Course Name: Chemistry
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Thermodynamics

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Thermodynamics

Definition: Thermodynamics is a branch of science that deals with heat, work, and temperature, and their relation to energy, radiation, and physical properties of matter.

The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics. Thermodynamics applies to a wide variety of topics in science and engineering.

Laws of thermodynamics

Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each.

Zeroth Law

The zeroth law of thermodynamics states that "If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other". This statement implies that thermal equilibrium is an equivalence relation on the set of thermodynamics systems under consideration. This law is tacitly assumed in every measurement of temperature.

First Law

The first law of thermodynamics states that "In a process without transfer of matter, the change in internal energy, ΔU of a thermodynamic system is equal to the energy gained as heat, Q, less the thermodynamic work, W, done by the system on its surroundings".

Mathematical expression of first law of thermodynamics

$$\Delta U = Q - W$$

This law is an expression of the principle of conservation of energy, which states that energy can be transformed but cannot be created or destroyed

Second Law

A traditional version of the second law of thermodynamics states that "Heat does not spontaneously flow from a colder body to a hotter".

Another form of second law

"It is impossible for a self acting machine to transfer heat from a body at lower temperature to higher temperature".

Mathematical expression of the second law of thermodynamics is

$$\Delta S \geq 0$$

Where S (randomness of a system) is entropy of the system.

The second law of thermodynamics can also be stated that "all spontaneous processes produce an increase in the entropy of the universe".

Third law of Thermodynamics

The third law of thermodynamics states that "As the temperature of a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value".

Another form of third law

The entropy of all pure crystalline solids may be taken as zero at the absolute zero of temperature.

The statement is confined to pure crystalline solids because theoretical argument and experimental evidence have shown that the entropy of solutions and super cooled liquids is not zero at 0 K.

Mathematical expression of third law of thermodynamics is

$$S_{T=0}=0 \text{ (For a perfect crystal)}$$

Work Done for Expansion of Gases

Constant Pressure and Volume

Isobaric process is one in which a gas does work at constant pressure, while an isochoric process is one in which volume is kept constant.

According to the first law of thermodynamics, heat transferred to a system can be either converted to internal energy or used to do work to the environment. A process in which a gas does work on its environment at constant pressure is called an isobaric process, while one in which volume is kept constant is called an isochoric process.

Isobaric Process (Constant Pressure)

