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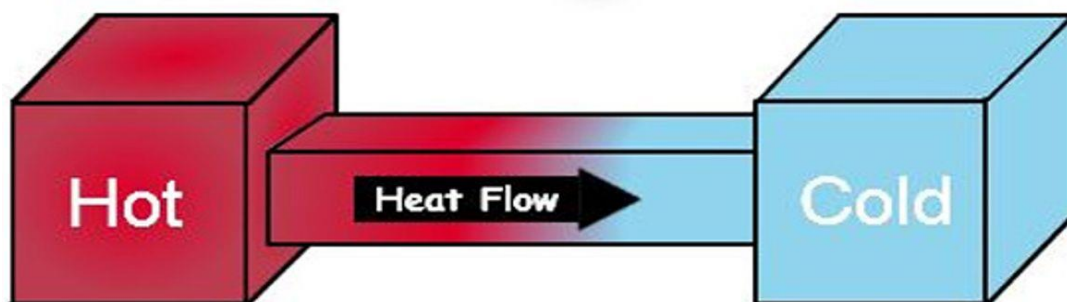
College of Science for women

Chemistry Department

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Introduction:

Rapid development of the study of external universe lead to the separation of chemistry as a special branch of natural science.

Chemical changes are always associated with a number of diversified physical changes like heat transfer, absorption or emission of electromagnetic radiations, electrical and surface phenomena.

Physical chemistry, branch **of chemistry concerned with interactions and transformations of materials**. Unlike other branches, it deals with the principles of physics underlying all chemical interactions (e.g., gas laws), seeking to measure, correlate, and explain the quantitative aspects of reactions.

Physical chemists are focused on understanding the physical properties of atoms and molecules, the way chemical reactions work, and what these properties reveal. Their discoveries are based on understanding chemical properties and describing their behavior using theories of physics and mathematical computations.

Thermodynamics is **the study of the relations between heat, work, temperature, and energy**. The laws of thermodynamics describe how the energy in a system changes and whether the system can perform useful work on its surroundings.

The most important laws of thermodynamics are:

- *The zeroth law of thermodynamics.* When two systems are each in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other. This property makes it meaningful to use thermometers as the "third system" and to define a temperature scale.

- *The first law of thermodynamics or the law of conservation of energy.* The change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings.

- *The second law of thermodynamics.* Heat does not flow spontaneously from a colder region to a hotter region, or, equivalently, heat at a given temperature cannot be converted entirely into work. Consequently, the entropy of a closed system, or heat energy per unit temperature, increases over time toward some maximum value. Thus, all closed systems tend toward an equilibrium state in which entropy is at a maximum and no energy is available to do useful work.

- *The third law of thermodynamics.* The entropy of a perfect crystal of an element in its most stable form tends to zero as the temperature approaches absolute zero. This allows an absolute scale for entropy to be established that, from a statistical point of view, determines the degree of randomness or disorder in a system.

International system of Units (SI)

The **International System of Units** (**SI**, abbreviated from the French *Système international (d'unités)* is the modern form of the metric system. It is the only system of measurement with an official status in nearly every country in the world. It comprises a coherent system of units of measurement starting with seven base units, which are the second (the unit of time with the symbol s), meter (length, m), kilogram (mass, kg), ampere (electric current, A), kelvin (thermodynamic temperature, K), mole (amount of substance, mol), and candela (luminous intensity, cd)

Units in the Metric System

In the metric and SI systems, one unit is used for each type of measurement.

Measurement	Metric	SI
Length	meter (m)	meter (m)
Volume	liter (L)	cubic meter (m³)
Mass	gram (g)	kilogram (kg)
Temperature	Celsius (°C)	Kelvin (K)
Time	second (s)	second (s)

Some principle derived from SI unit

Force	Newton	N	$Kg\ m\ s^{-2}$
Work, energy, quantity of heat	Joule	J	$N.m = Kg\ m^2\ s^{-2}$
Pressure	Pascal	Pa	$N\ m^{-2}$

Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	$1\ N\ m^{-2}, 1\ kg\ m^{-1}\ s^{-2}$
bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa
torr	1 Torr	$(101\ 325/760)$ Pa $= 133.32 \ldots$ Pa
millimetres of mercury	1 mmHg	$133.322 \ldots$ Pa
pound per square inch	1 psi	$6.894\ 757 \ldots$ kPa

Prefixes that modify of metric system of units

Prefiks	Symbol	Multiplying factor
yotta	Y	1 000 000 000 000 000 000 000 000 = 10^{24}
zetta	Z	1 000 000 000 000 000 000 000 = 10^{21}
exa	E	1 000 000 000 000 000 000 = 10^{18}
peta	P	1 000 000 000 000 000 = 10^{15}
tera	T	1 000 000 000 000 = 10^{12}
giga	G	1 000 000 000 = 10^{9}
mega	M	1 000 000 = 10^{6}
kilo	k	1 000 = 10^{3}
hecto	h	100 = 10^{2}
deka	da	10 = 10^{1}
deci	d	0,1 = 10^{-1}
centi	c	0,01 = 10^{-2}
milli	m	0,001 = 10^{-3}
mikro	μ	0,000 001 = 10^{-6}
nano	n	0,000 000 001 = 10^{-9}
piko	p	0,000 000 000 001 = 10^{-12}
femto	f	0,000 000 000 000 001 = 10^{-15}
atto	a	0,000 000 000 000 000 001 = 10^{-18}
zepto	z	0,000 000 000 000 000 000 001 = 10^{-21}
yocto	y	0,000 000 000 000 000 000 000 001 = 10^{-24}

THE DEFINING CONSTANTS OF THE INTERNATIONAL SYSTEM OF UNITS

Defining constant	Symbol	Numerical value	Unit
hyperfine transition frequency of Cs	$\Delta\nu_{Cs}$	9 192 631 770	Hz
speed of light in vacuum	c	299 792 458	$m\ s^{-1}$
Planck constant*	h	$6.626\,070\,15 \times 10^{-34}$	$J\ Hz^{-1}$
elementary charge*	e	$1.602\,176\,634 \times 10^{-19}$	C
Boltzmann constant*	k	$1.380\,649 \times 10^{-23}$	$J\ K^{-1}$
Avogadro constant*	N_A	$6.022\,140\,76 \times 10^{23}$	mol^{-1}
luminous efficacy	K_{cd}	683	$lm\ W^{-1}$

1. THE PROPERTIES OF GASES

Gas is a state of matter that has no fixed shape and no fixed volume. Gases have lower density than other states of matter, such as solids and liquids. There is a great deal of empty space between particles, which have a lot of kinetic energy. The particles move very fast and collide into one another, causing them to diffuse, or spread out, until they are evenly distributed throughout the volume of the container.
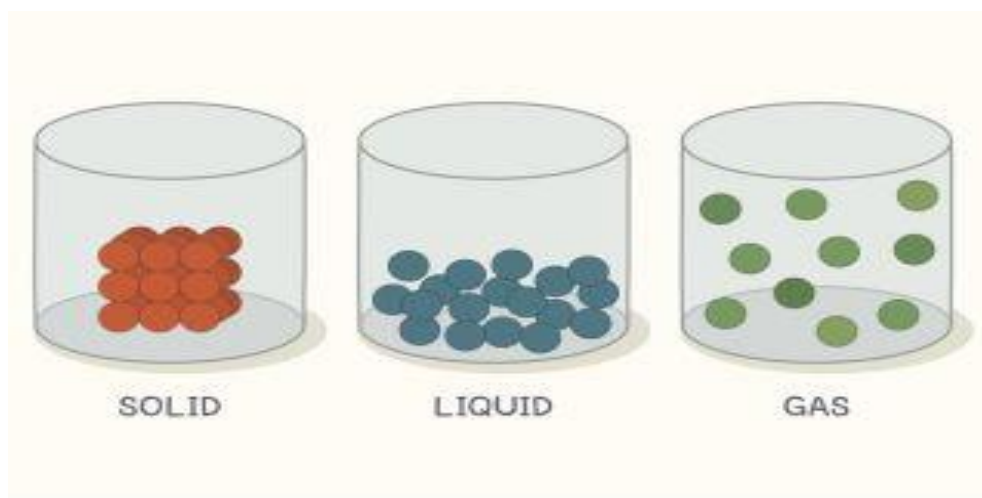
Gases are conveniently classified into two types, namely:

Ideal gas obeys all gas laws under all conditions of pressure and temperature.

An ideal gas is defined as one in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces

Real gas or nonideal gas is defined as a gas that at all standard pressure and temperature conditions does not obey gas laws. It deviates from its ideal behaviour and obeys gas laws only at conditions of low pressure and high temperature. They obey Vander Waal's real gas equation.

1.1. Ideal Gas Behaviour

- Boyle's law: Boyle's Law is a basic law in chemistry describing the behavior of a gas held at a constant temperature. The law, discovered by Robert A. Boyle in 1662, states that at a fixed temperature, the volume of gas is inversely proportional to the pressure exerted by the gas. In other words, when a gas is pumped into an enclosed space, it will shrink to fit into that space, but the pressure that gas puts on the container will increase.
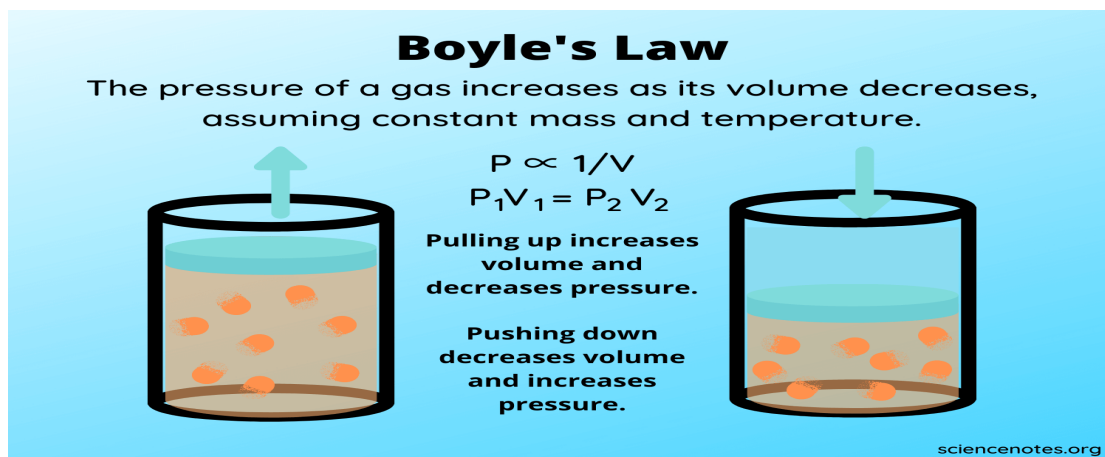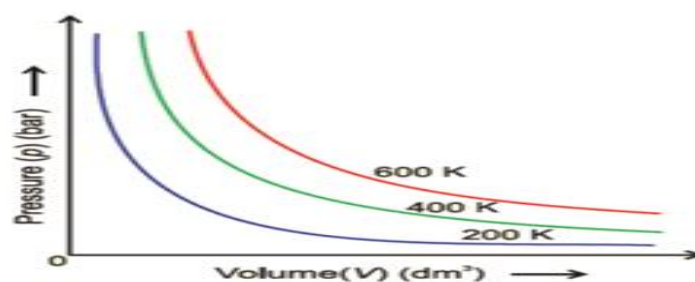

Mathematically:

$$P\alpha \frac{1}{V} \quad at\ constant\ temperature\ (T)$$

$$PV = constant$$

$$P_1V_1 = P_2V_2 \quad or \quad \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

Charles's law: A statement that the volume occupied by a fixed amount of gas is directly proportional to its absolute temperature, if the pressure remains constant. This empirical relation was first suggested by the French physicist J.-A.-C. Charles about 1787.
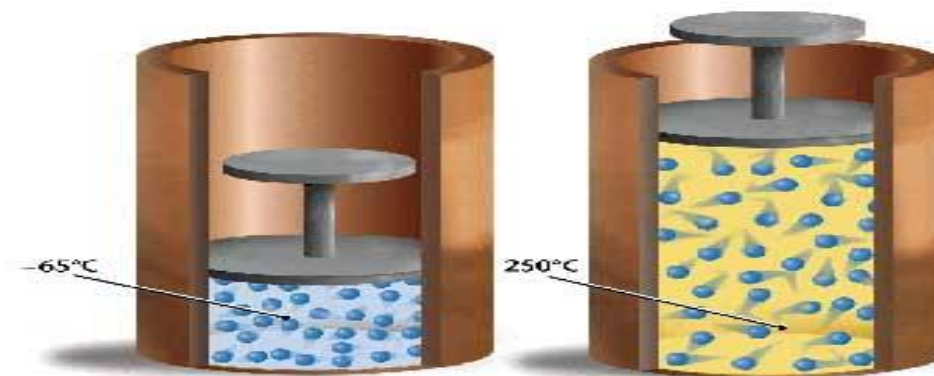
Mathematically:

$$V \alpha T \quad at\ constant\ pressure\ (P)$$

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

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad or \qquad V_1 T_2 = V_2 T_1$$

Charles's Law

- This suggests that -273°C is the lowest possible temperature
- In fact, experiments have shown that all matter cannot be cooled below this temperature
- This temperature is defined as **absolute zero**
- A scientist by the named of Lord Kelvin recognized this and devised a whole new temperature scaled based on **absolute zero**
- **On the Kelvin temperature scale, 0 is the lowest possible temperature**
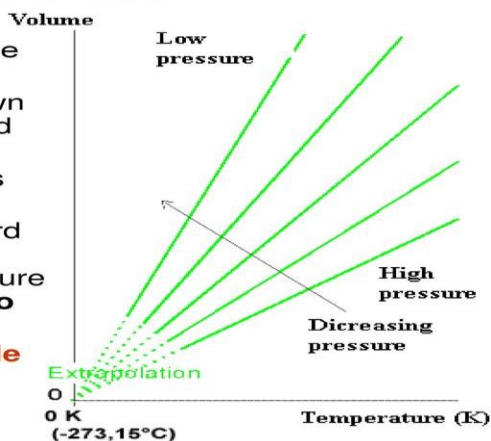
- **Avogadro's law:**

Avogadro's law states that "equal volumes of all gases, at the same temperature and pressure, have the same number of molecules.

The law is named after Amedeo Avogadro who, in 1812, hypothesized that two given samples of an ideal gas, of the same volume and at the same temperature and pressure, contain the same number of molecules. As an example, equal volumes of gaseous hydrogen and nitrogen contain the same number of atoms when they are at the same temperature and pressure, and observe ideal gas behavior.

Mathematically:

$$V \alpha\, n \quad at\ constant\ T\ and\ P$$

$$\frac{V}{n} = constant$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$N_A = 6.023 \times 10^{23}\ mol^{-1}$$

Equation of State of an Ideal Gas

For ideal gas, the equation of states is PV equal to nRT. It is a result of combination of Boyle's and Charles's laws.

$$PV = constant$$

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

$$\frac{PV}{T} = constant$$

The value of constant was calculated at standard temperature, volume and pressure for one mole of any gas;

STP= Pressure= 1atm, temperature= 273.15 K, volume= 22.414 liters

$$R = \frac{1atm \times 22.414L}{1\ mol\ \times 273.15K} = 0.08206 \text{ L. atm. mol}^{-1}.\text{K}^{-1}$$

R= 8.314 x 10^{7}erg mol^{-1}.K^{-1}

R= 8.314 J. mol^{-1}.K^{-1}

R= 1.987 cal. mol^{-1}.K^{-1}

Thermodynamic systems are specified by an equation of state that constrains the values that the state variables may assume. For a given amount of substance contained in a system, the temperature, volume, and pressure are not independent quantities; they are connected by a relationship of the general form**.**

$$PV = nRT$$

1. P is pressure measured in atmosphere
2. V is volume measured in Liters
3. n is moles of gas present
4. R is a constant that converts the units. Its value is 0.0821 atm.L/mol.K
5. T is temerature measured in Kelvin
6. Simple algebra can be used to solve for any of these values.

$$p = \frac{nRT}{V} \qquad V = \frac{nRT}{P} \qquad n = \frac{PV}{RT} \qquad T = \frac{PV}{nR} \qquad R = \frac{PV}{nT}$$

Applications of the Ideal Gas Law: Molar Mass, Density, and Volume

The volume occupied by one mole of a substance is its molar volume. The ideal gas law, $PV = nRT$, suggests that the volume of a given quantity of gas and the number of moles in a given volume of gas vary with changes in pressure and temperature. At standard temperature and pressure, or STP (273.15 K and 1 atm), one mole of an ideal gas (regardless of its identity) has a volume of about 22.4 L — this is referred to as the standard molar volume.

