

## CHM 231; BASIC PHYSICAL CHEMISTRY II

### SECTION A

#### CHEMICAL THERMODYNAMICS

**Thermodynamics:** This is the study of energy changes in chemical and physical processes and of the laws and relationships which govern them. Some terms are commonly used:

- (a) **System;** A system in thermodynamics is defined as collection of matter i.e that part of the universe under study. The rest of the universe of course being isolated.
- (b) **Surrounding:** The rest of the universe not under study. A system could be isolated from its surrounding i.e its completely insulated such that no heat flow exists between the system and its surrounding.
- (c) **State of a system:** The state of a system is specified by determining all its properties such as pressure, volume etc.
- (d) **Process:** A process is a change from one state A to another state B.
- (e) **State function:** A state function is a property or function of properties which depends only on the state and not on path by which the state was reached, a differential  $dx$  of a function  $x$  (not necessarily a state function) is termed a perfect differential if it can be integrated between two states to give a value  $X_{AB} = \int_A^B dx$  which is independent of the path from A to B. If this holds,  $X$  must be a state function. Kinetic energy, Internal energy are state functions.
- (f) **Intensive Properties.** Are those whose values are independent of the size of system taken i.e the properties will be the same whether small or great amount of the system is considered. E.g temperature, pressure, density, refractive index, etc.
- (g) **Extensive properties:** are those whose values depend or are proportional to size of the system. Increase in size of the system obviously will increase this property, e.g, heat capacity, mass, volume, enthalpy, and entropy.

There are four basic laws of thermodynamics, all having many different formulations that can be shown to be equivalent. The zeroth law states that if two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

#### First Law of thermodynamics.

The first law states that for any process the difference of the heat  $Q$  supplied to the system and the work  $W$  done by the system equal the change in internal energy,  $U$ .

$$\Delta U = Q - W$$

A chemist is often faced with the task of determining whether a particular process will occur under specified conditions, and if it does occur

### Measurement of Change in Internal Energy

From the first law  $\Delta U = q - w$ , when work done is zero then  $\Delta U = q$ . One way of making a system do work is to make it expand against external pressure. If however the process is performed in a rigid vessel (i.e. a vacuum) i.e. constant volume, then, no work is done and  $q = \Delta U$ . A process of making this happen can be done in a bomb calorimeter e.g. Figure (1 NOT SHOWN): Determination of heat of combustion in a bomb calorimeter.

In the bomb calorimeter combustion occurs at constant volume and as such heat changes is reflected in its internal energy  $\Delta u = q_v$ .

### Pressure – Volume work

Consider a cylinder of cross-sectional area  $x$ , with a frictionless and weightless piston, let the pressure on the piston be  $P$ . Pressure = Force/ Unit area.

Total force acting on the piston =  $Px$ , if as a result of expansion the piston moves a distance  $dl$ , therefore work is done ( $dw$ ) by the gas on the surroundings which is equivalent to  $dw = F \cdot dl = Px \cdot dl$ . But  $x \cdot dl = dv$  (sectional area  $\times$  length = volume) which is the increase in volume due to movement of the piston. Therefore,  $dw = Pdv$ .

The total work in the expansion of the gas from initial volume  $v_1$  to the final volume  $v_2$  is given by  $W = (V_1 < x < V_2) \square PdV$ . Therefore,  $\Delta u = q - Pdv$ , this means:

At constant volume (i.e. where there is no change in volume)  $dv = 0$ ,  $w = 0$  and  $\Delta U = q$ , and as such any thermal change in the calorimeter at constant volume must be the change in the internal energy due to the chemical reaction or physical reaction.

When the opposing pressure is zero (i.e. free expansion) that is the gas expands against a zero external pressure, no work is done  $\Delta U = q$ .

Opposing pressure is constant i.e. when opposing pressure is constant.