In the isobaric process since the pressure is constant, the force exerted is constant and the work done is given as PΔV. An example would be to have a movable piston in a cylinder (Figure below), so that the pressure inside the cylinder is always at atmospheric pressure, although it is isolated from the atmosphere. In other words, the system is dynamically connected, by a movable boundary, to a constant-pressure reservoir. If a gas is to expand at a constant pressure, heat should be transferred into the system at a certain rate. This process is called an isobaric expansion.
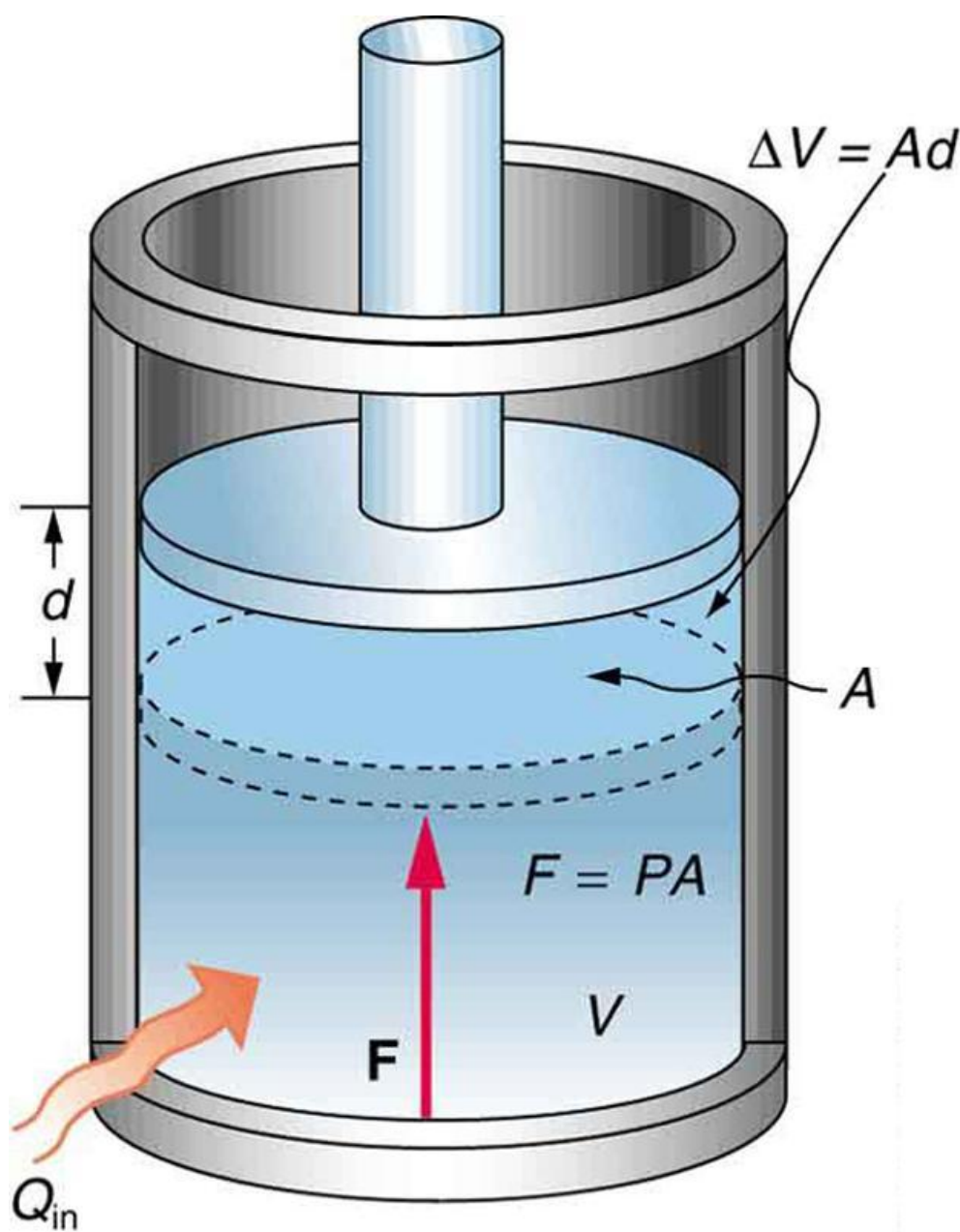
Figure: An isobaric expansion of a gas requires heat transfer during the expansion to keep the pressure constant. Since pressure is constant, the work done is PΔV.

Isochoric Process (Constant Volume)

An isochoric process is one in which the volume is held constant, meaning that the work done by the system will be zero. It follows that, for the simple system of two dimensions, any heat energy transferred to the system externally will be absorbed as internal energy. An example would be to place a closed tin can containing only air into a fire. To a first approximation, the can will not expand, and the only change will be that the gas gains internal energy, as evidenced by its increase in temperature and pressure. Mathematically,

$$\Delta Q = \Delta U$$

Isothermal Processes (Temperature Constant)

An isothermal process is a change of a thermodynamic system, in which the temperature remains constant.

An isothermal process in which the temperature remains constant ($\Delta T=0$). This typically occurs when a system is in contact with an outside thermal reservoir, and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange. In other words, in an isothermal process, the value $\Delta T=0$ but $Q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but $Q = 0$.

Ideal Gas in an Isothermal Process

For an ideal gas, the product of pressure and volume (PV) is a constant if the gas is kept at isothermal conditions. However, the cases where the product PV is an exponential term, does not comply. The value of the constant is nRT, where n is the number of moles of gas present and R is the ideal gas constant. In other words, the ideal gas law PV = nRT applies. This means that

$$P=nRT/V=Constant/V$$

holds.