For example, one mole each of hydrogen, oxygen, argon, or carbon dioxide occupies 22.4 liters at STP. This implies that 0.5 moles of any gas at STP occupies a volume of 11.2 L, and similarly, 2 moles of any gas at STP occupies a volume of 44.8 L.

The ideal gas law is universal, relating the pressure, volume, number of moles, and temperature of a gas regardless of the chemical identity of the gas:

$$PV = nRT$$

$$n = \frac{w}{M}$$

$$PV = \frac{w}{M} RT$$

$$M = \frac{wRT}{PV}$$

Density is the ratio of mass over volume. Rearranging the ideal gas equation to isolate V and substituting into the density equation yields:

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

$$M = \frac{\rho RT}{P}$$

This equation tells us that gas density is directly proportional to the pressure and molar mass, and inversely proportional to the temperature. For example, CO_2 (molar mass = 44 g/mol) is heavier than N_2 (molar mass = 28 g/mol) or O_2 (molar mass = 32 g/mol), and is therefore denser than air. For this reason, CO_2 released from a CO_2 fire extinguisher blankets a fire, preventing O_2 from reaching the combustible material. The phenomenon of the lifting of hot air balloons depends on the relationship that gases of equal molar masses (such as air) have lower densities at higher temperatures, and therefore hot air balloons can float.

First law of Thermodynamics

Thermodynamics: Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy in physico-chemical transformation. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter. Thermodynamics, then, is concerned with several properties of matter; foremost among these is heat. Heat is energy transferred between substances or systems due to a temperature difference between them.

- Thermodynamics based on three fundamental laws. These laws are not based on any theory but based on experimental facts.
- Thermodynamics can predict whether a given process will occur spontaneously or not.
- Thermodynamics deals with the state of the system and make no mention of the mechanism.
- Thermodynamics answer to why a change occurs but not how it occurs.

Thermodynamics terms

- **System:** is the part of the Universe which is chosen for thermodynamic consideration**.**

  The remaining portion of the universe, excluding the system, is called **surrounding.**

  <center>Universe = system + surrounding</center>

A system usually consists of a definite amount of one or more substance and is separated from the surrounding by a real or imaginary boundary through which matter and energy can flow from the system to the surrounding or vice versa**.**

Open system: A system is said to be an open system if it can exchange both matter and energy with the surrounding**.**

Closed system: If a system can exchange only energy with the surrounding but not matter.

Isolated system: If a system can neither exchange matter nor energy with the surrounding**.**
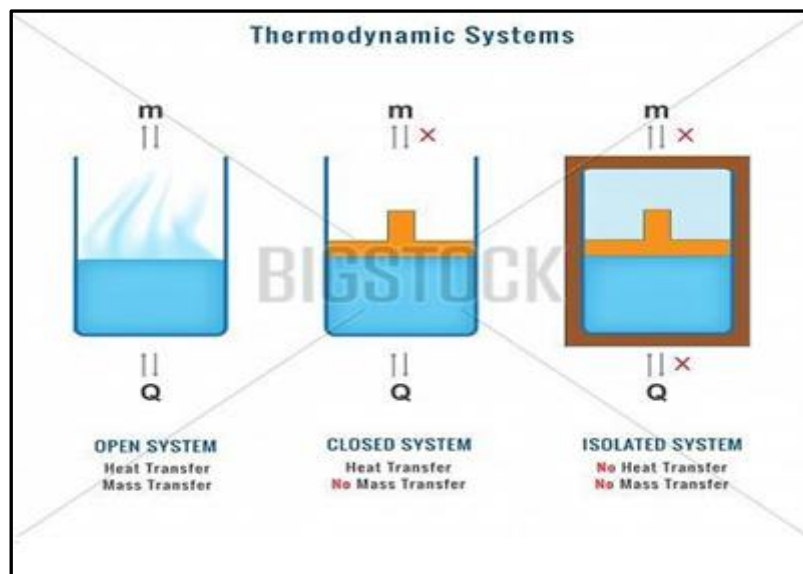
Properties of a System:

- **Extensive Properties**: the quantity of matter in the system. For example, the mass of a sample is an extensive quantity; it depends on the amount of substance like mass, volume, internal energy, heat contents, free energy, entropy, and heat capacity.

- **Intensive Properties**: is a property of matter that depends only on the type of matter in a sample and not on the amount. The electrical conductivity of a substance is a property that depends only on the type of substance. Silver, gold, and copper are excellent conductors of electricity, while glass and plastic are poor conductors. Other

intensive properties include color, temperature, pressure, density, surface tension, chemical potential, refractive index and solubility.

- **Process**: A thermodynamic process is defined as a change from one equilibrium state to another. The initial and final states are the defining elements of the process. ... In this process energy may be transferred form or into the system and also work can be done by or on the system.

- **Cyclic process**: It is a sequence of processes that leave the system in the same state in which it started. When a system undergoes a cyclic process, its initial and final internal energies are equal.

- **An isothermal process**: is a thermodynamic process in which the temperature of a system remains constant. The transfer of heat into or out of the system happens so slowly that thermal equilibrium is maintained.

- **An adiabatic process** is a process in which no heat is gained or lost by the system and surrounding.

- **An isochoric process**: also called a constant-volume process in which the volume of the system remains constant.

- **An isobaric process** is a process taking place at constant pressure.

- **Reversible Process:** is one which can be taken from its initial state to another state, and then back to the initial state without any change to either the system or the surroundings or during the transformation, the system does not deviate from equilibrium by more than infinitesimal amount.

- **Irreversible Process:** a process in which the system and the surroundings do not return to their original condition. This process is actual processes, carried out in finite time, occurs spontaneously and it does not remain in equilibrium during the transformation.

- **Quasi-static process:** is a thermodynamic process that happens slowly enough for the system to remain in internal thermodynamic equilibrium. An example of this is quasi-static expansion, where the volume of a system changes so slowly that the pressure remains uniform throughout the system at each instant of time during the process.

- **Work, Heat and Energy**

  Energy can be exchanged between a system and its surrounding by doing work or by heating. A system does work when it cause motion against an opposing force.

  Heating: is the process of transferring energy as a result of a temperature difference between the system and its surrounding. So we can define Heat is the energy transferred between two objects (or two parts of a system) because of a temperature difference.

  Work is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight.

  Mechanical work is defined as an energy transfer to the system through the change of an external parameter. Work is the only energy which is transferred to the system through external forces.
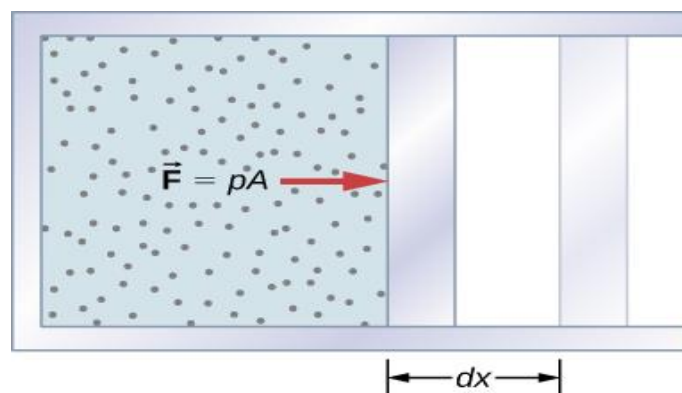

Figure (6) Work Done by a System

A force created from any source can do work by moving an object through a displacement. Then how does a thermodynamic system do work? (Figure 6) shows a gas confined to a cylinder that has a movable piston at one end. If the gas expands against the piston, it exerts a force through a distance and does work on the piston. If the piston compresses the gas as it is moved inward, work is also done - in this case, on the gas. The work associated with such volume changes can be determined as follows: Let the gas pressure on the piston face be p. Then the force on the piston due to the gas is pA, where A is the area of the face. When the piston is pushed outward an infinitesimal distance dx, the magnitude of the work done by the gas is

$$dW = Fdx = pAdx$$

Since the change in volume of the gas is dV= Adx , this becomes

$$dW = PdV$$

For a finite change in volume from V_1 to V_2 we can integrate this equation from V_1 to V_2 to find the net work:

$$W = \int_{V_1}^{V_2} PdV$$

This integral is only meaningful for a quasi-static process, which means a process that takes place in infinitesimally small steps, keeping the system at thermal equilibrium. Only then does a well-defined mathematical relationship (the equation of state) exist between the pressure and volume. This relationship can be plotted on a pV diagram of pressure versus volume, where the curve is the change of state. We can approximate such a process as one that occurs slowly, through a series of equilibrium states. The integral is interpreted graphically as the area under the PV curve (the

shaded area of (Figure7). Work done by the gas is positive for expansion and negative for compression.

When a gas expands slowly from V_1 to V_2 the work done by the system is represented by the shaded area under the *PV* curve.
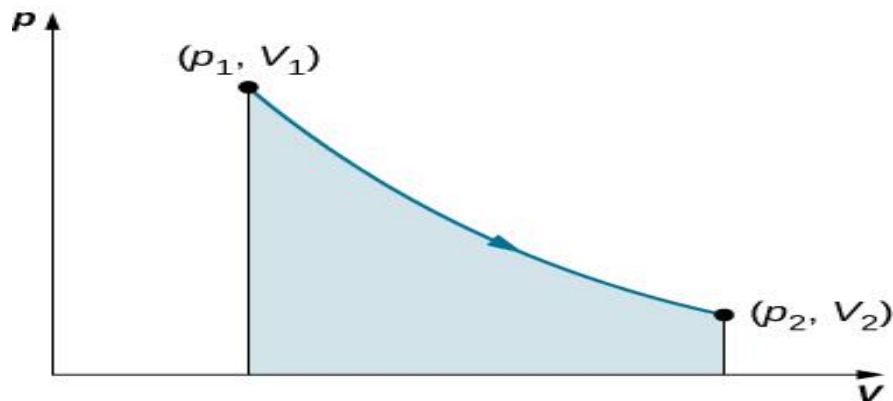
(Figure 7): *PV* curve

Consider the two processes involving an ideal gas that are represented by paths *AC* and *ABC* in (Figure 8). The first process is an isothermal expansion, with the volume of the gas changing its volume from V_1 to V_2. This isothermal process is represented by the curve between points *A* and *C*. The gas is kept at a constant temperature *T* by keeping it in thermal equilibrium with a heat reservoir at that temperature. From (Figure 8) and the ideal gas law,

$$W = \int_{V_1}^{V_2} P\, dV = W = \int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV$$
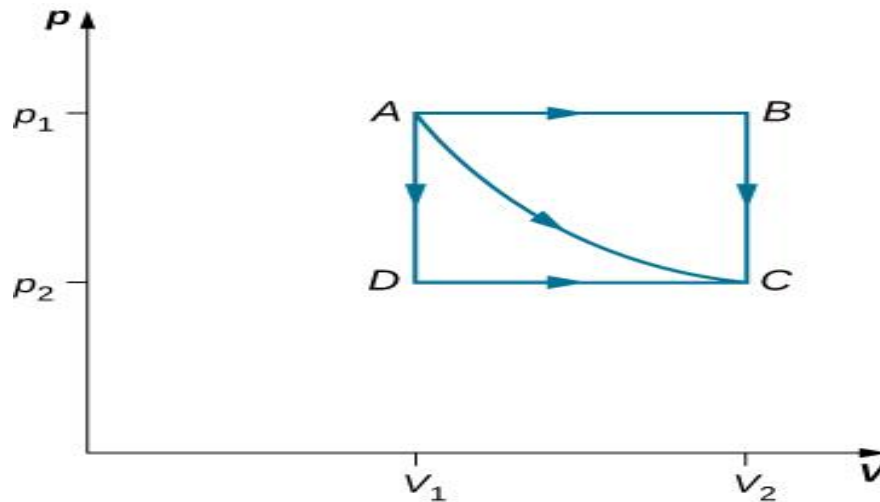
(Figure 8): work done in thermodynamic process

The expansion is isothermal, so *T* remains constant over the entire process. Since *n* and *R* are also constant, the only variable in the integrand is *V*, so the work done by an ideal gas in an isothermal process is:

$$W = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln\frac{V_2}{V_1}$$

Notice that if $V_2 > V_1$ (expansion), *W* is positive, as expected.

The straight lines from *A* to *B* and then from *B* to *C* represent a different process. Here, a gas at a pressure P_1 first expands isobarically (constant pressure) and quasi-statically from V_1 to V_2, after which it cools quasi-statically at the constant volume V_2 until its pressure drops to P_1. From *A* to *B*, the pressure is constant at *p*, so the work over this part of the path is:

$$W = \int_{V_1}^{V_2} PdV = P_1 \int_{V_1}^{V_2} dV = P_1(V_2 - V_1)$$

From *B* to *C*, there is no change in volume (dV=0) and therefore no work is done

$$W = \int_{V_1}^{V_2} PdV = 0$$

The net work over the path ABC is then:

$$W = P_1(V_2 - V_1) + 0 = P_1(V_2 - V_1)$$

A comparison of the expressions for the work done by the gas in the two processes of (Figure 8) shows that they are quite different. This illustrates a very important property of thermodynamic work: It is *path dependent*. We cannot determine the work done by a system as it goes from one equilibrium state to another unless we know its thermodynamic path. Different values of the work are associated with different paths.

Check Your Understanding How much work is done by the gas, as given in (Figure), when it expands quasi-statically along the path ADC?

State function a physical quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained. For examples: pressure, volume, temperature.

Energy, enthalpy, internal and entropy are state quantities because they describe quantitatively an equilibrium state of a thermodynamic system, irrespective of how the system arrived in that state.

Path functions are properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are heat and work.

Work in Reversible expansion of a gas

$$W_{rev} = -\int_{V_1}^{V_2} P_{ext}\, dV$$

For expansion of the gas, Pext should be less than the pressure (P) of the gas

$$P_{ext} = P - dP. \; dP \text{ is small} \rightarrow P_{ext} = P$$

$$W_{ext} = -\int_{V_1}^{V_2} P\, dV$$

If gas behaves ideally:

$$-W = \int_{V_1}^{V_2}\left(\frac{nRT}{V}\right)dV = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{P_1}{P_2}$$

$$\leftarrow isothermal\ reversible$$

Work in Irreversible expansion of a gas

$$W = -P_2(V_2 - V_1)$$

Expansion against constant pressure is irreversible expansion.

NOTE:

- When the system does work and loses energy (w is negative).
- In the Expansion $V_2 > V_1 \rightarrow$ **W= -**
- In the Expansion $V_2 < V_1 \rightarrow$ **W= +**
- When the energy increased work has become done on the system (W is positive).
- When the External pressure is zero (W=0). Expansion against zero external pressure is called free expansion. (or called gas expands in vacuum).

Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that if two bodies are each in thermal equilibrium with some third body, then they are also in equilibrium with each other. ... This basically explains that if objects A and B are each in thermal equilibrium with object C, then A and B are in thermal equilibrium with each other. Thermal equilibrium means that when two bodies are brought into contact with each other and separated by a barrier that is permeable to heat, there will be no transfer of heat from one to the other.

Zeroth law of thermodynamics
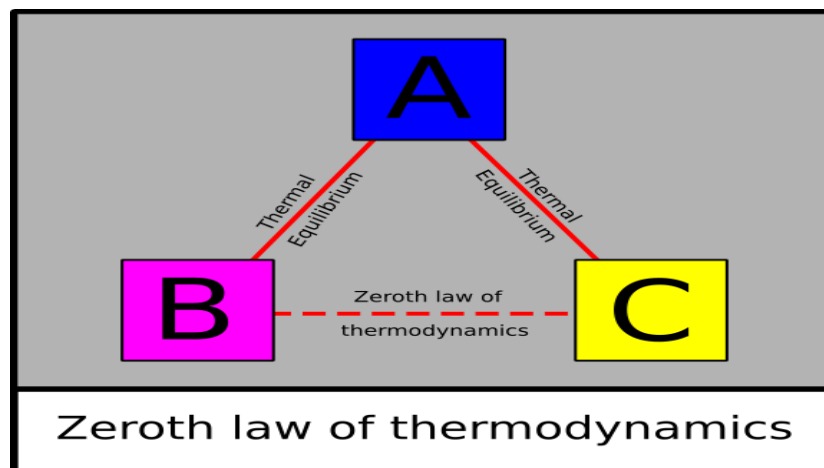
First Law of Thermodynamics

The first law of thermodynamics is a version of the law of conservation of energy (Energy cannot be created or destructed but may be transformed from one form to another).

