VIVEKANANDA COLLEGE, THAKURPUKUR

NAAC Accredited Grade—A

STUDY MATERIAL

Subject : GE2 - Chemistry

Course Title **: Chemical Thermodynamics continuation-2nd part**

Topic :

Calculations of q, w, ΔU and ΔH for reversible, irreversible and free expansion of gases. Standard states; Heats of reaction; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications; Laws of thermochemistry, Kirchhoff's equations.

Paper : CC 2 / GE2

Semester : 2nd Semester

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Isothermal Irreversible expansion:

Let us consider a given amount of confined in a cylinder fitted with a piston. The initial volume and pressure of the gas are V_1 and P_1 respectively. Let us also consider internal pressure is greater than the external pressure. The pressure is released suddenly to a final pressure P_2 and then the gas expands against the final

Thus, irreversible work (W_{irr}) is given by

$$W_{irr} = - P_2 (V_2 – V_1) = -nRT (1 – P_2/P_1)$$

Expression of reversible isothermal work ($W_{rev,\ iso}$) = $- n RT \ln(V_2/V_1)$

$W_{rev,iso} > W_{irrev,iso}$

$W_{rev,\ iso} - W_{irrev,iso} = - nRT \ln(P_1/P_2) = - n.RT \ln[1 + (P_1 – P_2)/P_2] – [- n RT (P_1 – P_2) /P_1]$

$\approx -nRT (P_1 – P_2)/P_2 – [- n RT (P_1 – P_2)/P_1] = - nRT (P_1 – P_2) [1 / P_2 – 1 / P_1)$

$= - nRT ((P_1 – P_2)^2 /P_1P_2$

$= + ve$

Five moles of an ideal gas at 27 °C are allowed to expand isothermally from an initial pressure of 10.0 atm to a final pressure of 4.0 atm against a constant pressure of 1.0 atm. Calculate W, Q, ΔE and ΔH.

Since the pressure difference value is high, so this is an isothermal irreversible process.

Thus, $W_{irrev,iso} = - P_{final} (V_2 – V_1) = - nRT (1/P_2 - 1 / P_1)$

$= - 5 \text{ mole} \times 0.082 \text{ lit. atm mole}^{-1} K^{-1} \times 300K (1/4 –1/10)$

∴ $W_{irrev,iso}$ = - 5 x1x 0.082 lit. atm x 300 x (0.25-0.1) = - 18.45 lit atm = - 1870.65 J

ΔE = 0 = ΔH since ΔT = 0

∴ Q = - $W_{irrev,iso}$ = + 1870.65 J

For the isothermal free expansion $P_{final} = 0$

∴ **W = 0,** since ΔT = 0, so, **ΔE = 0 = ΔH = Q**

Reversible Adiabatic Process:

Consider one-gram molecule of a perfect gas, enclosed in a perfectly non-conducting cylinder provided with a non-conducting piston. If the piston is now moved suddenly outwards, the gas expands, and does some work. Since no heat supplied from outside, adiabatic expansion has occurred. Therefore, the energy required for the expansion of the gas is taken from the gas itself so that its temperature falls.

Let the piston of area of cross section ‘A’ move through a small distance dx, so that the gas expands by a small amount dV. For a small expansion of the gas, pressure remains, practically constant, say P. Then the force acting on the piston,

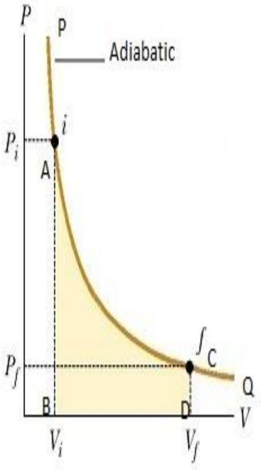
$F = P.A$

and small work done by the gas,

$dW = F\,dx$

$= PA\,dx$

$= P.\,dV$ (Since, $dW = P\,dV$) . The adiabatic curve PQ for the process is shown in below figure.



(a) Graphical Method

This case is different from the case of isothermal change in two respects.
(i) The container is made up an insulating material.
(ii) The curve is much sharper.

The net work done to expand the gas from a volume V1 to volume V2 will be, W = Area ABDC. Thus, area occupied below the curve in between AB and CD gives the required value of work done.

(b) Analytical Method

Analytically, network W can be calculated by integrating dW between the limits V_1 and V_2.

$$W = \int_0^W dW = \int_{V_1}^{V_2} P dV - - - - (1)$$

For an adiabatic change,

PV^γ = constant = K (say)

Or, $P = K / V^\gamma$

Equation (1) gives,

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

$$So,\ \mathrm{W} = \mathrm{K}\left|\frac{V^{1-\gamma}}{1-\gamma}\right|$$

$$= \frac{K}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

Now $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$

So, W = $[1/1-\gamma]$ $[P_2\ V_2^{\gamma}\ V_{2\text{-}}\gamma^{1} - P_1\ V_1^{\gamma}\ V_1^{1-\gamma}]$

Or, W = $[1/1-\gamma]$ $[P_2V_2 – P_1V_1]$ ------- (2)

If T_1 and T_2 are the initial and final temperatures of the gas,

$P_1V_1 = RT_1$ and $P_2V_2 = RT_2$

Substituting in equation (2) we get,

W = $[R/1-\gamma]$ $[T_2 - T_1]$

Or, W = $[R/\gamma-1]$ $[T_1 - T_2]$ --------(3)

The gas in a cloud chamber at a temperature of 292 K undergoes a reversible expansion. Assuming the process is adiabatic, calculate the final temperature if γ = 1.40 and the volume expansion ratio is 1.28.