In thermodynamics, the work involved when a gas changes from state A to state B is simply

$$W_{A \rightarrow B} = \int_{VA}^{VB} P dV$$

For an isothermal, reversible process, this integral equals the area under the relevant pressure-volume isotherm, and is indicated in blue in for an ideal gas. Again, P=nRT/V applies and with T being constant, we have

Figure: Work Done by Gas During Expansion: The blue area represents "work" done by the gas during expansion for this isothermal change.
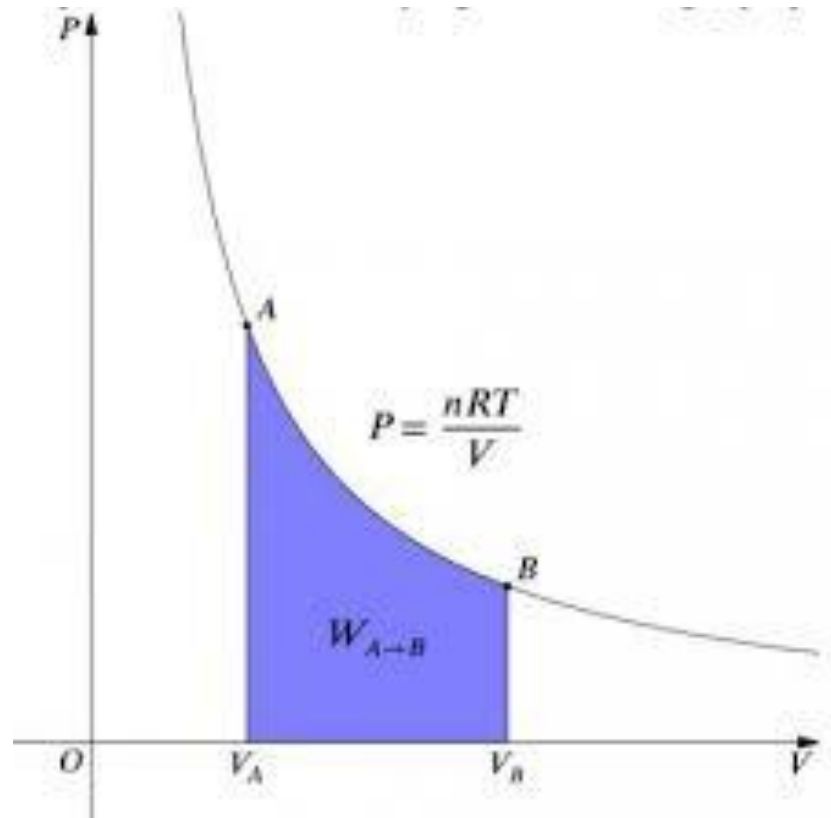
$$W_{A \to B} = nRT \int_{VA}^{VB} 1/V dV = nRT \ln V_B / V_A$$