Then,  $\Delta U = q - Pdv$  or

$$q = \Delta u + Pdv$$

$$= U_2 - U_1 + P(v_2 - v_1)$$

$$U_2 = U_1 + P v_2 - P v_1$$

$$q = U_2 + P v_2 - (U_1 + P v_1)$$

Since  $u$  is a state function and  $Pv$  are properties of a state, therefore  $U + Pv$  represents a state function which is represented as  $H$ . Then  $H = U + Pv$ , therefore heat absorbed at constant pressure is called the enthalpy.  $q_p = \Delta H$ .

### Opposing pressure variable

This can be calculated by putting  $P$  versus  $v$  and determine the area under the curve. In general  $w$ , will be positive if  $V_2 > V_1$  i.e. work is done by the gas on its surrounding (this is what happens when a system expands, pushing back its surroundings. If  $v_1 > v_2$  then  $w$ , is negative and a compression has taken place i.e. work is done by the surroundings on the gas.

### Heat capacities

From the Bomb calorimeter, heat capacities are calculated. There can be two types,,  $C_v$ :- heat capacity at constant volume and  $C_p$ :- heat capacity at constant pressure.

$$C_v = dq_v/dT \text{ and } C_p = dq_p/dT, \text{ since } \Delta U = q_v \text{ and } q_p = \Delta H, \text{ then } C_v = (du/dT)_v \text{ and } C_p = (dH/dT)_p$$

Heat capacity of a system is the heat required to raise the temperature of the system by one degree if  $dq$  is a small amount of heat added to a system, the temperature of the system will rise by  $dT$ . Therefore the heat capacity is represented by  $C = dq/dT$ .

$C_v = (dU/dT)_v$ , therefore  $C_v$  is the rate of change of internal energy with temperature at constant volume. While  $C_p = (dH/dT)_p$ ,  $C_p$  at constant pressure is the rate of change of enthalpy with temperature at constant pressure.

### Relationship between $C_v$ and $C_p$ (for an ideal gas)

$C_p - C_v = (dH/dT)_p - (dU/dT)_v$ , but  $H = U + PV$ , therefore  $dH/dT = dU/dT + d(PV)/dT$  for one mole of ideal gas  $PV = RT$

$C_p = C_v + R$ , therefore the difference between the molar heat capacities for an ideal gas is  $R$ , the gas constant.

### Internal Energy of an Ideal Gas (Joule Experiment)

When an ideal gas expands into a vacuum there is no gain or loss of heat.

Figure (2 NOT SHOWN): Joule experiment.

Two similar bulbs, one containing air under pressure and the other empty were connected by a wide tube with a control. The water was stirred and temperature noted. After thermal equilibrium the control was opened and temperature noted (No change in temperature). It was deduced that since the gas expands into a vacuum i.e. when the external pressure is zero, no work is done by the gas in its expansion i.e.  $w = 0$ , and as no change was recorded in the temperature, the  $q = 0$ . Therefore, it means that  $\Delta u = q - w = 0$  and that there is no change in the internal energy of an

ideal gas as a result of free expansion. ( The internal energy, U of an ideal gas is independent of volume at constant temperature)

$$(dU/dv)_T = 0, (dU/dv)_T dv + (dU/dT)_v dT = 0.$$

It can be calculated that the energy of the gas is a function of temperature only. The fact that  $(dU/dv)_T = 0$  indicate that for ideal gases intermolecular force of attraction is zero, but for real gas  $(dU/dv)_T$  is a small but positive quantity.

### Effect of Pressure and Temperature on $C_p$ and $C_v$

Since the internal energy du is independent of volume it is expected to be independent of pressure,  $C_v = dU/dT$ , indicating that heat capacity at constant volume of an ideal gas is independent of the volume or the pressure of the gas but a function of temperature. This is also similar for  $C_p$ ,  $C_p = dH/dT$ .

Show that by differentiating the equation  $H = U + Pv$  with respect to volume at constant temperature that  $(dH/dv)_T = 0$ .