The relation between temperature *T* and volume *V* from the adiabatic gas equation is,

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

Where *T* is the temperature and *V* is the volume of the gas.

Since the gas expand is expanding from its initial volume V_i and its initial temperature T_i to its final volume V_f and its final temperature T_f, therefore the equation (1) will be,

$T_i\ V_i^{\gamma-1} = T_f\ V_f^{\gamma-1}$

So,

$T_f = T_i\ (V_i/V_f)^{\gamma-1}$

Solution:-

To find out the final temperature of the gas T_f, substitute 292 K for T_i, 1.28 for volume expansion ratio V_f/V_i and 1.40 for γ in the equation $T_f = T_i\ (V_i/V_f)^{\gamma-1}$,

$T_f = T_i\ (V_i/V_f)^{\gamma-1}$

$= 292\ \mathrm{K}\ (1/1.28)^{1.40-1}$

$= 265\ \mathrm{K}$

Standard states; Heats of reaction; enthalpy of formation of molecules and ions and enthalpy of combustion and its applications:

The **standard enthalpy of formation** or **standard heat of formation** of a compound is the change of enthalpy during the formation of 1 mole of the substance from its constituent elements, with all substances in their standard states. The standard pressure value, recommended by IUPAC is one atm (101.325 kPa) and corresponding temperature will be 25 °C or 298.15 K.

The standard enthalpy of formation is measured in units of energy per amount of substance, usually stated in kilojoule per mole (kJ mol^{-1}), but also in kilocalorie per mole, joule per mole or kilocalorie per gram (any combination of these units conforming to the energy per mass or amount guideline).

All elements in their standard states (oxygen gas, solid carbon in the form of graphite, etc.) have a standard enthalpy of formation of zero, as there is no change involved in their formation.

Laws of Thermochemistry:

Law of Lavoisier and Laplace:

This law states that the heat-change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction.

Thus, H_2 (g) + ½ O_2 (g) → H_2O (l) $\Delta H = -68300$ cal

And H_2O (l) → H_2 (g) + ½ O_2 (g) $\Delta H = +68300$ cal

Hess's law:

For many substances, the formation reaction may be considered as the sum of a number of simpler reactions, either real or fictitious. The enthalpy of reaction can then be analysed by applying Hess's Law, which states that the sum of the enthalpy changes for a number of individual reaction steps equals the enthalpy change of the overall reaction. This is true because enthalpy is a state function, whose value for an overall process depends only on the initial and final states and not on any intermediate states. Examples are given in the following sections.

The formation reactions for most organic compounds are hypothetical. For instance, carbon and hydrogen will not directly react to form methane (CH_4), so that the standard enthalpy of formation cannot be measured directly. However the standard enthalpy of combustion is readily measurable using bomb calorimetry. The standard enthalpy of formation is then determined using Hess's law. The combustion of methane ($CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$) is equivalent to the sum of the hypothetical decomposition into elements followed by the combustion of the elements to form carbon dioxide and water:

$$CH_4 \rightarrow C + 2\,H_2$$
$$C + O_2 \rightarrow CO_2$$
$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Applying Hess's law,

$$\Delta_{comb}H^{\ominus}(CH_4) = [\Delta_f H^{\ominus}(CO_2) + 2\,\Delta_f H^{\ominus}(H_2O)] - \Delta_f H^{\ominus}(CH_4).$$

Solving for the standard of enthalpy of formation,

$$\Delta_f H^{\ominus}(CH_4) = [\Delta_f H^{\ominus}(CO_2) + 2\,\Delta_f H^{\ominus}(H_2O)] - \Delta_{comb}H^{\ominus}(CH_4).$$

The value of $\Delta_f H^{\ominus}(CH_4)$ is determined to be −74.8 kJ/mol. The negative sign shows that the reaction, if it were to proceed, would be exothermic; that is, methane is enthalpically more stable than hydrogen gas and carbon. It is possible to predict heats of formation for simple unstrained organic compounds with the heat of formation group additivity method.

Kirchhoff's equations: Influence of Temperature on ΔH and ΔU

If a system undergoes a change from one state to another given state, both the internal energy and heat content would alter. Therefore, we may write:

$U_f – U_i = ΔU$ and $H_f – H_i = ΔH$, the suffixes f anf i denote the initial and final states.

Differentiating these with respect to temperature at constant volume for the U and at constant pressure for the H, we get

$$[δ(ΔU) / δT]_v = [δU_f / δT]_v - [δU_i / δT]_v = C_{vf} - C_{vi} = ΔC_v$$

Similarly, $[δ(ΔH) / δT]_P = [δH_f / δT]_P - [δH_i / δT]_P = C_{Pf} - C_{Pi} = ΔC_P$

$$\int δ(ΔU) = \int ΔC_v.dT$$

Integrating between the limits T ºK and 0 ºK, we have,

$ΔU_T = ΔU_o + \int ΔC_v.\ dT$

$ΔH_T = ΔH_o + \int ΔC_P.\ dT$

These are called Kirchhoff's equations for chemical reactions for determining the internal energy changes at constant volume and the enthalpy changes at constant pressure.

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5. Patrick Fleming,Assistant Professor (Chemistry and Biochemistry) at California State University East Bay.