a reversible process, divided by the equilibrium temperature (T) of the system. ^[1]

$$dS = \frac{\delta Q}{T}$$

- For a closed thermodynamic system, it is a quantitative measure of the amount of thermal energy not available to do work.
- A measure of the disorder or randomness in a closed system.
- A measure of the loss of information in a transmitted message.
- The tendency for all matter and energy in the universe to evolve toward a state of inert uniformity.
- Inevitable and steady deterioration of a system or society.

In general, entropy increase is expected to increase in the following processes

1. Pure liquid or liquid solutions are made from solids
2. Gases are formed from solids or liquids
3. The # of moles of gases increases during a chemical reaction
4. The temperature of a substance increased

$\Delta S_{\text{universal}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$. All spontaneous or natural process produce an increase in the entropy of the universe.

Assignment: Predict whether there will be an increase or decrease in entropy in the following reactions



Answer: 1. There is a change from solid to gas, so there is an increase in entropy

2. 2 moles of gas produces 3 moles of gas. There is a decrease in the # of moles hence a decrease in entropy

3. Na and Cl ions are in random motion in the aqueous solution but forms a solid crystalline NaCl as product. There is an increase in orderliness hence an decrease in entropy
4. The net change in the # of moles of reactant and products are the same, hence there is no change in entropy.

Free Energy and Spontaneous Change

Consider a spontaneous process occurring at constant T, P, and where only PV work is done. There will be a heat change that will accompany the process and is equal to $q_p = \Delta H_{\text{system}}$. ΔH_{surr} is the negative of that of the system.

$\Delta S = q/T\Delta$. hence for this process, $q=q_{\text{sys}}$ and therefore

$$\Delta S_{\text{sys}} = \Delta H_{\text{sys}}/T \quad \text{and} \quad \Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$$

In essence

$$\Delta S_{\text{Univee}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T =$$

$$T\Delta S_{\text{univ}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} = -(\Delta H_{\text{sys}} - T\Delta S_{\text{sys}})$$

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

$-T\Delta S_{\text{univ}}$ is described as the Gibbs Free Energy G

$$\Delta G = \Delta H - T\Delta S$$

Assignment: The standard molar enthalpy of formation of silver oxide is -30.59 KJ/mol at 298K. The standard molar Gibbs free energy change, ΔG , for the decomposition of silver oxide at 298 K is shown below



What is the molar entropy change for this reaction?

$$\text{Answer: } \Delta S = (\Delta H_{\text{reac}} - \Delta G)/T$$

We need to calculate ΔH before we can solve for ΔS

$\Delta H_{\text{reac}} = \Delta H_{\text{pr}} \Delta H_{\text{react}} = [(4\Delta H_{\text{f}}\text{Ag}_s + \Delta H_{\text{f}}\text{O}_g) - (2\Delta H_{\text{f}}\text{Ag}_2\text{O}_s)]$ remember that ΔH_{f} of elements = 0. Therefore,

$$\Delta H_{\text{reac}} = [0+0 - 2(-30.59 \text{ KJ/mol})] = 61.18 \text{ KJ/mol}$$

Therefore, $\Delta S = (61.18 - 22.43)\text{KJ/mol}/298 \text{ K} = 0.130 \text{ KJ/mol K}$

Assignment 2

What is ΔG^0 @ 298K for the reaction



$$\Delta G_f^0(C_s) = 0 \text{ KJ/mol}$$

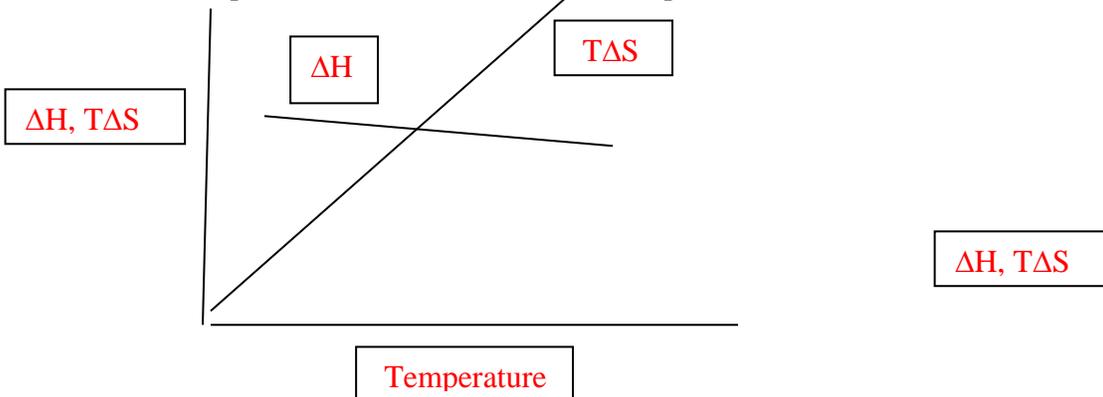
$$\Delta G_f^0(CO_{2g}) = -394.38 \text{ KJ/mol}$$