### Heat Capacity and Temperature Relationship

Both  $C_v$  and  $C_p$  increases with temperature. And the dependence on temperature is predicted from experimental measurements. Such relationship is  $C_p = a + bT + cT^2 + dT^3$

Where a, b, c and d are constant determined from experimental values of heat capacities over a range of temperatures (temperature in K ). Using this type of relationship, the amount of heat required to raise the temperature of a gas system from  $T_1$  to  $T_2$  at  $C_v$  and  $C_p$  is given by

$$\Delta U = (T_2 < x < T_1) \int C_v dT = (T_2 < x < T_1) \int (a + bT + cT^2 + dT^3) dT$$

$$\Delta H = (T_2 < x < T_1) \int C_p dT = (T_2 < x < T_1) \int (a + bT + cT^2 + dT^3) dT$$

### Isothermal Process

Temperature is constant, and since U varies with temperature, it means that at constant temperature  $\Delta U = \text{constant}$ , therefore for isothermal process  $\Delta U = 0$  and  $q = w$ .

$$q = (v_2 < x < v_1) \int PdV, q = \Delta U + w \text{ and } \Delta U = \int PdV$$

The magnitude of q will vary with w from zero, for a free expansion (when exert pressure against which expansion occur is zero) to a maximum for reversible process. (In which exert pressure and internal pressure only differ by an infinitesimal amount).

$$q = W = (v_2 < x < v_1) \int PdV, \text{ for an ideal gas } PV = nRT$$

$$q = (V_2 < x < V_1) \int (nRT/V) dV,$$

$$W_{\max} = nRT \ln(V_2/V_1) \text{ or } 2.303nRT \log(V_2/V_1),$$

but for an ideal gas at constant temperature the relationship  $P_1V_1 = P_2V_2$  holds (Boyle's law), thus  $P_1/P_2 = V_2/V_1$

$$W_{\max} = nRT \ln(P_1/P_2).$$

For real gases  $\Delta u \neq 0$  under isothermal conditions because even when temperature is constant, internal energy will change due to change in volume or pressure. The same is true  $\Delta H$ . Therefore for real gases expanding,  $W_{\max}$  will be less than the volume above depending on the degree of non-ideality.

Example 1:- Calculate the maximum work obtainable by the isothermal reversible expansion of 2 mole of Nitrogen from 10 litres to 20 litres at 25°C.

Solution:-

$$\begin{aligned} W_{\max} &= nRT \ln(V_2/V_1) \\ &= 2.303nRT \log(V_2/V_1) \\ &= 2 \times 2.303 \times 8.314 \times 298 \times \log(20/10) \\ &= 3.44 \text{ kJ mol}^{-1} \\ &= 0.821 \text{ kcal mol}^{-1} \end{aligned}$$

Tutorial:- An ideal gas undergoes a reversible isothermal expansion from an initial volume  $V_1$  to a final volume  $10V_1$  and thereby does 16.628 Joules of work. The initial pressure was  $100 \text{ Nm}^{-2}$ . (a) Calculate  $V_1$  (b) if there were 2 moles of gas. What must its temperature have been?

### Adiabatic Process

An adiabatic process is one which there is no exchange of heat between the system and its surroundings i.e.  $q = 0$ . Work done is at the expense of the internal energy  $\Delta U = -W$ , this implies that if work is done on the system, the internal energy of the system will increase and  $\Delta u$  will decrease if work is done by the system. From the first law;

$$\Delta U = -PdV$$

$$C_v dT = -PdV, \text{ but for an ideal gas } P = RT/V$$

$$C_v dT = -R(dV/V)$$

For a process that takes the gas from  $V_1$  at  $T_1$  to  $V_2$  at  $T_2$

$$(T_1 < x < T_2) \quad C_v \int dT/T = -(V_1 < x < V_2) \quad R \int dV/V$$

$(C_v/R)\ln(T_2/T_1) = -\ln(V_2/V_1)$ , by rearranging

$$\ln(T_2/T_1) = \ln(V_1/V_2)^{R/C_v}$$

But we know that  $C_p - C_v = R$ ,

$$\text{therefore } \ln(T_2/T_1) = \ln(V_1/V_2)^{(C_p - C_v)/C_v}$$

Let  $C_p/C_v = \gamma$ , this is the ratio of heat capacities at constant pressure and constant volume.