This is mean:

- Whenever a quantity of one kind of energy is produced, an exactly equivalent of other kinds must disappear.
- The total energy of a system and its surrounding must remain constant, although it may be changed from one form to another.

The first law of thermodynamics defines the internal energy (ΔU) as equal to the difference of the heat transfer (q) **into** a system and the work (W) done **by** the system.

The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\Delta U = Q - W$$

Change in internal energy   Heat added to the system   Work done by the system

This is a particularly important law when discussing heat engines (like car engines), because it helps to understand that heat must go somewhere—the basis for cogeneration. As an engine creates heat, if the heat is not vented, the engine will become hotter and hotter, which will eventually lead to melting. Therefore, because it is impossible to achieve 100% efficiency , heat must be vented. This can either be treated as waste heat, or used for cogeneration, which is applying the waste heat to another cause, like heating a car, or heating houses.

Heat Capacity:

The internal energy of a substance increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the sample is confined to a constant volume. For example, the sample may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that

temperature. The **heat capacity at constant volume** is denoted C_V and is defined formally as:

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$
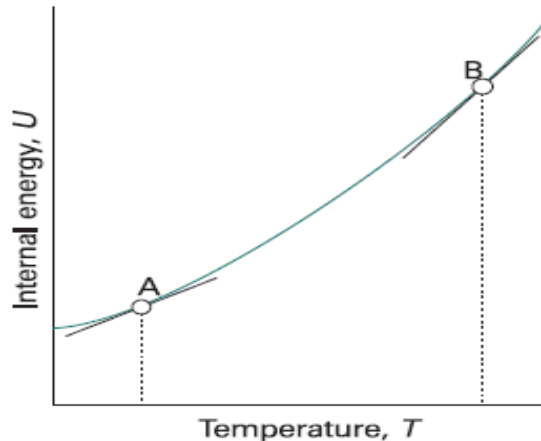
Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**, $C_{V,m} = C_V/n$, is the heat capacity per mole of material, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,m}$ for polyatomic gases are close to 25 J K^{-1} mol^{-1}. For certain applications it is useful to know the **specific heat capacity** (more informally, the 'specific heat') of a substance, which is the heat capacity of the sample divided by the mass or is defined by the amount of heat needed to raise the temperature of 1 gram of a substance 1 degree Celsius, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to 4 J K^{-1} g^{-1}. In general, heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system:

$$dU = C_V dT \quad at\ constant\ volume$$

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is C_V. If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature, ΔT, brings about a measurable increase in internal energy, ΔU, where

$$\Delta U = C_V \Delta T \quad at\ constant\ volume$$

Because a change in internal energy can be identified with the heat supplied at constant Volume, the last equation can be written:

$$q_V = C_V \Delta T$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature raise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

Heat Content or Enthalpy

When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat. So dU is less than dq. However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy.
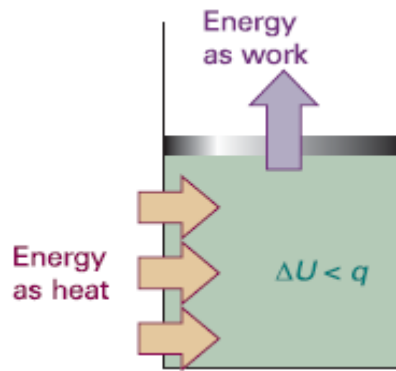
The **enthalpy**, H, is defined as:

$$H = U + PV$$

Where P is the pressure of the system and V is its volume. Because U, p, and V are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy, ΔH, between any pair of initial and final states is independent of the path between them.

When a process is carried out at constant volume, no mechanical work is done:

$$V = constant \rightarrow \Delta V = 0$$

$$W = P\Delta V \rightarrow W = 0$$

$$\Delta U = q - W \rightarrow \Delta U = q$$

If the process is carried out at constant pressure:

$$\Delta U = U_2 - U_1 = q_P - W = q_P - P(V_2 - V_1)$$

$$U_2 - U_1 = q_P - P(V_2 - V_1)$$

$$q_P = (U_2 - U_1) + P(V_2 - V_1)$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

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

$$as \ \Delta P = 0 \rightarrow q_P = U + P\Delta V$$

$$q_P \text{ is the Enthalpy} = H$$

$$H = q_P \ (at \ constant \ pressure \ the \ enthalpy \ is \ equal \ heat)$$

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

The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H:

$$H = U + PV = U + nRT$$

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is:

$$\Delta H = U + \Delta nRT$$

Where Δn is the change in the amount of gas molecules in the reaction

.

The variation of enthalpy with temperature

The enthalpy of a substance increases as its temperature is raised. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The most important condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**, C_p, at a given. More formally:

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$
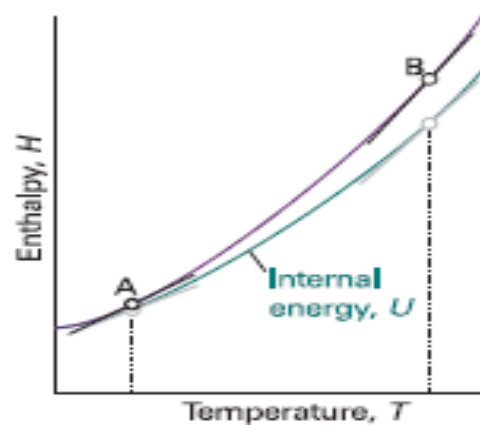
The heat capacity at constant pressure is the analogue of the heat capacity at constant volume, and is an extensive property. The **molar heat capacity at constant pressure**, $C_{p,m}$, is the heat capacity per mole of material; it is an intensive property.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature:

$$dH = C_P dT \quad at\ constant\ pressure$$

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature:

$$\Delta H = C_P \Delta T \quad at\ constant\ pressure$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_P = C_P \Delta T$$

Relation between C_P and C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \quad \text{... ... ...} (1)$$

As H= U+ P∆V

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \dots\dots (2)$$

$$U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \dots\dots (3)$$

$$dU = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Divided the equation on dT at constant pressure:

$$\left(\frac{dU}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{\partial T}\right)_P \dots\dots (4)$$

Substitute eq. 4 in eq. 2

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{dV}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

$\left(\frac{\partial U}{\partial V}\right)_T$ *is very small in gas and equal zero for ideal gas*

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

for one mole of ideal gas $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

$$C_P - C_V = P \times \frac{R}{P} = R$$

$$\boxed{C_P - C_V = R}$$

Joule's Experiment

For a closed system, the state function U is determined by T and V alone

$$dU = C_V \, dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Joule tried to measure this partial derivative $\left(\frac{\partial U}{\partial V} \right)_T$

In this experiment, Joule introduced a gas in a container linked to another one where a vacuum had been made. The complete system is isolated from the outside world so that it cannot exchange any type of energy in the form of heat. A valve that is initially closed separates both containers. When the valve is opened the gas expands freely towards the container where the vacuum is made until it fills the complete volume of the two containers and allowed to attain equilibrium and the temperature of the bath is recorded. Joule observed no change in temperature of thermostat. If we wait until the gas completely returns to the initial container while the other ones is completely empty, we will probably lose our time and will get old because the process is irreversible.
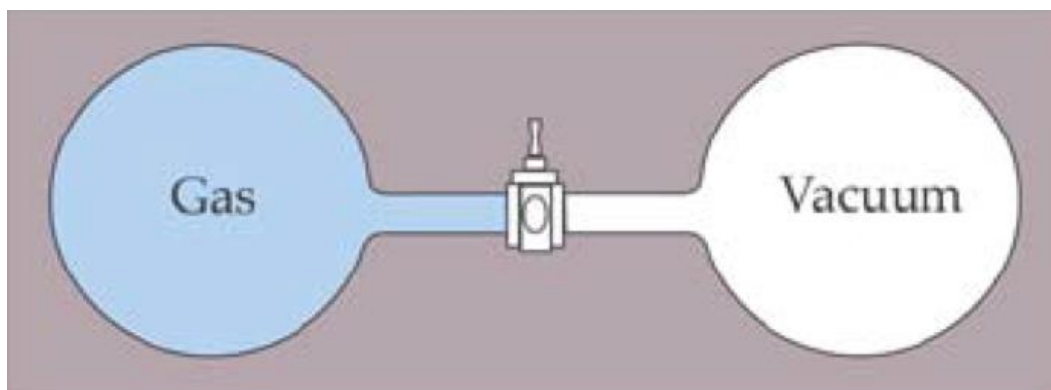
The thermodynamic implications of the experiment are as follows. No work was done in the expansion into a vacuum, so $w = 0$. No energy entered or left the system (the gas) as heat because the temperature of the bath did not change, so $q = 0$. Consequently, within the accuracy of the experiment, $\Delta U = 0$. It follows that U does not change much when a gas expands isothermally:

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

For ideal gas when T constant and V changes

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

For ideal gas when T constant and P changes

$$\left(\frac{\partial U}{\partial P} \right)_T = 0$$

Joule – Thomson effect

Joule-Thomson effect can be defined as the phenomenon of temperature change produced when a gas is allowed to expand adiabatically from a region of high pressure to a region of extremely low pressure. This cooling of the gas is basically due to the decrease in the kinetic energy of the gaseous molecules as some part of this kinetic energy is utilized in overcoming intermolecular van der Waals force of attraction during expansion. The Joule-Thomson effect is very small when a gas approaches ideal behavior. Thus for an ideal gas, Joule Thomson effect is zero. Therefore, no absorption or evolution of heat takes place when expansion of an ideal gas occurs i.e. q = 0.This is because in an ideal gas there are no intermolecular van der Waals forces of attraction thus there is no expenditure of energy in overcoming these forces during expansion. Further, when expansion of ideal gas occurs in vacuum then no work is done since pressure against which it expands is zero. From the first law

equation we can say that ΔU is also equal to zero. Thus, when an ideal gas undergoes expansion under adiabatic conditions in vacuum, no change takes place in its internal energy. In other words, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

Joule Thomson Coefficient ($\mu_{J.T.}$)

Joule and Thomson derived the relationship between fall of pressure of gas on expansion and resulting lowering of temperature by performing the following technique:
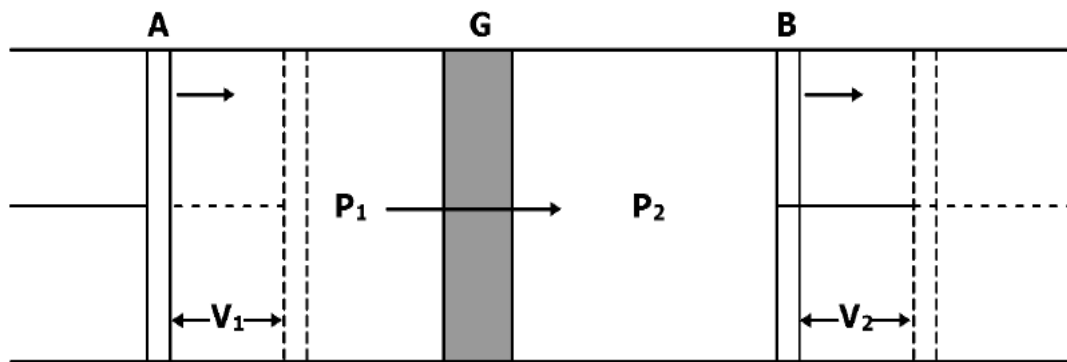
A tube made of a non-conducting material is fitted with a porous plug G in the middle and two pistons A and B on the sides, as shown. The tube is thoroughly insulated to ensure adiabatic conditions. Let the volume of gas enclosed between the piston A and the porous plug G at pressure P_1 is V_1. This volume is forced to pass through porous plug by moving the piston A inwards. At the same time the volume of gas enclosed between porous plug G and piston B i.e. V_2 is allowed to expand at a lower pressure P_2 by moving the piston B outward, as shown.

Therefore, work done on the system at the piston A = +P_1V_1 and work done by the system at the piston B = –P_2V_2.

Since the expansion of the gas is done adiabatically i.e. no exchange of heat takes place between the system and surroundings. Thus the work is done by the system at the expense of internal energy only. Let the internal energy of the system changes from U_1 to U_2.

$$-P_2V_2 = P_1V_1 = U_2 - U_1$$

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

$$H_2 = H_1$$

This states that the Joule-Thomson expansion of a real gas occurs with constant enthalpy and not with constant internal energy. According to this the process is known as **isoenthalpic process**.

Taking enthalpy as the function of temperature and pressure, then the total differential of the enthalpy H can be written as:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\text{But } \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT$$

Since for adiabatic expansion, dH = 0, hence

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT = 0$$

Rearranging the above equation

$$\left(\frac{dT}{dP}\right)_H = \frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P} \text{ ... ... (6)}$$

The quantity $\left(\frac{dT}{dP}\right)_H$ is called Joule-Thomson coefficient and it is denoted as **(μ.т.)** .

Joule-Thomson Coefficient for an Ideal Gas.

Since H = U + PV, substituting this in equation 6 we get**:**

$$\left(\frac{dT}{dP}\right)_H = \mu_{J.t} = -\frac{[\partial(U + PV)/\partial P)T]}{C_P}$$

$$= -\frac{\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial PV}{\partial P}\right)_T}{C_P}$$

$$= -\frac{\left(\frac{\partial U}{\partial P} \times \frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial PV}{\partial P}\right)_T}{C_P}$$

As the internal energy of an ideal gas at constant temperature is independent of its volume i.e. for an ideal gas, $(\Delta U / \Delta V)_T$ is zero, therefore

$$\left(\frac{\partial U}{\partial V}\right)_T \times \left(\frac{\partial V}{\partial P}\right)_T = 0$$

Also, PV is independent of temperature in the case of ideal gas $\left(\frac{\partial PV}{\partial P}\right)_T = 0$

Hence $\mu_{J.t} = 0 \; for \; ideal \; gas$

Adiabatic change in state

The thermodynamic process in which there is no exchange of heat from the system to its surrounding neither during expansion nor during compression**.**

The adiabatic process can be either *reversible or irreversible.* Following are the essential conditions for the adiabatic process to take place:

- The system must be perfectly insulated from the surrounding.
- The process must be carried out quickly so that there is a sufficient amount of time for heat transfer to take place.
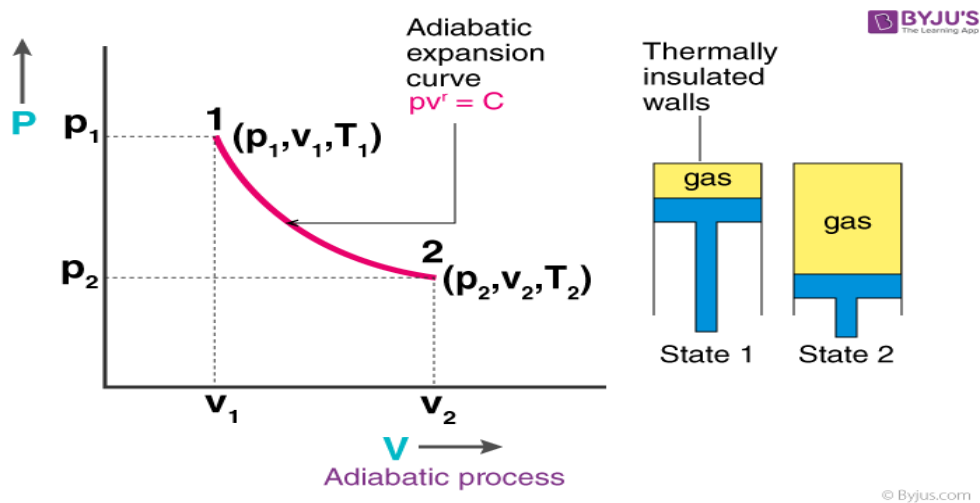
Adiabatic process

Reversible Adiabatic Process

Reversible adiabatic process is also called an Isentropic Process. It is an idealized thermodynamic process that is adiabatic and in which the work transfers of the system are frictionless; there is no transfer of heat or of matter and the process is reversible. Such an idealized process is useful in engineering as a model of and basis of comparison for real processes.