It is also worth noting that, for many systems, if the temperature is held constant, the internal energy of the system also is constant, and so $\Delta U = 0$. From the first law of thermodynamics, it follows that $Q = -W$ for this same isothermal process.
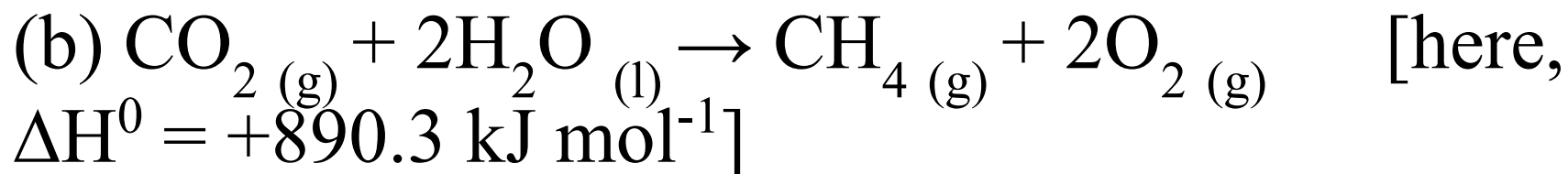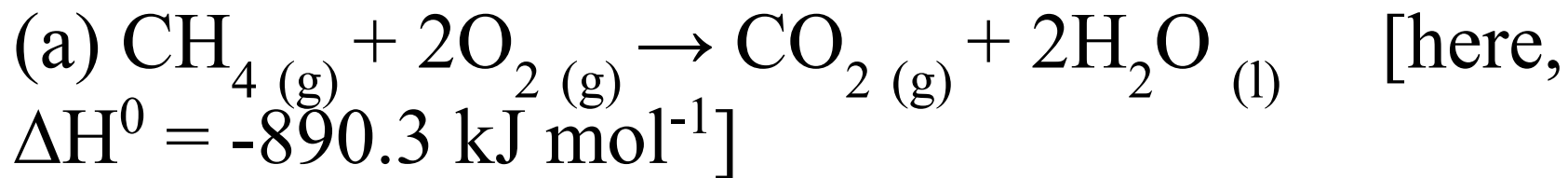
Thermochemistry

Thermochemistry is the study of the heat energy which is associated with chemical reactions and/or physical transformations. A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings. Thermochemistry is useful in predicting reactant and product quantities throughout the course of a given reaction.

Thermochemistry rests on two generalizations. Stated in modern terms, they are as follows:

Lavoisier and Laplace's law of Thermochemistry

Lavoisier and Laplace law states that the energy change accompanying any transformation is equal and opposite to energy change accompanying the reverse process.

This is evident from the following two fractions:

(a) $CH_{4\ (g)} + 2O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2H_2O_{(l)}$ [here, $\Delta H^0 = -890.3$ kJ mol^{-1}]

(b) $CO_{2\ (g)} + 2H_2O_{(l)} \rightarrow CH_{4\ (g)} + 2O_{2\ (g)}$ [here, $\Delta H^0 = +890.3$ kJ mol^{-1}]

Thus, it can be concluded that $\Delta H_{\text{forward reaction}} = \Delta H_{\text{backword reaction}}$