$$\ln(T_2/T_1) = \ln(V_1/V_2)^{\gamma-1}$$

Other equivalent relationships are:  $T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$  or  $P_2 V_2^\gamma = P_1 V_1^\gamma$

$$\text{Or } T_2^\gamma P_2^{\gamma-1} = T_1^\gamma P_1^{\gamma-1}$$

and  $W = nR (T_2 - T_1) / (\gamma - 1)$

**The Joules Thompson Effect:** Use in measuring quantitative deviation from ideal law.

Figure (3 'NOT SHOWN')

A gas from a high pressure region A is allowed to pass to a low pressure region C through a porous plug B. Temperature of the gas is then taken at C. The entire system is thermally insulated (i.e. an adiabatic process,  $q = 0$ ).

Then  $\Delta U = -PdV$ , work done before gas is forced through is  $-PdV$  and work done by expansion is  $PdV$ .

But  $H = U + PdV$ , therefore  $\Delta H = -PdV + PdV$

$\Delta H = 0$ , heat content of a system during its expansion through a porous plug remains constant.

Joule-Thompson Coefficient ( $\alpha_{JT}$ ):- It is the rate of change of temperature with the pressure when a gas flows through a plug from a higher pressure to a low pressure

$$\alpha_{JT} = (dT/dp)_H$$

For an ideal gas  $\alpha_{JT} = 0$ . That is no change of temperature is observed in expanding through a porous plug. For real gases it is not zero but becomes smaller and approaches zero as conditions for ideality are approached. For most gases at normal temperature except for  $H_2$  &  $He$   $\alpha_{JT}$  is positive, showing that expansion results in cooling. For  $H_2$  and  $He$  at a very low temperature i.e.  $-80^\circ C$  for  $H_2$  is required before  $\alpha_{JT}$ , can be positive. This is responsible for the extremely great difficulty of obtaining liquid  $H_2$  and liquid  $He$ .

## Variation of Enthalpy with Temperature

Consider a reaction, Reactant  $\rightarrow$  Products

$\Delta H = H_p - H_r$ , differentiating both sides with respect to temperatures;

$$(d\Delta H/dT)_p = (dH_{\text{product}}/dT)_p - (dH_{\text{reactant}}/dT)_p$$

Therefore  $(d\Delta H/dT)_p = C_{p(\text{product})} - C_{p(\text{reactant})}$ .

Or  $(d\Delta H/dT)_p = \Delta C_p$ , Kirchoffs equation, where  $\Delta C_p = \sum C_{p(\text{product})} - \sum C_{p(\text{reactant})}$ .

For a small range of temperature  $\square d(\Delta H) = \square \Delta C_p dT$ , that is  $C_p$  can be taken as constant. If it is constant then  $(\Delta H_1 < x < \Delta H_2) \square d(\Delta H) = (T_1 < x < T_2) \square \Delta C_p dT$

$$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$$

$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$ . Where  $\Delta H_2$  is the heat of reaction at  $T_2$  and  $\Delta H_1$  is that at  $T_1$ .

However if the temperature interval is very large then  $\Delta C_p$  is not constant, and also a function of temperature. Note that generally heat capacities of gases vary with temperature as a function of power series of  $T$ .

$$\Delta C_p = a + bT + cT^2 + dT^3.$$

$$\Delta H_2 = \Delta H_1 + (T_1 < x < T_2) \square \Delta C_p dT.$$

$$\Delta H_2 = \Delta H_1 + (T_1 < x < T_2) \square (a + bT + cT^2 + dT^3) dT$$

Tutorial: - The standard heat of formation for  $\text{NH}_3$  is  $-11.02 \text{ kcal mol}^{-1}$  at 298k. Heat capacities at this temperature for  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  are 6.96, 6.89 and  $8.38 \text{ cal mol}^{-1}$ ; determine  $\Delta H_{298\text{k}}^0$  and  $\Delta H_{773\text{k}}$  for the reaction.