In adiabatic process $\partial q = 0 \rightarrow \Delta U = w$

$$\int_{U_1}^{U_2} dU = nC_V\, dT = -PdV \qquad , dT = T_2 - T_1$$

For one mole of ideal gas, $T = \dfrac{PV}{R}$

$$\Delta U = C_V \left(\frac{P_2 V_2}{R} - \frac{P_1 V_1}{R} \right)$$

$$\Delta U = \frac{C_V}{R}(P_2V_2 - P_1V_1)$$

$$R = C_P - C_V$$

$$\Delta U = C_V \frac{(P_2V_2 - P_1V_1)}{(C_P - C_V)}$$

Divided on C_V

$$\Delta U = \frac{(P_2V_2 - P_1V_1)}{\frac{(C_P - C_V)}{C_V}}$$

$$U = \frac{(P_2V_2 - P_1V_1)}{\frac{C_P}{C_V} - 1} \qquad , \frac{C_P}{C_V} = \gamma$$

$$U = \frac{(P_2V_2 - P_1V_1)}{\gamma - 1}$$

Relation between temperature and volume in reversible adiabatic changes

$$\Delta U = C_V dT = -PdV \qquad , for\ one\ mole\ of\ ideal\ gas\ P = \frac{RT}{V}$$

$$C_V dT = -\frac{RT}{V}\ dV$$
$$C_V \frac{dT}{T} = -R \frac{dV}{V}$$

If C_v is assumed to be temperature independent, then it is possible to integrate the above equation within specified limit. The result is

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1}$$

$$C_V \ln\frac{T_2}{T_1} = R \ln\frac{V_1}{V_2}$$

$$\ln\frac{T_2}{T_1} = \frac{R}{C_V} \ln\frac{V_1}{V_2}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_P - C_V}{C_V}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$$(TV)^{\gamma - 1} = constant$$

Relation between volume and pressure in reversible adiabatic changes

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

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

Substitute the following value in the above equation:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\left(\frac{R}{C_V}\right)-1}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

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

Relation between temperature and pressure in reversible adiabatic changes

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

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

Substitute in:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

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

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

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

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

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

$$\left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}} = \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\frac{T_2}{(P_2)^{\frac{R}{C_P}}} = \frac{T_1}{(P_1)^{\frac{R}{C_P}}} = constant$$

We can summarize the results as

$$\frac{1}{R} \ln \frac{T_2}{T_1} = \frac{1}{C_V} \ln \frac{V_1}{V_2} = \frac{1}{C_P} \ln \frac{P_2}{P_1}$$

Adiabatic Irreversible Changes

$$-W_{irr} = P_{ext} \Delta V$$

$$if \ P_{ext} = P_2 \quad , \quad -W_{irr} = P_2 (V_2 - V_1)$$

$$\Delta U = W_{irr} = -P_2 (V_2 - V_1) = nC_V (T_2 - T_1)$$

$$V_2 = \frac{nRT_2}{P_2} \quad , \quad V_1 = \frac{nRT_1}{P_1}$$

$$\Delta U = W_{irr} = -P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) = nC_V (T_2 - T_1)$$

Adiabatic free expansion

$$W = 0 \quad , \quad q = 0$$

$$\Delta U = W_{irr} = nC_V (T_2 - T_1) = 0$$

$$\Delta H = nC_P (T_2 - T_1) = 0, \quad T_2 = T_1$$

Solved Exercises

Example 1: Two mole of nitrogen gas at 25 C was expanded reversibly and isothermally from 10 L to 20 L. calculate the work done.

$$W_{rev} = -nRT \ln \frac{V_2}{V_1}$$

$$W_{rev} = -2.303nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 2 \times 8.314 \times 298 \, log \, \frac{20}{10}$$

$$= 3435.2 \, J$$

Example 2: One mole of oxygen at 300 K expands isothermally from 3 atm to 1 atm. Assuming that oxygen behaves ideally, calculate W: 1) if the expansion is reversible 2) if the expansion against constant pressure of 1 atm.

Solution: the initial volume of the gas V_1 is given by:

$$V_1 = \frac{nRT}{P} = \frac{1 \, mol \; \times (0.08021) \times 300}{3 \, atm} = 8.21 \, L$$

$$V_2 = \frac{nRT}{P} = \frac{1 \, mol \; \times (0.08021) \times 300}{1 \, atm} = 24.63 \, L$$

For process (1)

$$-W_{rev} = \, nRT \, ln\frac{P_1}{P_2} = 1 \, mol \; \times (8.314) \times 300 \; \times 2.303 \, log\frac{3}{1} = 2.74 \, J$$

For process (2) $-W_{rev} = P\Delta V = \, P_2(V_2 - V_1)$

$$= 1 \times 101325 \, N.m^{-2}(24.63 - 8.21) \times 10^{-3}m^3 = 16.637 \, kJ/mol$$

Example3: An ideal gas was expanded reversibly and isothermally from V_1 to 10 V_1 when 10000 cal of work was achieved, if the initial pressure was 100 atm. Calculate V_1.

$$-W_{rev} = \, nRT \, ln\frac{V_2}{V_1} = nRT \, ln\frac{10V_1}{V_1}$$

$$10000 = nRT \, ln \, 10$$

$$\frac{10000}{2.303} = nRT = PV \ for \ ideal \ gas$$

$$4342.16 = 100 \ \times V_1$$

$$V_1 = \frac{4342.16}{100} = 43.42 \ L$$

Example 4: A sample consisting of 2 mol He is expanded isothermally at 22°C from 22.8 dm^3 to 31.7 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

(a) reversibly

$$-W_{rev} = \ nRT \ ln\frac{V_2}{V_1} = \ -2 \ \times 8.314 \times 295 \times ln\frac{31.7}{22.8} = 6.82kJ$$

$$for \ isothermal \ process \ \Delta T = 0 \ \rightarrow \ \Delta U = 0 \rightarrow q = w$$

$$or \ isothermal \ process \ \Delta T = 0 \ \rightarrow \ \Delta H = 0$$

(b) against a constant external pressure

$$-W_{irr} = P\Delta V = \ P_2(V_2 - V_1)$$

$$P_2 = \ \frac{nRT}{V_2} = \frac{2 \times 0.0821 \times 295}{31.7} = 1.528 \ atm$$

$$-W_{rev} = 1.528 \times 101325 \ Nm^{-2}(31.7 - 22.8) \times 10^{-3}m^3 = 1.378 \ kJ$$

$$for \ isothermal \ process \ \Delta T = 0 \ \rightarrow \ \Delta U = 0 \rightarrow q = w$$

$$or \ isothermal \ process \ \Delta T = 0 \ \rightarrow \ \Delta H = 0$$

(c) against zero external pressure (W=0)

$$for \ isothermal \ process \ \Delta T = 0 \ \rightarrow \ \Delta U = 0 \rightarrow q = w{=}0, \Delta H = 0$$

Example 5: Calculate ΔU, and ΔH when 100 dm^3 of helium at STP are heated in a closed container. Assume that the gas behaves ideally and its C$_v$ is 12.55 J mol^{-1} K^{-1}.

Solution:

$$\Delta U = nC_V\Delta T$$

$$\Delta U = \left(\frac{100}{22.414}\, mol\right)\,(12.55\, J\, mol^{-1}K^{-1})(373 - 273\, K)$$

$$= 5226\, J = 5.226\, kJ$$

$$\Delta H = nC_P\Delta T$$

$$= \left(\frac{100}{22.414}\, mol\right)\,(12.55 + 8.314\, J\, mol^{-1}K^{-1})(373 - 273\, K)$$

$$= 9317\, J = 9.317\, kJ$$

Example 6: One mole of an ideal gas (C_v = 12.55 J mol^{-1} K^{-1}) at 300 K is compressed adiabatically and reversibly to one fourth its original volume. What is the final temperature of the gas?

Solution:

$$T_1 = 300K \quad , \quad V_1 = 4x \quad , \quad V_2 = x$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

$$\frac{T_2}{300} = \left(\frac{4x}{x}\right)^{\frac{8.314}{12.55}}$$

$$\frac{T_2}{300} = 4^{0.66247} \quad \rightarrow T_2 = 752K$$

Example 6: To what pressure must a given volume of nitrogen at 100 °C and 1 atm be adiabatically compressed in order to raise the temperature to 400 °C. $\gamma = 1.4$

Solution:

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

$$\left(\frac{673}{373}\right)\left(\frac{P_2}{1}\right)^{\frac{1.4-1}{1.4}} \quad \rightarrow P_2 = 7.891\, atm$$

Example 7: One mole of nitrogen at 300 K and 20 atm expands to 2 atm. Calculate W, q, ΔU, and ΔH if expansion were: (Given C_v = 20.816 J mol^{-1} K^{-1})

(1) isothermal and reversible.

(2) isothermal and irreversible.

(3) adiabatic and reversible.

Solution:

(1) For isothermal process $\Delta U = \Delta H = 0$

$$q = -W_{rev} = nRT \ln\frac{P_1}{P_2} = 1 \times 8.314 \times 300 \times \ln\frac{20}{2} = 5.744 kJ$$

(2) For isothermal and irreversible $\Delta U = \Delta H = 0$

$$q = -W_{irr} = P\Delta V = P_2(V_2 - V_1)$$

$$V_1 = \frac{nRT}{P} = \frac{1\ mol\ \times (0.08021) \times 300}{20\ atm} = 1.23\ L$$

$$V_2 = \frac{nRT}{P} = \frac{1\ mol\ \times (0.08021) \times 300}{2\ atm} = 12.3\ L$$

$$q = -W_{irr} = (2 \times 101325\ Nm^{-2})\ (12.31 - 1.23) \times 10^{-3} m^3$$

$$q = -W_{irr} = 2245\ J \rightarrow 2.245 kJ/mol$$

(3) Adiabatic reversible expansion:

$$q = 0\ \rightarrow \Delta U = w = nC_V\Delta T$$

$$\left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$$

$$\left(\frac{T_2}{300}\right)\left(\frac{2}{20}\right)^{\frac{8.314}{29.13}}$$

$$T_2 = 150.8 K$$

$$\Delta U = w = (1 \times 20.816)(150.8 - 300\ K) = -3.106\ kJ/mol$$

$$\Delta H = nC_P\Delta T = (1 \times 29.13)(150.8 - 300\ K) = -4.346\ kJ/mol$$

Exercises

1- A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm^3 to 44.8 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

2- A sample of 4.50 g of methane occupies 12.7 dm^3 at 310 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm^3. (b) Calculate the work that would be done if the same expansion occurred reversibly.

3- Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm^3 at 298.15 K to 2.00 dm^3.

4- Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm^3 to a final volume of 3.0 dm^3. $\gamma = 1.3$.

5- Sample of 4.0 mol O$_2$ is originally confined in 20 dm^3 at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate q, w, ΔT, ΔU, and ΔH. (The final pressure of the gas is not necessarily 600 Torr.)

6- A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8$ J K^{-1} is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and final temperature and the work done.

7- One mole of air at 750K is expanded reversibly and adiabatically from 1 L to 3 L. Taking $C_V = 20.92$ J K^{-1} and assuming ideal behavior calculate the final temperature, ΔU, ΔH and w.

8- When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

Thermochemistry

Thermochemistry 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 the surroundings. Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy (if the reaction occurs at constant volume) or a change in enthalpy (if the reaction occurs at constant pressure). Conversely, if we know ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) the reaction can produce.
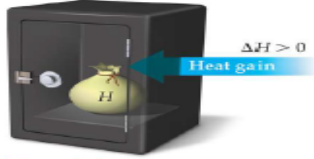
We have already remarked that a process that releases energy by heating the surroundings is classified as exothermic and one that absorbs energy by cooling the surroundings is classified as endothermic. Because the release of energy by heating the surroundings signifies a decrease in the enthalpy of a system (at constant pressure), we can now see that an exothermic process at constant pressure is one for which $\Delta H < 0$.

Conversely, because the absorption of energy by cooling the surroundings results in an increase in enthalpy, an endothermic process at constant pressure has $\Delta H > 0$. **Endothermic** reactions absorb heat, while **exothermic** reactions release heat.

Endothermic and Exothermic

$$\Delta H = H_{final} - H_{initial} \quad \text{or} \quad \Delta H = H_{products} - H_{reactants}$$
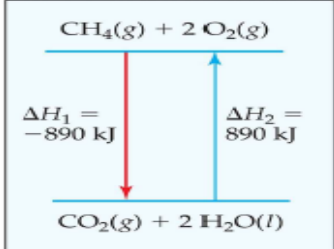
- A process is **endothermic** when ΔH is positive (>0).

- A process is **exothermic** when ΔH is negative (<0).

Standard enthalpy changes

The standard enthalpy change for a reaction or a physical process is the difference between the products in their standard states and the reactants in their standard states, all at the same specified temperature. In most of our discussions we shall consider the **standard enthalpy change**, $\Delta H°$, 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.

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at

298 K and 1 bar; the standard state of solid iron at 500 K is pure iron at 500 K and 1 bar.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*,

$\Delta_{vap}H$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in

$$H_2O\ (l) \rightarrow H_2O\ (g) \qquad \Delta_{vap}H^0(373K) = +40.66 kJ\ mol^{-1}$$

As implied by the examples, standard enthalpies may be reported for any temperature.

However, the conventional temperature for reporting thermodynamic data is 298.15K (corresponding to 25°C). Unless otherwise mentioned, all thermodynamic data in this text will refer to this conventional temperature.
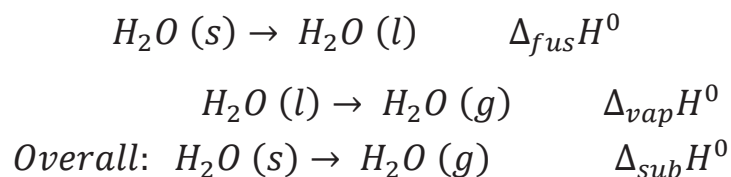
Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_{trs}H°$ .The **standard enthalpy of vaporization**, $\Delta_{vap}H°$, is one example. Another is the **standard enthalpy of fusion**, $\Delta_{fus}H°$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

$$H_2O\ (s) \rightarrow H_2O\ (l) \qquad \Delta_{fus}H^0(373K) = +6.1 kJ\ mol^{-1}$$

Because enthalpy is a state function, a change in enthalpy is independent of the path between the two states. This feature is of great importance in thermochemistry, for it implies that the same value of $\Delta H°$ will be obtained however the change is brought about between the same initial and final states. For example, we can picture the conversion of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour),

$$H_2O\ (s) \rightarrow H_2O\ (g) \qquad \Delta_{sub}H^0$$

or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:

$$H_2O\ (s) \rightarrow H_2O\ (l) \qquad \Delta_{fus}H^0$$
$$H_2O\ (l) \rightarrow H_2O\ (g) \qquad \Delta_{vap}H^0$$
$$Overall:\ H_2O\ (s) \rightarrow H_2O\ (g) \qquad \Delta_{sub}H^0$$

Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (**1**), and we can conclude that (for processes occurring at the same temperature)

$$\Delta_{sub}H^0 = \Delta_{fus}H^0 + (g)\,\Delta_{vap}H^0$$

An immediate conclusion is that, because all enthalpies of fusion are positive, the enthalpy of sublimation of a substance is greater than its enthalpy of vaporization (at a given temperature).
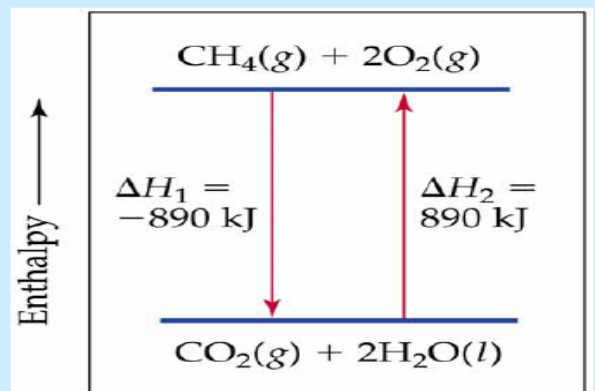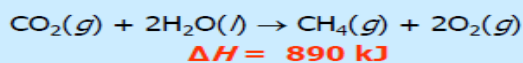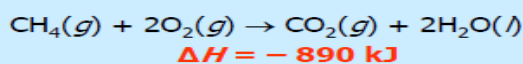
Laws of Thermochemistry

Another consequence of H being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign and equal in magnitude:

$$\Delta H^0(A \rightarrow B) = -\Delta H^0(B \rightarrow H)$$

For instance, because the enthalpy of vaporization of water is +44 kJ mol^{-1} at 298 K, its enthalpy of condensation at that temperature is −44 kJ mol^{-1}.

The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.