Hess's Law

The enthalpy change accompanying a chemical change is independent of the route by which the chemical change occurs. or
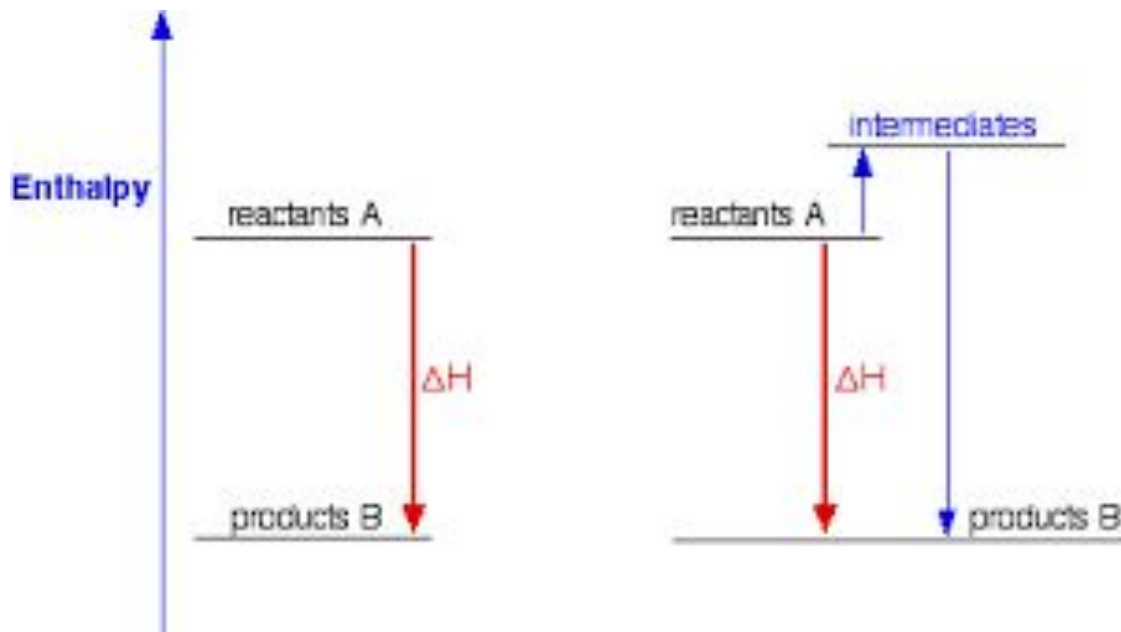
Hess's law states that the energy change accompanying any transformation is the same whether the process occurs in one step or many.
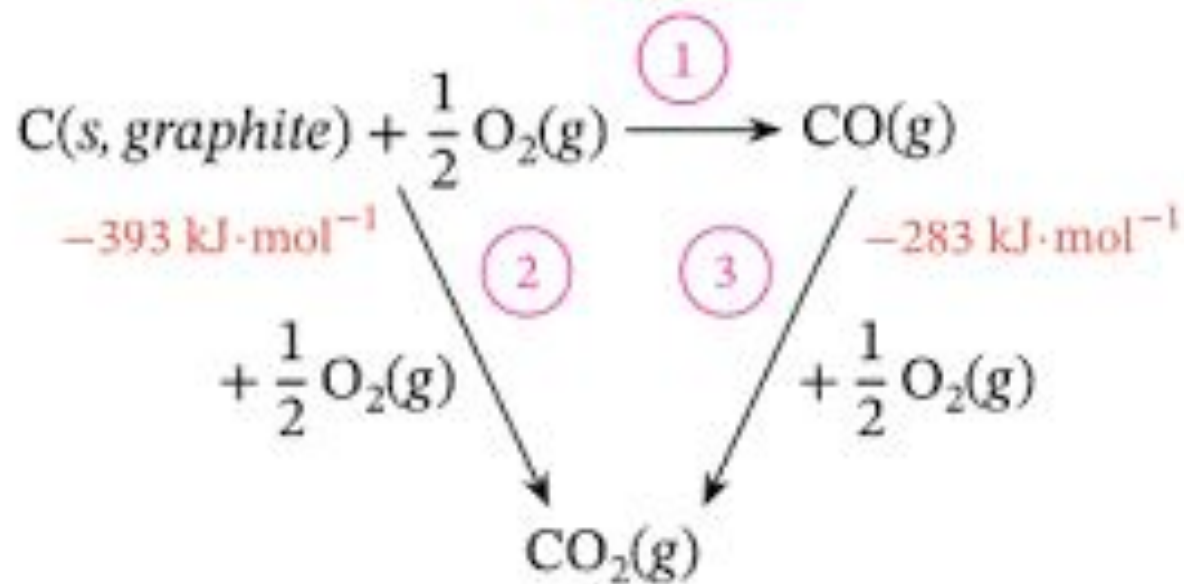
Explaining Hess's Law

Hess's Law is saying that if you convert reactants A into products B, the overall enthalpy change will be exactly the same whether you do it in one step or two steps or however many steps.

If you look at the change on an enthalpy diagram, that is actually fairly obvious.

Figure: This shows the enthalpy changes for an exothermic reaction using two different ways of getting from reactants A to products B.

Unknown

$$C(s, \textit{graphite}) + \frac{1}{2}O_2(g) \xrightarrow{\;\;①\;\;} CO(g)$$

$-393 \text{ kJ} \cdot \text{mol}^{-1}$ ②   ③ $-283 \text{ kJ} \cdot \text{mol}^{-1}$

$+\frac{1}{2}O_2(g)$ $+\frac{1}{2}O_2(g)$

$$CO_2(g)$$

State Function

State function is defined as the property whose value depends only upon the state of the system and is independent of the path by which state has been reached.

For example: a person standing on the roof of the building has a fixed value of potential energy and the potential energy of person does not depend whether he has reached there by stairs or lift.