## Questions

Explain the terms:-

1. System, surroundings, state of system, change of system.
2. What do you understand by the term internal energy and enthalpy of a system? How are they related?
3. Two litres of  $\text{N}_2$  at  $0^\circ\text{C}$  and 5 atm pressure are expanded isothermally against a constant pressure of 1 atm until the pressure of the gas is also 1 atm, assuming ideal behaviour. What are the values of  $W$ ,  $\Delta u$ ,  $\Delta H$  and  $q$ ?
4. One mole of an ideal gas is allowed to expand reversibly against a confining pressure that is at all-time infinitesimally less than the gas pressure of 0.1 atm, the temperature being

kept constant at 0°C. (a) How much work is done by the gas (b) What is the change in u and H. (c) How much heat is absorbed?

### Second Law of Thermodynamics

A chemist is often faced with the task of determining whether a particular process will occur under specified conditions, and if it does occur, it is important to estimate its extent. This is the essence of the second law of thermodynamics.

Many natural processes are known to occur spontaneously in one direction only. (1) For example a gas expands to occupy all the space made available to it. No gas is ever known to collect its molecule together leaving or vacating some available space and congregating in only a section of the space. (2) Heat flows spontaneously from a hot body when placed in contact with cold body. (3) A mixture of hydrogen and water in ratio 1:2 by volume explodes when exposed to sunlight forming water. All these processes and their un-natural reverse processes satisfy the 1st law which predicts energetics of change but not direction of change.

General experience such as these show that systems tend to make from a non-equilibrium state to the one of equilibrium and once in this state they remain unchanged unless disturbed by some external agent. This means that the path to equilibrium is normally thermodynamically irreversible. Example one is not at equilibrium because of difference in pressure, and example two because of temperature difference while example three is a chemical change. What then determines the direction of change?

The second law predicts the criterion of chemical change and the direction of change, 1st law predicts energetics of change, but not the direction of change. There is a quantity called entropy, which is a function of the state of the system. In a reversible process the entropy of the universe remains constant. Therefore, **second law of thermodynamics states that spontaneous reaction occurs in the direction of increasing entropy.**

### Entropy a state function

That entropy is a state function can be proved from the axiom called the inequality of Clausius. This states that for all thermodynamic cycles  $\oint dq/dT \leq 0$ , the equality holds for a reversible cycle while the inequality holds for the irreversible cycle. Let a system undergo a reversible process from state 1 to 2 along path A and let the cycle be completed along path B, which is also reversible.

$$\oint dq/T = 0 = (1A \rightarrow 2A) \int dq/T + (2B \rightarrow 1B) \int dq/T \dots\dots\dots (1)$$

Now consider another reversible cycle which has the same initial path A but is completed along path C (which is also reversible) thus

$$\int_{1A}^{2A} dq/T = 0 = \int_{1A}^{2A} dq/T + \int_{2A}^{1C} dq/T + \int_{1C}^{2C} dq/T \dots\dots\dots (2)$$

Substituting eqn (2) from (1);  $\int_{1B}^{2B} dq/T = \int_{1C}^{2C} dq/T$

Therefore  $\int_{1}^{2} dq/T$  is the same for all reversible paths between states 1 and 2 and is independent of the reversible path between state 1 and 2;  $dq/T$  is a state function and thus property is called entropy and denoted by S thus,  $dS = (dq/T)_{rev}$  and  $\int_{1}^{2} dS = \int_{1}^{2} (dq/T)_{rev}$ .

Therefore,  $S_2 - S_1 = \Delta S = \int_{1}^{2} (dq/T)_{rev}$ .

Note that the definition involves only the heat released or absorbed in a reversible path only. When the path is irreversible the heat absorbed or released is not usable in calculation of  $\Delta S$ .

Therefore,  $(dq/T)_{rev} \neq (dq/T)_{irr}$ ,  $dq/T$  depends on path, but  $\Delta S$  does not.

**How the second law does predicts the direction of change**

Note that a spontaneous change is irreversible and 2<sup>nd</sup> law state that during this process, the entropy of the universe increases. To predict whether a change is spontaneous or not  $\Delta S$  is completed for system and its surroundings which contribute the universe during the change. If  $\Delta S$  is +ve, process is spontaneous, if  $\Delta S$  is zero or -ve, no spontaneous change will occur and the process is already in equilibrium.