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

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

- ΔH_f° - **standard enthalpy of formation:** ΔH for forming one mole of product directly from its reactants with products and reactants in standard states.
  - The standard enthalpy of formation of the most stable form of any element is zero.
- ΔH_{vap}° — **standard enthalpy of vaporization:** ΔH for converting liquids to gases with products and reactants in standard states.
- ΔH_{fus}° — **standard enthalpy of fusion:** ΔH for melting solids.
- ΔH_{sub}° — **standard enthalpy of sublimation:** ΔH for converting solids to gases
- ΔH_{comb}° — **enthalpy of combustion:** ΔH for combusting a substance with oxygen)
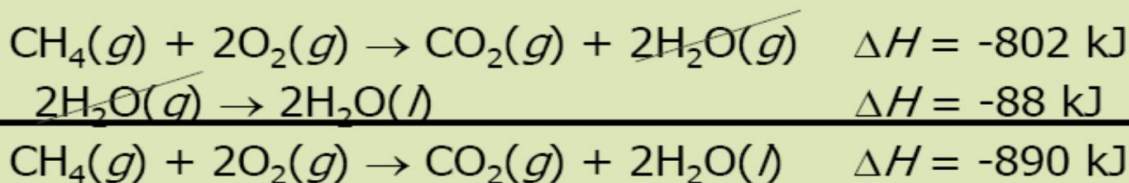
Hess's law

Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction or the resultant heat change at constant volume or pressure in a given chemical reaction is the same whether it take place in one or several steps. This application of the First Law is called **Hess's law**:
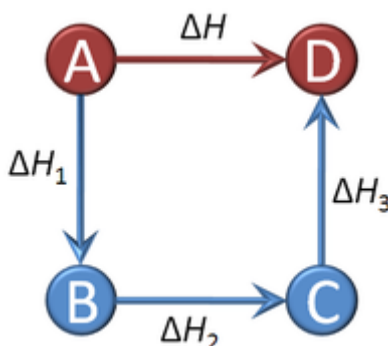
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Hess's law: if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802 \text{ kJ}$$
$$\underline{2H_2O(g) \rightarrow 2H_2O(l) \qquad\qquad\qquad\qquad \Delta H = -88 \text{ kJ}}$$
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890 \text{ kJ}$$

Calculate the enthalpy of the reaction: $C_2H_{4(g)} + HCl_{(g)} = C_2H_5 Cl_g$

From the following reaction:

(i) $2 C_{(s)} + \frac{5}{2} H_{2(g)} + \frac{1}{2} Cl_{2(g)} = C_2H_5 Cl_g$ $\qquad \Delta H^\circ = -112.1 \ kJ$

(ii) $\frac{1}{2} H_{2(g)} + \frac{1}{2} Cl_{2(g)} = HCl_{(g)}$ $\qquad \Delta H^\circ = -92.35 \ kJ$

(iii) $2 C_{(s)} + 2 H_{2(g)} = C_2H_{4 \ (g)}$ $\qquad \Delta H^\circ = 52.3 \ kJ$
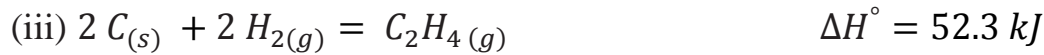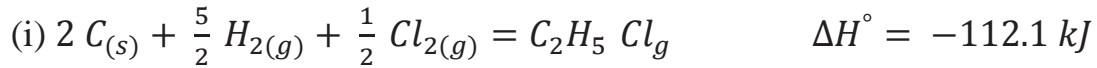
Solution:

By adding eq (ii) to eq (iii) we get:

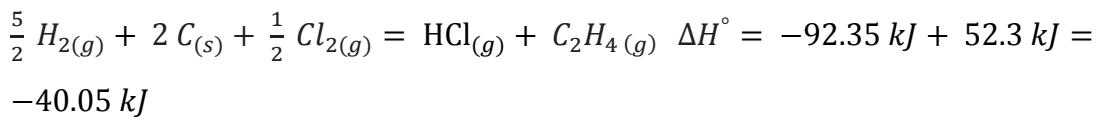$\frac{5}{2} H_{2(g)} + 2 C_{(s)} + \frac{1}{2} Cl_{2(g)} = HCl_{(g)} + C_2H_{4 \ (g)}$ $\Delta H^\circ = -92.35 \ kJ + 52.3 \ kJ =$ $-40.05 \ kJ$

Subtracted eq (i) from the result equation:

$\frac{5}{2} H_{2(g)} + 2 C_{(s)} + \frac{1}{2} Cl_{2(g)} = HCl_{(g)} + C_2H_{4 \ (g)}$

$2 C_{(s)} + \frac{5}{2} H_{2(g)} + \frac{1}{2} Cl_{2(g)} = C_2H_5 Cl_g$

_____

_____

$C_2H_5 Cl_g = HCl_{(g)} + C_2H_{4 \ (g)}$ $\Delta H^\circ = -40.05 \ kJ - (-112.1 \ kJ)$

$= +72.05 \ kJ$

$C_2H_{4(g)} + HCl_{(g)} = C_2H_5 Cl_g$ $\qquad \Delta H^\circ = -72.05 \ kJ$
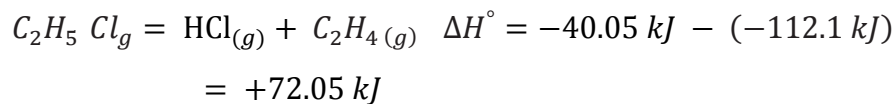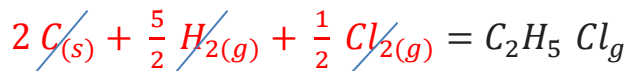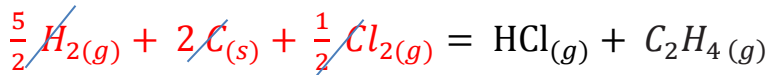
Example:

The standard reaction enthalpy for the hydrogenation of propene,

$$CH_2{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$
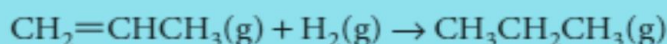
is -124 kJ mol^{-1}. The standard reaction enthalpy for the combustion of propane,

$$CH_3CH_2CH_3(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$
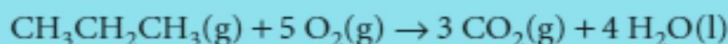
is -2220 kJ mol^{-1}. Calculate the standard enthalpy of combustion of propene.

Answer The combustion reaction we require is

$$C_3H_6(g) + \tfrac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$
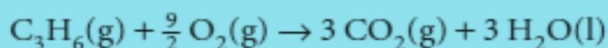
This reaction can be recreated from the following sum:

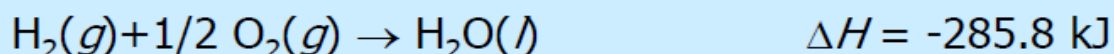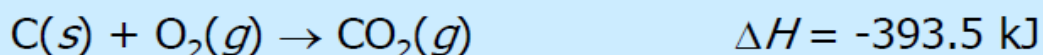|	$\Delta_r H^{\oplus}/(kJ\ mol^{-1})$
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	-124
$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$	-2220
$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$	$+286$
$C_3H_6(g) + \tfrac{9}{2}O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$	-2058

- Calculate ΔH for the reaction

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$

$C_2H_2(g) + 5/2\,O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$	$\Delta H = -1299.6$ kJ
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H = -393.5$ kJ
$H_2(g) + 1/2\,O_2(g) \rightarrow H_2O(l)$	$\Delta H = -285.8$ kJ

- Calculate ΔH for the reaction

$$NO(g) + O(g) \rightarrow NO_2(g)$$

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$	$\Delta H = -198.9$ kJ
$O_3(g) \rightarrow 3/2\,O_2(g)$	$\Delta H = -142.3$ kJ
$O_2(g) \rightarrow 2\,O(g)$	$\Delta H = +495.0$ kJ
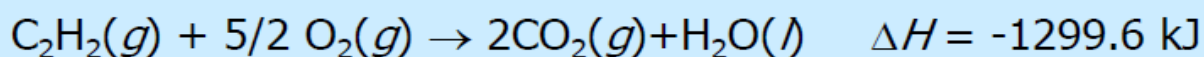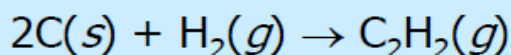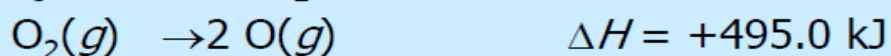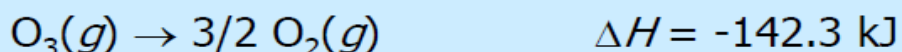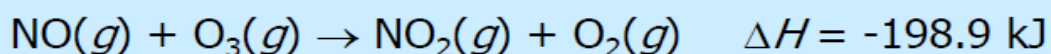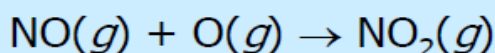
The following conventions apply when we use ΔH

In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -286\,\text{kJ}$$
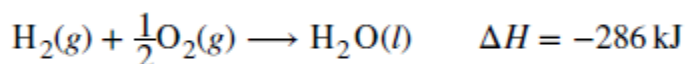
This equation indicates that when 1 mole of hydrogen gas and 1/2 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

(two-fold increase in amounts)

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = 2 \times (-286\,\text{kJ}) = -572\,\text{kJ}$$

(two-fold decrease in amounts)

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{4}O_2(g) \longrightarrow \tfrac{1}{2}H_2O(l) \qquad \Delta H = \tfrac{1}{2} \times (-286\,\text{kJ}) = -143\,\text{kJ}$$

The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 1/2 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -242\,\text{kJ}$$
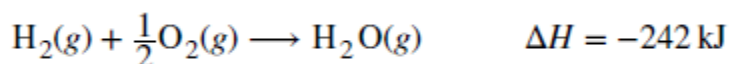
A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH

is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Enthalpies of chemical change

Standard enthalpies of formation ($\Delta_f H^\bullet$)

The **standard enthalpy of formation**, $\Delta_f H°$, 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. For example, at 298 K the reference state of nitrogen is a gas of N_2 molecules, that of mercury is liquid mercury, that of carbon is graphite, and that of tin is the white (metallic) form. Standard enthalpies of formation are expressed as 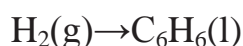enthalpies per mole of molecules or (for ionic substances) formula units of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction   6 C(s, graphite) + 3 $H_2(g) \rightarrow C_6H_6(l)$

and is +49.0 kJ mol^{-1}. The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such 'null' reactions as $N_2(g) \rightarrow N_2(g)$

Enthalpy of Combustion ($\Delta_f H^\bullet$)

Standard enthalpy of combustion ($\Delta_c H °$) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes

complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2 + 3H_2O(l) \qquad \Delta H^{\circ}_{298} = -1366.8 \text{ kJ}$$
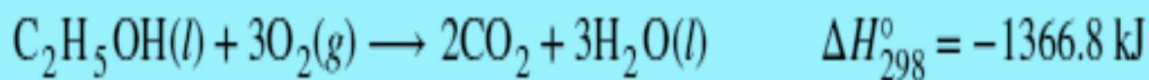
$$\Delta_c H^{\circ} = \left[3\Delta_f H^{\circ} H_2O + 2\Delta_c H^{\circ} CO_2\right] - \left[\Delta_f H^{\circ}(C_2H_5OH + \Delta_f H^{\circ}(O_2)\right]$$
$$\Delta_f H^{\circ}(O_2) = 0 \ for \ elements$$

Enthalpy of neutralization (ΔH_n)

The **enthalpy of neutralization** (ΔH_n) is the change in enthalpy that occurs when one equivalent of an acid and a base undergo a neutralization reaction to form water and a salt.

Dilute solution should be used to avoid enthalpy changes due to mixing of acid and base. If one mole of a strong monoprotic acid (HCl, HNO_3 etc…) is mixed with 1 mole of strong base (NaOH, KOH etc…) neutralization take place as:

$$H_3O^+(aq) + OH^-(aq) = 2H_2O \ (l) \qquad \Delta H^{\circ} = -57.32 kJ$$
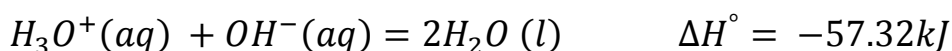
Since these acid and base are completely ionized in dilute solution, the enthalpy change is always -57.32kJ.

For a weak acid or base the enthalpy of neutralization is not the same, but less than -57.32kJ. In this case neutralization involves ionization of the acid or the base in addition to neutralization. The heat required to ionize the weak acid or the weak base is known as the **enthalpy of ionization**. The enthalpy of ionization of a weak acid can be calculated from the enthalpies of neutralization of strong acid and weak acid by strong base. For example, in the neutralization of acetic acid by sodium hydroxide, the enthalpy of neutralization is -55.43kJ mol^{-1}. The enthalpy of ionization will therefore be equal to+1.89 kJmol^{-1}.

Bond enthalpies

The amount of enthalpy required to break 1mole of a particular bond in a given compound and separate the resulting gaseous atoms or radicals from one another. It depends on the nature of the atoms linked by the bond and the nature of the molecule as a whole. The bond dissociation enthalpy of a hydrogen molecule is 435.9kJ mol^{-1}.

$$H_{2(g)} = 2H_{(g)} \qquad \Delta H^{\circ} = 435.9 kJ\ mol^{-1}$$

In the case of water, the bond dissociation of an OH linkage is 497.8kJ and the enthalpy required to break the O-H bond in the residual group is 428.5 kJ.

$$H_2O_{(g)} = H_{(g)} + \quad OH_{(g)} \qquad \Delta H^{\circ} = 497.8\ kJ\ mol^{-1}$$

$$OH_{(g)} = H_{(g)} + \quad O_{(g)} \qquad \Delta H^{\circ} = 428.5\ kJ\ mol^{-1}$$
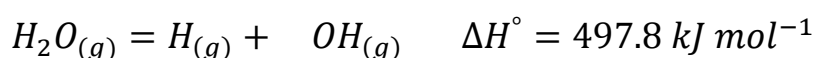
ΔH = breaking bonds + forming bonds

[this is exothermic (negative)]

C$_2$H$_5$OH (g) + 3O$_2$(g) ⟶ 2CO$_2$(g) + 3H$_2$O (g)

$$\Delta H = [(5 \times 413) + 348 + 360 + 463 + (3 \times 498)]$$
$$+ [(4 \times -743) + (6 \times -463)]$$
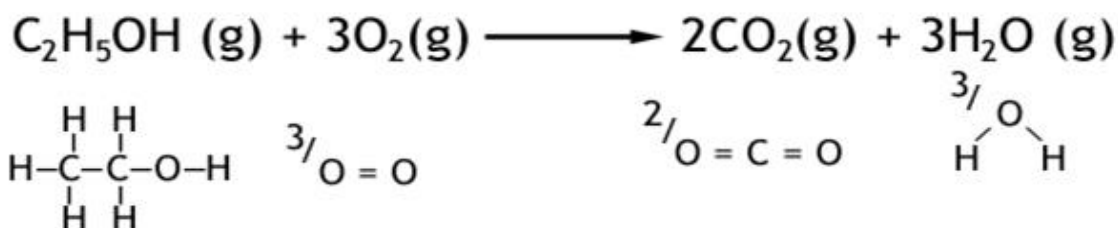
$$= -1020\ kJ\ mol^{-1}$$

B(X-Y) / kJ mol^{-1}	
H−C = 413	O−H = 463
C−C = 348	O=O = 498
C−O = 360	C=O = 743

Example: calculate the bond enthalpy for a C-O bond in methanol from the following date:

(i) $C_{(s)} + 2\ H_{2(g)} + \frac{1}{2}O_{2(g)} = CH_3OH = -200\ kJ/mol$

(ii) $C_{(s)} = C_{(g)}$ $\qquad\qquad\qquad\qquad \Delta H^{\circ} = 716.8\ kJ\ /mol$

(iii) $2 H_{2(g)} + = 4H_{(g)}$ $\qquad\qquad\qquad$ $\Delta H° = 872 \, kJ/mol$

(iv) $\frac{1}{2}O_{2(g)} = O_{(g)}$ $\qquad\qquad\qquad$ $\Delta H° = 249 \, kJ/mol$
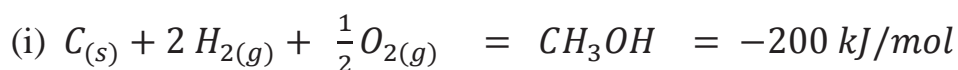
The bond enthalpy of C-H is 413 kJ/mol and for O-H is 463.6 kJ/mol.