Potential energy, pressure, volume, temperature internal energy, enthalpy, entropy, free energy etc. are examples of state functions.

State functions are written as uppercase letters (E, H, P, V, T, S…….)

Internal Energy (U)

Internal energy of a system is the sum of kinetic energies of all of its constituent particles, plus the sum of the potential energies of interaction among these particles. It is symbolized by U.

$\Delta U = U_2 - U_1$

Where, ΔU = Change in internal energy

U_1 = Initial internal energy

U_2 = Final internal energy

Enthalpy (H)

Enthalpy is the amount of heat (energy) absorbed (required) by the system to cause a change a in the system, or the amount of heat expelled by the system as a result of a change in the system. or

Enthalpy (H) is the sum of the internal energy (U) and the product of pressure and volume (PV) given by the equation: $H=U+PV$. When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy.

Enthalpy is a state function whose value for a particular system can not be measured.

We can however, measure enthalpy changes (ΔH). Since, $\Delta H = H_{final} - H_{initial}$

Sign of ΔH	Type of Reaction	Heat
Negative	Exothermic	Released
Positive	Endothermic	Absorbed

Entropy (S)

Entropy is a state function, as well as a measurable physical property that is most commonly associated with a state of disorder, randomness, or uncertainty.
Or
Entropy can be defined in a simple qualitative way as a measure of the degree of randomness of the particles, such as molecules, in a system.

2nd law of thermodynamic, $S_2 - S_1 = \Delta Q/T$
Differential form of entropy, $dS = dQ/T$

Gibbs Free Energy

In thermodynamics, the Gibbs free energy is a thermodynamic potential that can be used to calculate the maximum reversible work that may be performed by a thermodynamic system at a constant temperature and pressure. or

A state function, Gibbs free energy determines whether or a chemical reaction is favorable or not. Gibbs free energy is the energy associated with a chemical reaction that is available to do work.
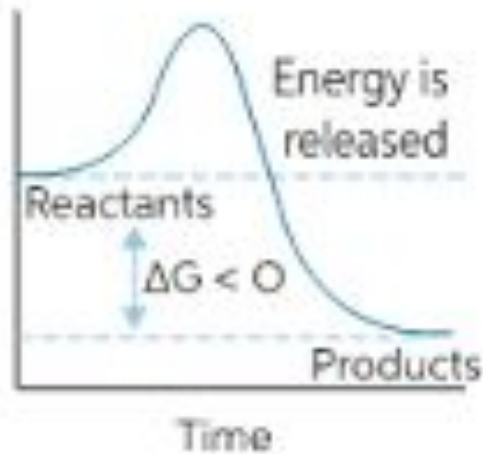
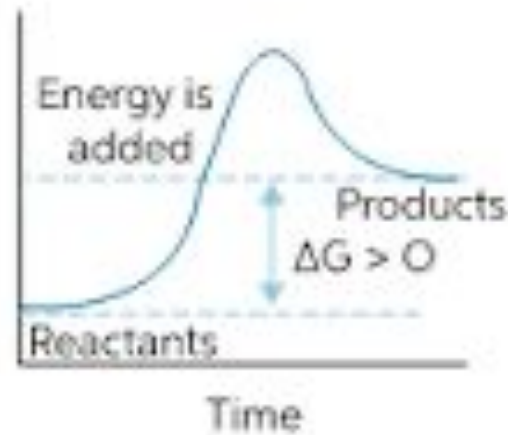Mathematically
$\Delta G = \Delta H - T\Delta S$

Where, ΔG is the change in free energy, ΔH is the change in enthalpy, T is the thermodynamic temperature, and ΔS is the change in entropy.

Gibbs free energy

Exergonic reaction:ΔG < O
Reaction is spontaneous

Endergonic reaction:ΔG > O
Reaction is not spontaneous

Reaction conditions depend on ΔG value

ΔG = -ve Spontaneous reaction
ΔG = +ve Non-Spontaneous reaction
ΔG = 0 in Equilibrium