$$\Delta G_f^0(CO_g) = -137.78 \text{ KJ/mol}$$

$$\begin{aligned} \text{Answer: } \Delta G_r^0 &= \Delta G_{\text{prod}}^0 - \Delta G_{\text{reac}}^0 \\ &= [2\Delta G_f^0(CO_g) - (\Delta G_f^0(CO_{2g}) + \Delta G_f^0(C_s))] \\ &= [2x(-137.78) - (0 - 394.38)] \\ &= 119.82 \text{ KJ/mol} \end{aligned}$$

3/4/2012 Free Energy and Equilibrium

For a spontaneous process $\Delta G^0 < 0$, and for a non-spontaneous process, $\Delta G^0 > 0$. At equilibrium, $\Delta G^0 = 0$. There is an equal tendency for a process to proceed in the forward/backward direction at equilibrium. An infinitesimal change in any variable at equilibrium (e.g. T, P), will cause a net change or a shift in the position of equilibrium. An hypothetical situation at equilibrium can be represented as shown in the diagram below for a phase diagram of two processes. Equilibrium is reached at the intersection of the two processes. The plot shows the variation of ΔH and $T\Delta S$ with temperature. ΔH has a positive and negative slope which decreases gradually and is not temperature sensitive. $T\Delta S$ slope is steep because T is involved in the expression.

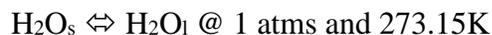


On the left side of the diagram, the vertical distance between ΔH and $T\Delta S$ lines is ΔH and $T\Delta S$ is $\Delta G = \Delta H - T\Delta S$. ΔG is large and positive hence $\Delta G > 0$. At the intersection $\Delta G = 0$ (equilibrium). On the right side $T\Delta S$ is larger than ΔH hence ΔG is negative.

Phase Transition

We can liken the transition of ice to liquid water (melting of ice) to the graph shown above.. If we deal with solid and liquid ice in their standard states, the intersection will be the melting point of ice, which is 273.15 K. This means that the melting point of ice is spontaneous above 273.15K and vice versa. We can use the equilibrium to determine entropy of change for melting ice.

For the melting process



$$\Delta G^0 = \Delta H - T\Delta S = 0$$

$$\text{Therefore, } \Delta H = T\Delta S$$

$$\text{Hence } \Delta S = \Delta H/T$$

Molar heat of fusion of ice @273.15K = 6.02 KJ/mol

$$\text{Then, } \Delta S = 6.02/273.15 = 2.2 \times 10^{-2} \text{ KJ/mol}$$

Assignment 1

What is the standard molar entropy of vaporization of water at 100°C? The standard molar enthalpy of vaporization @ 100°C is 40.7 KJ/mol

Answer



$$\Delta S = \Delta H_{\text{vap}}/T_{\text{vap}} = 40.7/273.15 = 0.149 \text{ KJ/mol}$$

Relationship between ΔG^0 and K

if ΔG – the free energy for non standard states, then,

$$\Delta G = \Delta G^0 + RT \ln Q \text{ where } Q = [\text{product}]/[\text{reactant}] \text{ or the equilibrium constant, K}$$

$$\overline{G} = \Delta G^0 + 2.303RT \log K = 0 \text{ at equilibrium}$$

$$\text{Therefore, } \Delta G^0 = -RT \ln K = 2.303 \log K$$

The Third Law of Thermodynamics

Absolute values of most thermodynamic properties cannot be determined except that of entropy. This is made possible by the third law of thermodynamics which says: **the entropy of a pure and perfect compound at the absolute zero of temperature is zero.**

- A pure perfect crystal @ absolute zero of temperature is the greatest order possible for a thermodynamic system
- As the temperature increases, the entropy also increases
- Absolute entropies are always positive
- If more than one form of a solid exist, there will be a small entropy increase when converting from one form to the other.
- Such increase occur when ice melts or water turns into vapor or Iodine sublimes.

Term Assignment(15%)

1. Draw the variation of enthalpy and $T\Delta S$ with temperature for the phase transition process of liquid water to gaseous water.
2. Use the phase transition diagram to explain the relationship between free energy, enthalpy, and entropy
3. Use the equation derived in question 2 to relate entropy to enthalpy and temperature at standard conditions.