Solution: the enthalpy change for the dissociation of $CH_3OH_{(g)}$ is :

$$CH_3OH = C_{(g)} + 4H_{(g)} + O_{(g)} \qquad \Delta H° = ?$$
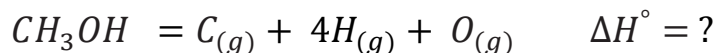
Adding (ii), (iii) and (iv) gives

$$C_{(s)} + 2 H_{2(g)} + \frac{1}{2}O_{2(g)} = C_{(g)} + 4H_{(g)} + O_{(g)} \quad \Delta H° = 1837.9 kJ$$
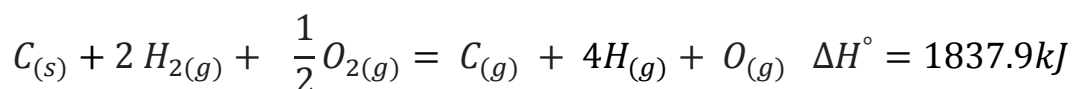
Now subtracting eq (i) from the above equation gives:

$$CH_3OH = C_{(g)} + 4H_{(g)} + O_{(g)} \qquad \Delta H° = 2037.8 kJ$$
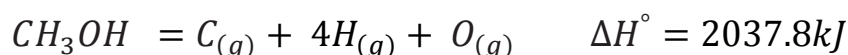
Since in methanol, there are three C-H, one C-O and one O-H bonds

$$2037.8 kJ = 3(\Delta H°_{(C-H)} + 1(\Delta H°_{(o-H)}) + (\Delta H°_{(C-O)})$$

$$2037.8 kJ = 3 \times (415) + (463.6) + (\Delta H°_{(C-O)})$$

$$(\Delta H°_{(C-O)} = 329 \, kJ/mol$$

Unsolved example:

- Calculate the enthalpy of the reaction:

$$C_2H_{4(g)} + Br_{2(g)} = C_2H_4Br_{2(g)}$$
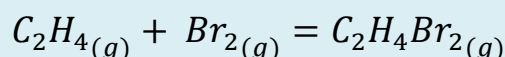
The bond enthalpies ($kJmol^{-1}$) are $\Delta H°_{(C-H)} = 415$, $\Delta H°_{(C=C)} = 610$,

$\Delta H°_{(C-C)} = 348$, $\Delta H°_{(C-Br)} = 276$, $\Delta H°_{(Br-Br)} = 193$.

The Temperature-Dependence of Reaction Enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature. In many cases heat capacity data are more accurate that reaction

enthalpies so, providing the information is available, the procedure we are about to describe is more accurate that a direct measurement of a reaction enthalpy at an elevated temperature.

when a substance is heated from T_1 to T_2, its enthalpy changes from $H(T_1)$

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

Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_P^\circ \, dT$$

$$\Delta_r C_P^\circ = \Sigma_{Products} \, C_P^\circ - \Sigma_{reactants} \, C_P^\circ$$

This equation is known as **Kirchhoff's law** which expressing the temperature dependence of the thermal quantities associated with a chemical reaction through the difference in heat capacities between the products and reactants. It is normally a good approximation to assume that $\Delta_r C_p$ is independent of the temperature.

Example:

The standard enthalpy of formation of gaseous H_2O at 298 K is -241.82 kJ mol^{-1}. Estimate the value at 100 ^{0}C given the following values of molar heat capacities at constant pressure: $H_2O(g)$: 33.58 kJ mol^{-1}; H_2 (g) : 28.84 kJ mol^{-1}; O_2 (g) : 29.37 kJ mol^{-1}. Assume heat capacities are independent of T.

$$\Delta_r H^0(T_2) = \Delta_r H^0(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^0 dT = \Delta_r H^0(T_1) + (T_2 - T_1)\Delta_r C_p^0$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$
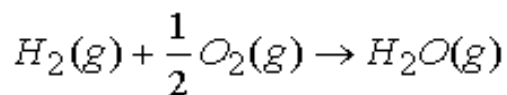
$$\Delta_r C_p^0 = \Delta_r C_{p,m}^0(H_2O,g) - \{C_{p,m}^0(H_2,g) + \frac{1}{2}C_{p,m}^0(O_2,g)\}$$

It follows that

$$\Delta_r H^0(373\,K) = -241.82\,kJ\,mol^{-1} + (75\,K)(-9.94\,kJ\,mol^{-1})$$
$$= -242.6\,kJ\,mol^{-1}$$

Unsolved example:

The enthalpy of fusion of water at 273K is 6.0kJ/mol-1 at constant pressure of 1 atm. Calculate its value at 263K.

$$C_{p(H2O)l} = 74.46\,Jmol^{-1}K^{-1}$$

$$C_{p(H2O)s} = 37.2\,Jmol^{-1}K^{-1}$$

The Second Law of Thermodynamics

The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or not.

The second law of thermodynamics asserts that processes occur in a certain direction and that the energy has *quality* as well as *quantity*.
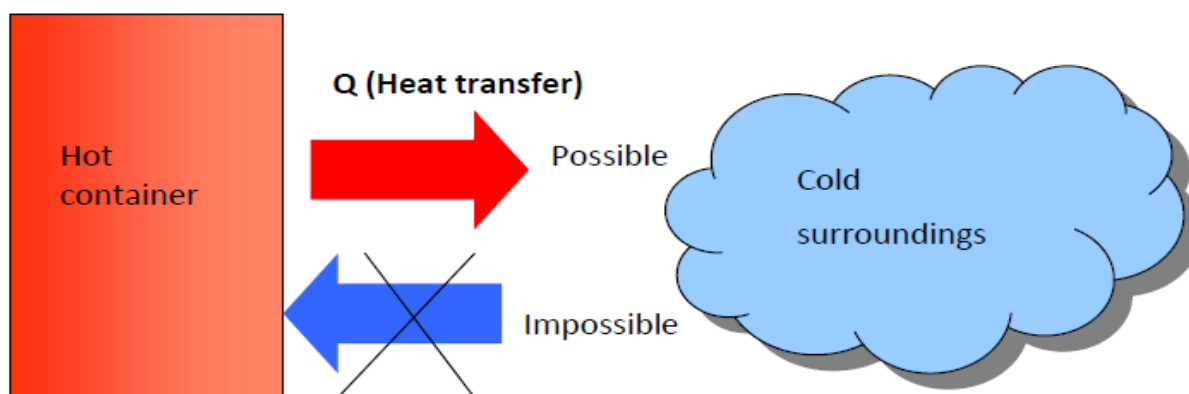
- Heat transfer from a hot container to the cold surroundings is possible; however, the reveres process (although satisfying the first law) is impossible.
- It is impossible to construct a machine working in cycles which will transfer heat from a lower temperature to a higher temperature.
- Heat cannot be completely converted into work without leaving changes either in the system or in the surroundings.
- Heat cannot be pass from a colder to a warmer body.
- No machine has yet been made with efficiency of a unity.

A process can occur when and only when it satisfies both the first and the second laws of thermodynamics.

The second law is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators etc.

Thermal Energy Reservoirs

Thermal energy reservoirs are hypothetical bodies with a *relatively* large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of **heat without undergoing any change in temperature**. Lakes, rivers, atmosphere, oceans are example of thermal reservoirs.

A two-phase system can be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature.

A reservoir that supplies energy in the form of heat is called a **source** and one that absorbs energy in the form of heat is called a **sink.**

Heat Engines

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

1-They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)

2-They convert part of this heat to work.

3-They reject the remaining waste heat to a low-temperature sink

4-They operate in a cycle.

The efficiency: is the fraction of the heat input that is converted to the net work output.

$$\eta = \frac{W_{net,out}}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

$$W_{net} = Q_{in} + Q_{out}$$
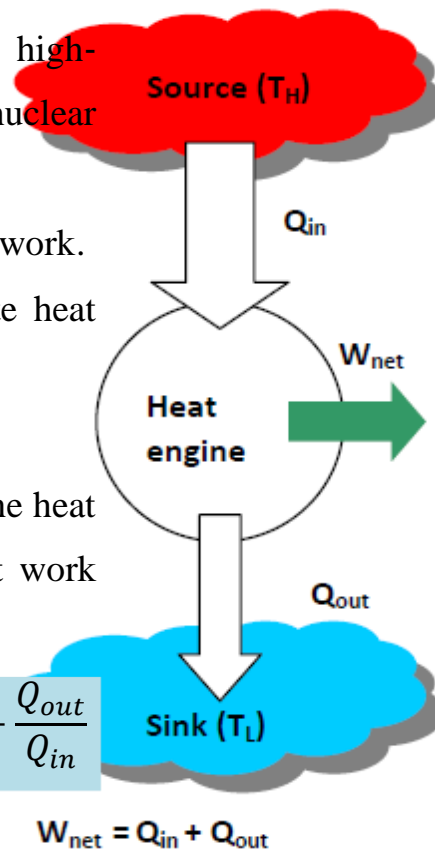
The Second Law: Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine can have a thermal efficiency of 100%.
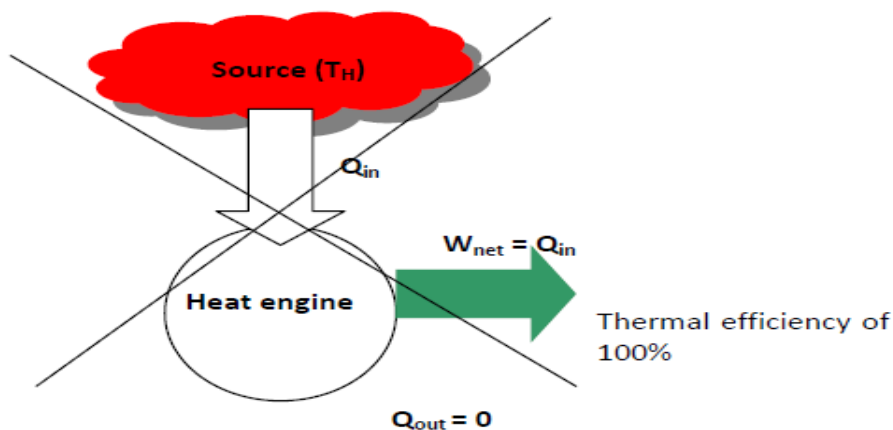
Refrigerators and Heat Pumps

In nature, heat flows from high-temperature regions to low-temperature ones. The reverse process, however, cannot occur by itself. The transfer

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of heat from a low temperature region to a high-temperature one requires special devices called ***refrigerators***. Refrigerators are cyclic devices, and the working fluids used in the cycles are called refrigerant.

Heat pumps transfer heat from a low-temperature medium to a high-temperature one some work is done on it by the surrounding and rejects heat at the higher temperature. It thus functions as a refrigerator, that is, it extracts heat from a cold reservoir and passes it to a hot reservoir. The ratio of work done on the engine to the heat absorbed at lower temperature is the coefficient of performance of the engine and is given as:

$$\frac{W}{Q_1} = \frac{(T_2 - T_1)}{T_2}$$

$$W = Q_1 \frac{(T_2 - T_1)}{T_2}$$

This equation represents the minimum amount of work which must be done to remove a quantity of heat (Q_1) at T_1 and giving it at higher temperature T_2.

The Second Law of Thermodynamics: Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body. In other words, a refrigerator will not operate unless its compressor is driven by an external power source.

Kelvin-Planck and Clausius statements of the second law are negative statements, and a negative statement cannot be proved. So, the second law, like the first law, is based on experimental observations.

The two statements of the second law are equivalent. In other words, any device violates the Kelvin-Planck statement also violates the Clausius statement and vice versa.
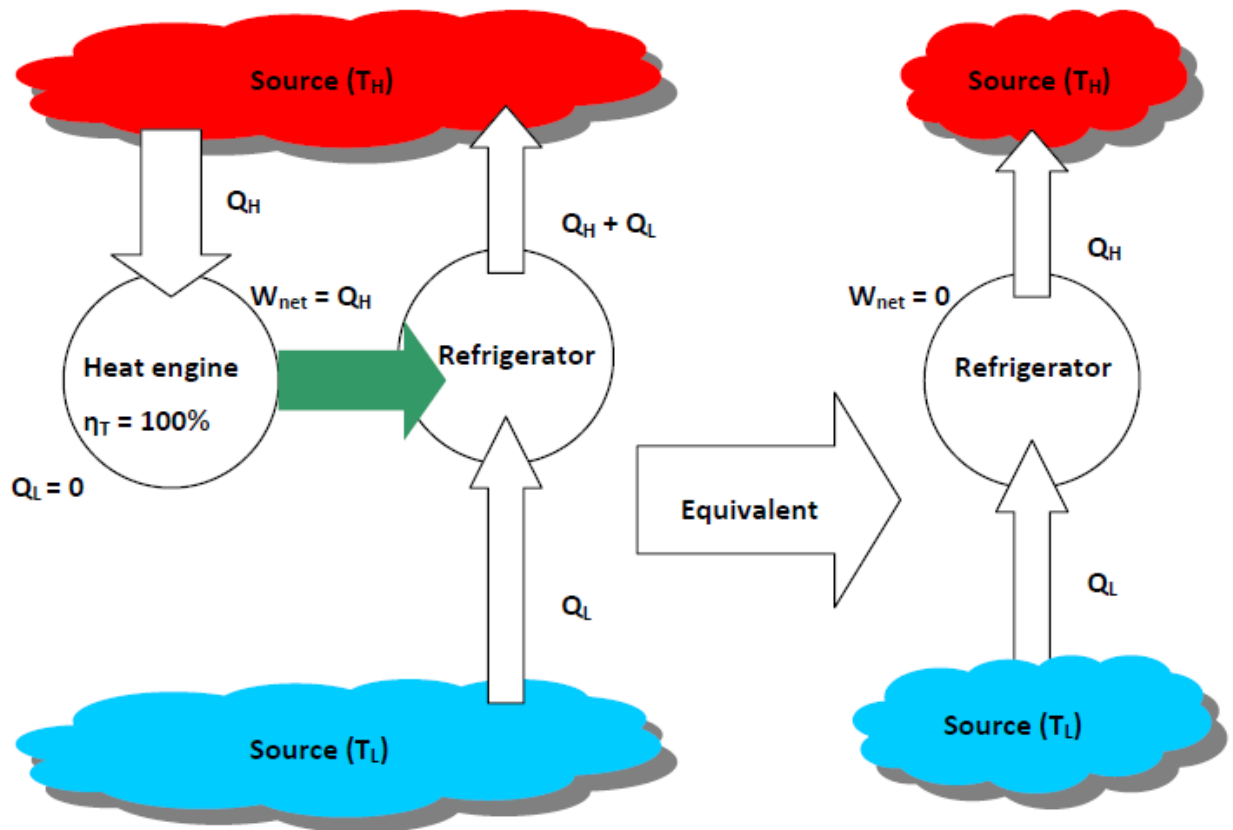
- Clausius introduced the function of entropy (S). Entropy function is a measure of randomness.
- Spontaneous processes are the processes which take place of their own without the external intervention of any kind.
- Spontaneous processes happen in one direction and are irreversible.
- Spontaneous processes pass from a less probable to more probable.

The Carnot Cycle

The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net

work (or efficiency) can be maximized by using reversible processes. The best known reversible cycle is the *Carnot cycle*.

Note that the reversible cycles cannot be achieved in practice because of irreversibility associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles.

- Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:
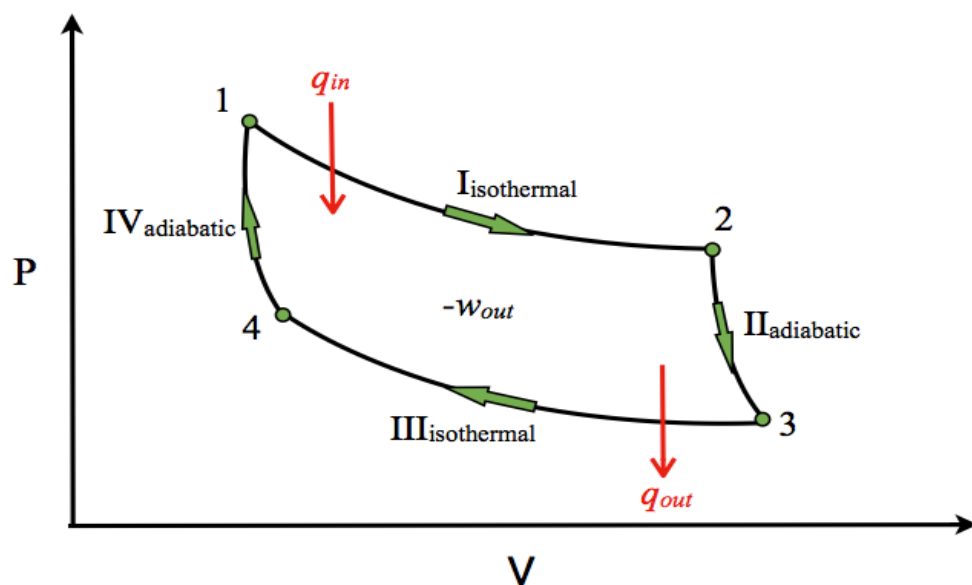
Carnot Cycle

(Step 1)Reversible isothermal expansion: The cylinder containing the gas is placed in contact with the reservoir T_2. It absorbs a certain quantity of heat q_2. The gas expands slowly, doing work on the surrounding; it expands isothermally and reversibly at the temperature T_2 of the source. The volume changes from V_1 to V_2. So there is no change in the internal energy $\Delta U = 0$

$$\Delta U = 0 \rightarrow q_2 = -W_1 = nRT_2 \ln\frac{V_2}{V_1}$$

(Step 2)Reversible adiabatic expansion: The cylinder is removed from the source. It is surrounding by a thermally insulated enclosure and the gas is allowed to expand reversibly and adiabatically from its volume V_2 to V_3 until its temperature drops to T_1, the temperature of the sink. The expansion is adiabatic: no heat enters or leaves the system. $q = 0$

$$W_2 = C_V(T_1 - T_2)$$

(Step 3)Reversible isothermal compression: The gas is allowed to exchange heat with a sink at temperature T_1 as the gas is being slowly compressed. So, the surrounding is doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at T_1 until it volume changes from V_3 to V_4.

$$\Delta U = 0 \rightarrow q_2 = -W_3 = nRT_1 \ln\frac{V_4}{V_3}$$

(Step 4)Reversible adiabatic compression: the cylinder is removed from the sink, surrounded by the thermal insulation and compressed adiabatically and reversibly until its temperature rises to that of source and volume decrease from V_4 to V_1.

$$W_4 = C_V(T_2 - T_1)$$

$$W = W_1 + W_2 + W_3 + W_4$$

$$W = -nRT \ln\frac{V_2}{V_1} + C_V(T_1 - T_2) - nRT \ln\frac{V_4}{V_3} + C_V(T_2 - T_1)$$

$$C_V(T_1 - T_2) = -C_V(T_2 - T_1)$$

$$W = -RT_2 \ln\frac{V_2}{V_1} + RT_1 \ln\frac{V_4}{V_3}$$

V_2, V_3 lie on the adiabatic I, V_1, V_4 on the adiabatic II.

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\left[\frac{V_3}{V_2} = \frac{V_4}{V_1}\right] \div \frac{V_2}{V_4} \rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

The net work is:

$$-W = RT_2 \ln\frac{V_2}{V_1} - RT_1 \ln\frac{V_3}{V_4} = R(T_2 - T_1)\ln\frac{V_2}{V_1}$$

The efficiency of the engine is thus:

$$\eta = \frac{-W}{q_2} = \frac{R(T_2 - T_1)\ln\frac{V_2}{V_1}}{RT_2 \ln\frac{V_2}{V_1}} = \frac{(T_2 - T_1)}{T_2} = 1 - \frac{T_1}{T_2}$$

Mathematical Formulation of Entropy

We now from Carnot cycle:-

$$\frac{-W}{q_2} = \frac{q_1 + q_2}{q_2} = \frac{(T_2 - T_1)}{T_2} = 1 + \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

In the Carnot cycle, heat is exchanged only in the isothermal steps and the sum of q/T terms represents a definite thermodynamic property of the system. It is called entropy which for an infinitesimally small changes in the state of the system is defined as the heat absorbed isothermally and reversibly divided by the temperature at which the absorption of heat takes place,

$$dS = \frac{q}{T}$$

$$for\ a\ finite\ changes\ in\ the\ state\ of\ the\ sstem\ \ \Delta S = \frac{q}{T}$$

$$\Delta S_{cycle} = \sum \frac{q_{rev}}{T} = 0$$

$$\oint dS \text{ is zero}$$

Relation between energy, enthalpy and entropy- combined form of the first law and the second law

$$\Delta U = q - w = q - PdV$$

$$dS = \frac{dq}{T} \rightarrow dq = TdS$$

$$\Delta U = TdS - PdV$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$\boxed{dH = TdS + VdP}$$

Entropy changes in reversible process (noncyclic process)

$$\Delta S_{sys} = \frac{q_{rev}}{T} \quad , \quad \Delta S_{surr} = -\frac{q_{rev}}{T}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

(i) Isothermal reversible process

$$\Delta S_{sys} = \frac{q_{rev}}{T}$$

$$q = -w = nRT_2 \ln\frac{V_2}{V_1} = nRT \ln\frac{P_1}{P_2}$$

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{nRT \ln\frac{V_2}{V_1}}{T} = nR \ln\frac{V_2}{V_1} = nR \ln\frac{P_1}{P_2}$$

$$\Delta S_{sys} = -\Delta S_{surr}$$

(ii) Isobaric Reversible process involving changes in Temperature

$$\Delta S_{sys} = \sum \left(\frac{q_{rev}}{T}\right)_P \quad , \quad q_P = \Delta H = C_P \Delta T$$

When C_p is independent on temperature

$$\Delta S_{sys} = \sum \frac{C_P \Delta T}{T}$$

By integration

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_P \Delta T}{T} = C_P ln \frac{T_2}{T_1} = 2.303 \, C_P ln \frac{T_2}{T_1}$$

(iii) Isochoric Reversible process involving changes in Temperature

$$\Delta S_{sys} = \sum \left(\frac{q_{rev}}{T}\right)_V \quad , \quad q_V = \Delta U = C_V \Delta T$$

$$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{C_V \Delta T}{T} = C_V ln \frac{T_2}{T_1} = 2.303 \, C_V ln \frac{T_2}{T_1}$$

(iv)Entropy changes in vacuum or against zero opposing pressure.

In this process no work is done by the system and the expansion is isothermally

$$\Delta U = 0 \rightarrow q_{free} = W = nRT \, ln \frac{V_2}{V_1} = nRT \, ln \frac{P_1}{P_2}$$

$$\Delta S_{sys} = \frac{q_{free}}{T}$$

As no heat is exchange between the system and the surrounding

$$\Delta S_{surr} = 0$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = nR \, ln \frac{V_2}{V_1} = nR \, ln \frac{P_1}{P_2}$$

(v) Reversible phase Transition

Transformation of substance from one phase to another can be carried out reversibly at constant temperature and constant pressure usually 1 atm.

$$q_{trans} = \Delta H_{trans}$$

$$\Delta S_{trans} = \frac{q_{trans}}{T}$$

Example:

$$(+)\quad \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \qquad Entropy\ of\ vaporization$$

$$(+)\quad \Delta S_{fus} = \frac{\Delta H_{fus}}{T_{fus}} \qquad Entropy\ of\ fusion$$

$$(+)\quad \Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}} \qquad Entropy\ of\ sublimation$$

$$(-)\quad \Delta S_{frez} = \frac{\Delta H_{frez}}{T_f} \qquad Entropy\ of\ freezing$$

Tronton's Rule

A wide range of liquids give approximately the same standard entropy of vaporization (about 85 JK^{-1} mol^{-1})

$$\Delta_{vap}S^{\circ} \approx 85\,JK^{-1}mol^{-1}$$

It is used to predict the standard molar enthalpy of vaporization $\Delta_{vap}H^{\circ}$ at boiling point.

$$\Delta_{vap}S^{\circ} = \frac{\Delta_{vap}H^{\circ}}{T}$$

$$\Delta_{vap}H^{\circ} = \Delta_{vap}S^{\circ} \times T_b = T_b \times 85\,JK^{-1}mol^{-1}$$

Variation of entropy with Temperature and volume

Considering entropy as a function of volume and temperature. For infinitesimal changes, dS can be written as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \ldots (1)$$

Considering U= f(V,T) we get:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= n\, C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Substituting this value of dU in this equation

$$TdS = dU + PdV$$

$$dS = \frac{n\, C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \ldots (2)$$

This equation is general and applicable to all substances solids, liquids, and gases. The first term on the right hand side of the equation gives the change in entropy due to change in temperature and the second expression denotes the contribution to entropy changes due to variation in volume. Comparing equation (1) and equation (2)

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n\, C_V}{T} \ldots \ldots (3)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \ldots \ldots (4)$$

For ideal gases $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{P}{T}$$

For one mole of ideal gas $\dfrac{P}{T} = \dfrac{R}{V}$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V}$$

$$\Delta S = R \ln \frac{V_2}{V_1}$$

For a mole of an ideal gas equation (2) reduces to:

$$dS = \frac{C_V \, dT}{T} + \frac{P}{T} dV = \frac{C_V \, dT}{T} + \frac{R}{V} dV$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{n \, C_V}{T}$$

Integration yields the total change in entropy resulting from simultaneous changes in volume and temperature. The expression is:

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For one mole of ideal gas $V = \frac{T}{P}$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \frac{T_2}{T_1}$$

$$\Delta S = (C_V + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Entropy of Mixing of Ideal gas

Mixing of two or more gases is irreversible and accompanied by an increase of entropy. We shall derive an expression for the entropy of mixing of ideal and nonreacting gases

Let consider two gases A and B, n_A is the number of moles of A and n_B is the number of moles of B. $n_t = n_A + n_B$

V= $V_A + V_B$

$$\Delta S_{mixing} = n_A R \ln \frac{V}{V_A} + n_B R \ln \frac{V}{V_B}$$

$$\Delta S_{mixing} = -n_A R \ln \frac{V_A}{V} - n_B R \ln \frac{V_B}{V}$$

$$\frac{V_A}{V} = \frac{n_A}{n_t} = X_A \ , \ \ \frac{V_B}{V} = \frac{n_B}{n_t} = X_B$$

$$\Delta S_{mixing} = -n_A R \ ln \ X_A - n_B R \ ln \ X_B$$

$$\Delta S_{mixing} = -R \sum n_i \ ln \ X_i$$

The entropy of mixing per mole of the mixture is obtained by dividing both sides of the above equation by n_i , the total number of moles;

$$\Delta S_{mixing} = -R \sum X_i \ ln \ X_i$$

The Third Law of thermodynamics

Variation of entropy of a substance with temperature at constant pressure is given by:

$$dS = \frac{C_P}{T} dT$$

Integrating this equation from T=0K to some temperature T below the melting point of the substance we get:

$$T_1 = 0K$$

$$T_2 = T$$

$$S_T - S_0 = \int_0^T \frac{C_P}{T} \ dT = C_P \ d \ln T$$

Where S_0 is the hypothetical value of entropy at absolute zero. C_P/T is positive, the entropy at some higher temperature must be greater than that at the absolute zero. In 1913, Plank suggested that entropy of a pure and perfectly crystalline substance is zero at the absolute zero of temperature. This known as the third law of thermodynamics.

If S_0 is taken to be zero at zero Kelvin:

$$S_T = \int_0^T \frac{C_P}{T} \ dT$$

Knowing the temperature dependence of heat capacity, entropy of a substance at any specified temperature can be calculated using the above equation. In evaluating the absolute value of entropy contributions to entropy due to phase transformations such as melting, vaporization, sublimation and transition from one allotropic form into other must be taken into account.

The entropy of a substance at any temperature above its boiling point is then given as:

$$S_T = \int_{trans}^{T_m} \frac{C_{P(s)}}{T}\,dT + \frac{\Delta H_{fus}}{T_m} + \int_{Tm}^{T_s} \frac{C_{P(l)}}{T}\,dT + \frac{\Delta H_{vap}}{T_b}$$
$$+ \int_{Tb}^{Tm} \frac{C_{P(g)}}{T}\,dT$$

Some Fundamental relation based on the second law of thermodynamics:

Prove that:

(1) $\quad \left(\dfrac{\partial P}{\partial T}\right)_S = \dfrac{C_P}{T\left(\dfrac{\partial V}{\partial T}\right)_P}$

$\left(\dfrac{\partial S}{\partial T}\right)_P = \dfrac{C_P}{T}$

$\left(\dfrac{\partial S}{\partial V}\right)_P \left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{C_P}{T}$

$dH = VdP + TdS$

$\left(\dfrac{\partial S}{\partial V}\right)_P = \left(\dfrac{\partial P}{\partial T}\right)_S$

Replacing $\quad \left(\dfrac{\partial S}{\partial V}\right)_P \quad by \quad \left(\dfrac{\partial P}{\partial T}\right)_S$

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{T\left(\frac{\partial V}{\partial T}\right)_P}$$

(2) For an ideal gas

$$\left(\frac{\partial P}{\partial V}\right)_S = \frac{\gamma\, P}{V}$$

Consider $\quad S = f(P.V)$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

If $\quad dS = 0 \quad$ then:

$$\left(\frac{\partial S}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P$$

$$\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial P}{\partial S}\right)_V$$

$$= \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$

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

$$= -\frac{C_P}{C_V}\frac{R}{V}\frac{P}{R} = \gamma\,\frac{P}{V}$$

(3) $\quad \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial H}{\partial P}\right)_S = -R \left(\frac{\partial U}{\partial S}\right)_V$

$$dU = TdS - PdV$$

$$dT = TdS + VdP$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad and \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

The left hand side is thus –PV which is equal to RT. The right hand side is:

$$-R \ \left(\frac{\partial U}{\partial V}\right)_S = -R \ \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$

$$= -RC_V \frac{T}{C_V} = -RT$$

Solved Examples

Example1: Two moles of an ideal monoatomic gas $C_P=5/2$ R initially at 1 atm and 300 K are subjected through the following reversible cycle:

(1) isothermal compression to 2 atm.

$$\Delta S_{sys} = -nR \ln \frac{P_2}{P_1} = -2 \times 8.314 \ln \frac{2}{1} = -11.52 JK^{-1}$$

(2) isobaric temperature increase to 400K.

$$\Delta S = nC_P \ \ln \frac{T_2}{T_1} = 2 \times \frac{5}{2} \times 8.314 \ln \frac{400}{300} = 11.97 JK^{-1}$$

(3) Return to the initial state by a different path.

$$\Delta S_{cycl} = 0 = \Delta S_1 + \ \Delta S_2 + \Delta S_3 = -11.52 + 11.97 + \ \Delta S_3$$

$$\Delta S_{cycl} = \ -0.45 JK^{-1}$$

Example2: One mole of an ideal gas C_V= 12.55 JK^{-1} mol^{-1} is transferred from 298K and 2 atm to 233K and 0.4 atm. Calculate for the change in the state of the system.

Solution:

$$C_V = 12.55 JK^{-1}mol^{-1} \rightarrow C_P = 12.55 + 8.314 = 20.86 JK^{-1}mol^{-1}$$

$$\Delta S = nC_P \ \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

$$\Delta S = (1mol)(20.864) \ln \frac{233}{298} - (1mol)(8.314) \ln \frac{0.4}{2}$$

$$= -3.308 + 13.40 = 10.092 JK^{-1}mol^{-1}$$

Example3: the temperature of an ideal monoatomic gas is increase from 273K to 819K. Calculate the pressure change in order that the entropy of the gas remains unchanged in the process?

$$\Delta S_{sys} = nC_P \ln\frac{T_2}{T_1} - nR \ln\frac{P_2}{P_1}$$

$$\Delta S_{sys} = 0$$

$$nC_P \ln\frac{T_2}{T_1} = nR \ln\frac{P_2}{P_1}$$

$$\frac{5}{2}R \ln\frac{T_2}{T_1} = R \ln\frac{P_2}{P_1}$$

$$\frac{5}{2}\ln\frac{819}{273} = \ln\frac{P_2}{P_1}$$

$$\ln\frac{P_2}{P_1} = 2.74 \rightarrow \frac{P_2}{P_1} = 15.588$$

Example4: One mole of hydrogen and nine moles of nitrogen are mixed at 298K and 1 atm pressure. Assuming ideal behavior for the gases, calculate the entropy of mixing per mole of the mixture formed.

For ideal gases, the entropy of mixing per mole of mixture is given by:

$$\Delta S_{mix} = -R \sum X_i \ln X_i$$

$$X_{H_2O} = 0.1 \ and \ X_{N_2} = 0.9$$

$$\Delta S_{mix} = -R \ [0.1 \ln 0.1 + 0.9 \ln 0.9]$$

$$= -8.314 \times -0.3248 = 2.704 JK^{-1}mol^{-1}$$

Example4: Predict the enthalpy of vaporization of ethane from its boiling point,

−88.6°C.

$$\Delta_{vap}H^° = \Delta_{vap}S^° \times T_b$$

$$\Delta_{vap}H^° = 85 \ JK^{-1}mol^{-1} \times (-88.6 + 273)K = 15.6 \ kJ \ mol^{-1}$$

Example 5: A reversible heat engine absorbs 40kJ of heat at 500 K and performs 10kJ of work rejecting the remaining amount to the sink at 300K. Calculate the entropy change for the source, sink and universe.

$$q_2 = 40000J$$

$$\Delta S_{source} = -\frac{40000}{500} = -80 JK^{-1}$$

$$q_1 = 40kJ - 10kJ = 30000J$$

$$\Delta S_{sink} = \frac{30000\ J}{300K} = 100 JK^{-1}$$

$$\Delta S_{univ} = \Delta S_{source} + \Delta S_{sink} = -80 + 100 = 20\ JK^{-1}$$

Exercises

(1) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = 5/2R$, is changed from 25°C and 1.00 atm to 125°C and 5.00 atm.

(2) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = 7/2R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm.

(3) A sample consisting of 3mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,m} = 27.5$ J K^{-1} mol^{-1}, calculate q, w, ΔU, ΔH, and ΔS.

(4) A carnot engine whose low temperature reservoir is at 280 K has an efficiency of 40%. It is desired to increase this to 50 %. By how much many degrees must the temperature of the low temperature reservoir be decreased if that of the high temperature reservoir remains constant.

(5) 2 moles of an ideal monoatomic gas at 300K and 10 atm pressure is expanded to 20 times its original volume by (i) isothermal reversible path and (ii) adiabatic reversible path.

(6) 10 moles of an ideal monoatomic gas ($C_{P,m} = 28.314$ J K^{-1} mol^{-1}) at 400K and 10 atm are expanded adiabatically to 2 atm. Calculate the entropy change for the system, surrounding and universe if the process is (1) reversible (2) expansion is a free expansion.

Free Energy Functions

An irreversible change is always spontaneous and in an isolated system the entropy must increase and should be maximum at equilibrium. All the natural processes are spontaneous and rarely occur in isolated systems. In selecting entropy as a criterion of spontaneity is not convenient. So it desirable to introduce new functions as criteria of spontaneity. These functions are the Helmholtz free energy or the work function denoted by A and the Gibbs free energy or Gibbs potential represented by G. They are defined as:

$$A = U - TS$$

$$G = H - TS$$

The values of A and G are defined by the state of the system and are independent of the path followed for the change in the state of the system, both are single-valud thermodynamic functions of the system. dA and aG are exact differentials and the cyclic integrals are zero. They are extensive properties of the system and depend on the quantity of the matter and nature of the system.

$$\oint dA = 0 \quad , \quad \oint dG = 0$$

Relation between A and G

From the definition of enthalpy $H = U + PV$

$$G = H - TS$$

$$G = U + PV - TS$$

$$as \ \ A = U - TS$$

$$G = A + PV$$

Changes in A and G in isothermal processes

The change in A for an isothermal process is given by:

$$\Delta A = A_2 - A_1$$

$$\Delta A = (U_2 - TS_2) - (U_1 - TS_1)$$

$$\Delta A = (U_2 - U_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta U - T\Delta S$$

For infinitesimal change

$$dA = dU - TdS$$

Similarly, the change in Gibbs free energy for isothermal process is given by:

$$\Delta G = G_2 - G_1$$

$$\Delta G = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

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

For infinitesimal change

$$dG = dH - TdS$$

Significant of A and G

For a system of fixed composition:

$$dA = dU - TdS - SdT$$

$$dU = TdS + W_{rev}$$

W_{rev}: reversible work done by the system and include both mechanical and non mechanical work.

$$dA = TdS - TdS - SdT + W_{rev} = -SdT + W_{rev}$$

If the process is isothermal dT=0

$$d(A)_T = -P(dV)_T$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \qquad , P = \frac{nRT}{V}$$

$$\int_{A_1}^{A_2} dA = -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$\Delta A = A_2 - A_1 = -nRT \ln \frac{V_2}{V_1}$$

$$= nRT \ln \frac{V_1}{V_2} = \boldsymbol{n}RT \ln \frac{P_2}{P_1}$$

$$dG = dH - TdS - SdT$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = TdS - PdV + VdP + PdV - TdS - SdT$$

$$dG = VdP - SdT$$

At constant T, -SdT =0

$$\Delta G = VdP$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad , \qquad V = \frac{nRT}{P}$$

$$\int_{G_1}^{G_2} dG = -\int_{P_1}^{P_2} \frac{nRT}{P} =$$

$$\Delta\boldsymbol{G} = \boldsymbol{n}RT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

We show that ΔG=ΔA in isothermal process.

If the change from G^0 to G and from P^0 to P , where G^0 is Gibbs energy at standard state.

$$\int_{G^0}^{G} dG = nRT \int_{P^0}^{P} \frac{dP}{P}$$

$$G = G^0 + RT \ln \frac{P}{P^0}$$

Maxwell's Relation

The four fundamental thermodynamics equation are:

$$dU = TdS - PdV \ldots \ldots (1)$$

$$dH = TdS + VdP \ldots \ldots (2)$$

$$dA = -SdT - PdV \ldots \ldots (3)$$

$$dG = -SdT + VdP \ldots \ldots (4)$$

From these relations we can be derived four relations known as Maxwell's relation as follow:

$$U = f(S,V) \qquad , \qquad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$H = f(S,P) \qquad , \qquad dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$A = f(T,V) \qquad , \qquad dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S, \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$G = f(T,P) \qquad , \qquad dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T \qquad , \qquad \left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T = V \qquad , \qquad \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$Z = f(x, y)$$

$$dZ = MdX + NdY$$

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y = M \quad , \quad \left(\frac{\partial Z}{\partial Y}\right)_X = N$$

Since the mixed partial derivatives

$$\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y$$

$$dU = TdS - PdV$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \dots\dots (a)$$

$$dH = TdS + VdP$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \dots\dots.. (b)$$

$$dA = -SdT - PdV$$

$$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V \quad \dots\dots.. (c)$$

$$dG = -SdT + VdP$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad \dots\dots\dots. (d)$$

A, b, c and d are called **Maxwell's relation**.

Variation of Gibbs energy with Temperature at constant pressure

$$dG = -SdT + VdP$$

At constant pressure dP=0

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \dots\dots (1)$$

From the definition: $G = H - TS$

$$S = \frac{H - G}{T} \dots\dots\dots (2)$$

Substitute eq(2) in eq(1) yields:

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{G - H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = \frac{H}{T} \dots\dots\dots (3)$$

The left side of eq (3) is simplified as:

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\frac{d}{dT}\frac{1}{T}$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2}$$

$$= \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right] \dots\dots (4)$$

Substitute eq (3) in (4) we get:

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = \frac{1}{T}\left[-\frac{H}{T}\right]$$

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{H}{T^2}$$

This is Gibbs-Helmholtz equation.

For change between final and initial state:

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{\partial T}\right)_P = -\frac{H}{T^2}$$

If we can determine ΔG for reactions, we can calculate ΔH without using a calorimetry.

If ΔH and ΔG are known at one temperature, we can calculate ΔG at another temperature assuming ΔH is independent on T.

Chemical Potential of an Ideal gas

The quantity μ_i defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n}$$

μ_i is known as the chemical potential of the I component.

" The increase in G per mole that results when a small amount dn_i moles are added to the system keeping temperature, pressure and all other compositions constant.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

For pure substance G= n$\bar{G}$, $\bar{G}$ is the molar Gibbs energy.

$$\mu_i = \left(\frac{\partial nG}{\partial n_i}\right)_{T,P}$$

From equation: $G = G^0 + RT \ln\frac{P}{P^0}$

$\mu = \mu^0 + RT \ln\frac{P}{P^0}$, μ^0 : chemical potential in the standard state

In a mixture of ideal gases, chemical potential of the ith component is given by:

$$\mu_i = \mu^0_i + RT \ln P_i \quad , \quad P_0 = 1\ atm$$

$$P_i = X_i\ P \quad , \quad P = total\ pressure, \quad X_i = mole\ fraction$$

$$\mu_i = \mu^0_i + RT \ln X_i\ P$$

$$\mu_i = \mu^0_{\ i} + RT \ln P + RT \ln X_i$$

$\boldsymbol{\mu^0_{\ i} + RT \ln P}$: *is the chemical potential of pure substance*

Thermodynamics of Mixing of Ideal Gases

$$\Delta G_{mix} = RT \sum_i X_i \ln X_i$$

$$\Delta S_{mix} = -R \sum_i X_i \ln X_i$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = RT \sum_i X_i \ln X_i - RT \sum_i X_i \ln X_i = \boldsymbol{0}$$

ΔV_{mix}
$= 0$, *no change in volume occurs when ideal gases were mixed*

The Clapeyron Equation

For a pure substance present in two phase 1 and 2 at a pressure P and temperature T, the condition of equilibrium:

$$G_{m,1} = G_{m,2} \quad , \quad \Delta G = 0$$

Where $G_{m,1}$ and $G_{m,2}$ are the free energies per mole in phase 2 and 1, respectively.

If the pressure of the system is changed to P+dP and temperature to T+dT, the value of G will changed to G_m+dG_m :

$$G_1 + dG_1 = G_2 + dG_2$$

$$G_1 = G_2 \quad , \quad dG_1 = dG_2$$

$$dG_1 = V_1 dP - S_1 dT$$

$$dG_2 = V_2 dP - S_2 dT$$

$$S_2 - S_1 = dT = (V_2 - V_1)dP$$

$$\frac{dT}{dP} = \frac{(V_2 - V_1)}{(S_2 - S_1)} = \frac{\Delta V}{\Delta S}$$

This is known as the **Clapeyron equation** and holds for the equilibrium between two phases of a substance.

i) For liquid- vapour equilibrium: the molar entropy of a gas are higher than those for the liquids, therefore ΔS_m and ΔV_m are always positive for liquid vapour transformation and the quantity dP/dT will be positive. A rise in temperature increases the equilibrium vapour pressure of the liquid.

(ii) For solid- vapour transformation: for solid –vapour transformation

$$\Delta S_m = S_{m,g} - S_{m,s} = \frac{\Delta H_{sub}}{T} = positive$$

$$\Delta V_m = V_{m,g} - V_{m,s} = positive \quad , \quad \frac{dP}{dT} = positive$$

Increase in temperature increase the equilibrium vapour of the solid. Further

$$\Delta H_{sub,m} = \Delta H_{fus,m} + \Delta H_{vap,m}$$

$$\Delta H_{sub,m} > \Delta H_{vap,m}$$

(iii) For solid- liquid equilibrium: in this case

$$\Delta S_m = S_{m,l} - S_{m,s} = \frac{\Delta H_{fus,m}}{T} = positive$$

For most of the substance $\quad \Delta V_m = V_{m,l} - V_{m,s} = positive \quad , \frac{dP}{dT} = positive$

Clausius- Clapeyron Equation

In solid-vapour or liquid-vapour equilibrium if $V_{m,l}$ or $V_{m,S}$ can be neglected in comparison to $V_{m,g}$, then the calpeyron equation becomes:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_{vap,m}}{T V_{m,g}}$$

$$\Delta S_m = \frac{\Delta H_{vap,m}}{T}$$

If the vapours are assumed to behave ideally, then $V_{m,g}$ can be replaced by $\frac{RT}{P}$

$$\frac{dP}{dT} = \frac{\Delta H_{vap,m} \, P}{T.RT}$$

$$\frac{dP}{P} = \frac{\Delta H_{vap,m}}{RT^2} dT$$

For small temperature variation, $\Delta H_{vap,m}$ may be assumed to be constant. Integration of the above equation then yields Clausius- Clapeyron Equation:
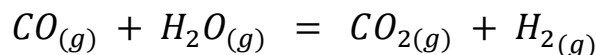
$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vap,m}}{R}\frac{(T_2 - T_1)}{T_1 T_2}$$

Solved Examples

Example 1: the entropy and enthalpy changes for the reaction :

$$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$$

At 300 K and 1 atm pressure are respectively -42.4 JK^{-1} and -41.2 kJ. Calculate the free energy change for the reaction, predict if the reaction is feasible and the temperature at which the reaction will go in the opposite direction.

**Solution:** the free energy of the reaction is given by:

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

$$= (-41.2 + 300 \times 42.4) = -28.48\ kJ$$

Since ΔG < 0 , the reaction is spontaneous.

It will go in the opposite direction as soon as ΔG start changing its sign, so the minimum temperature at which ΔG becomes zero can be calculated as:

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

$$T = \frac{\Delta H}{\Delta S} = \frac{41.2 \times 10^3}{42.4} = 971.7K$$

Example 2: It is found that ΔH= -2810 kJ mol^{-1} and ΔS= 182.4JK^{-1} when glucose is oxidized at 300 K according to the reaction: Calculate the free energy.

$$C_6H_2O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$$
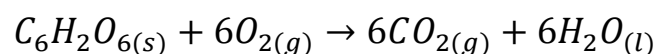
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-2810) - (300)(182.4 \times 10^{-3})kJ\ mol^{-1}$$

$$\Delta G = (-2810) - 54.72)\ kJmol^{-1} = -2864.72kJmol^{-1}$$

Example 3: one mole of an ideal gas expands isothermally and reversibly from 5 dm^3 to 10 dm^3 at 300K. Calculate q, W, ΔU, ΔH, ΔS , ΔA, and ΔG.

For isothermal process ΔT=0, ΔU=0, ΔH=0

$$q = -W_{rev} = nRT \ln\frac{V_2}{V_1} = 1729 Jmol^{-1}$$

$$\Delta S = nR \ln\frac{V_2}{V_1} = 1 \times 8.314 \times ln\frac{10}{5} = 5.76\ JK^{-1}mol^{-1}$$

$$\Delta G = \Delta A = -nRT \ln\frac{V_2}{V_1} = -1729 Jmol^{-1}$$

Example 4: the boiling point of water is 373K at 1atm pressure. Calculate q, W, ΔU, ΔH, ΔS , ΔA, and ΔG when a mole of steam is compressed isothermally and reversibly. The heat of vaporization of water is 40.67 kJmol^{-1}.

$$-W = P\Delta V = P(V_l - V_g) = -PV_g = -RT = -8.314 \times 373$$
$$= -3100 Jmol^{-1}$$

$$q_P = \Delta H = -40.67\ kJmol^{-1}$$

$$\Delta U = \Delta H - P\Delta V = -40.67kJmol^{-1} + 3.1kJmol^{-1}$$
$$= -37.57kJmol^{-1}$$

$$\Delta A = W = 3.1kJmol^{-1}$$

$$\Delta S = \frac{q_{rev}}{T} = -\frac{40.67}{373} = -109\ J\ K^{-1}mol^{-1}$$

Exercises

1- Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

2- Calculate ΔG and ΔA when 4 moles of an ideal gas are expanded isothermally and reversibly from 5 atm to 1 atm at 323K.

3- 1mole of perfect gas molecules at 27°C is expanded isothermally and reversibly from an initial pressure of 3.00 atm to a final pressure of 1.00 atm. determine the values of q, w, ΔU, ΔH, ΔS, ΔA and ΔG.

4- Assuming that He and N_2 form an ideal gaseous mixture, calculate ΔU, ΔH, ΔS, ΔV, ΔA and ΔG when 5 moles of He and 3 moles of N_2 are mixed at 298K.

5- 1 mole of an ideal gas (C_v= 30J K^{-1}mol^{-1}) initially at 300 K and 1 atm is heated at constant pressure until the final volume is doubled. Calculate of q, w, ΔU, ΔH, ΔS, and ΔG for the process.

6- For the reaction below ΔH is -562.59 kJ and ΔS is -194.75 JK^{-1} at 298K, show that the reaction is non-spontaneous and calculate the minimum temperature at which the reaction will be reversed.

$$H_2S_{(g)} + \frac{3}{2}O_{2(g)} = H_2S_{(l)} + SO_{2(g)}$$
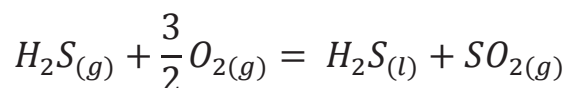
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