

Answer the following questions

Total Marks 50

أجب عن الأسئلة الآتية:

(N=14, C=12, H=1 and O=16)

Question No. (1) (10 Marks)

- (a) Define the concept of partial pressure and derive the relationship between partial pressure, total pressure and mole fraction of a component gas in a gas mixture? (3 Marks)
- (b) List two conditions under which gas can deviate from ideal behaviour and show how you can obtain van der Waals equation of state by the modification of the ideal gas equation of state? (3 Marks)
- (c) Compute the molecular weight of gas mixture and its density at 27 °C and 750 torr, if the mixture of gases has the following composition by weight: CO₂=0.44%, O₂=22.4%, N₂=75.36% H₂O=1.8%? (4Marks)

Question No. (2): (10 Marks)

- (a) State the three laws of thermodynamic? (3 Marks)
- (b) Derive the relationship between C_p and C_v for Real gases? (3 Marks)
- (c) Referring to the information in the table at 25°C: (4 Marks)

(1) Calculate ΔS°, at 25°C for the reaction:



(2) Calculate ΔS° for CO_(g) at 25°C.

(3) Discuss the effect of temperature on the spontaneity of the above reaction

Compound	ΔH° _f kcal/mole	ΔG° _f kcal/mole	S° cal/mole K
H _{2(g)}	0.00	0.00	31.212
CO _(g)	-26.415	-32.808	—
CH ₃ OH _(l)	-57.036	-39.747	30.26

Question No. (3): (10 Marks)

- (a) What is meant by colligative properties of solutions? (2Marks)
- (b) Ethylene glycol C₂H₆O₂ is used as anti-coolant in vehicle's engine cooler (رديتير السيارات), specially in cold climates. If the temperature reached to -10°C, what weight of ethylene glycol C₂H₆O₂ must be added to 100 gm of water to prevent the formation of ice? (consider ΔH_{fusion} =1436 cal/mol for water) (4Marks)
- (c) What is the density at 17°C of aqueous solution containing 0.75 gm of sucrose, (C₁₂H₂₂O₁₁), per 2 litre of a solution developed a rise of 26.4 cm at osmotic equilibrium? (4Marks)

Question No. (4): (10 Marks)

- (a) Explain the main features of the phase diagram of water? State the phase rule and explain what is meant by its parameters? Apply this rule to interpret the tripple point of water on its phase diagram? (4Marks)
- (b) Study the effect of pressure on the melting point of water, starting from a pressure of 1 to 101 atm with an incremental change of 20 atm, where the density of liquid water at 0°C is given as 0.99 gm/cm³ and that for ice at 0°C is 0.92 gm/cm³. (consider ΔH_{fusion} =1436 cal/mol for water) (6Marks)

Question No. (5): (10Marks)

- (a) Give different Four examples of cathodic reactions and different five examples of anodic reactions? (3Marks)
- (b) Based on the relation between electrode potentials and free energy change, derive the Nernst equation? (2Marks)
- (c) I- Calculate E°_{cell} for the reaction: Cu⁺⁺ + Zn = Cu + Zn⁺⁺ (5Marks)
- II- What is the potential of the cell containing (Zn⁺⁺/Zn) and (Cu⁺⁺/Cu)couples if the Zn⁺⁺ and Cu⁺⁺ concentrations are 0.1 and 10⁻⁹ molar, respectively, at a temperature of 25°C.
- III- What is the value of ΔG for the reduction of one mole of Cu⁺⁺ ions by Zn at the indicated concentrations of the ions, given in (b), at temperature of 25°C. Also, what is the value of ΔG° for the reaction at 25°C.
- If you are taken that: Zn⁺⁺ + 2e = Zn E° = -0.763 v and Cu⁺⁺ + 2e = Cu E° = 0.337 v.

انتهت الأسئلة مع أطيب التمنيات بالتوفيق والنجاح
أ/د/ أحمد أحمد الصروي

Question No. (1):

(10 Marks)

(a) Define the concept of partial pressure and derive the relationship between partial pressure, total pressure and mole fraction of a component gas in a gas mixture?

(3Marks)

The partial pressure of any component in a gas mixture, is the pressure that the component would exert if it was alone occupying the entire volume of the gas mixture at the same temperature.

The ideal gas equation can be applied to a mixture of gases, where each gas in the mixture behaves ideally and independently. Assume that a mixture of (N) components, each behaves as an ideal gas, contained in a container of volume (V) at a temperature (T). The ideal gas equation can be applied to each component individually as follows:

For the first component → $P_1 V = n_1 R T$

For the second component → $P_2 V = n_2 R T$

For the third component → $P_3 V = n_3 R T$

.....
and so on for the Nth → $P_N V = n_N R T$

Summing up these system of equations :

$$(P_1 + P_2 + P_3 + \dots + P_N) V = (n_1 + n_2 + n_3 + \dots + n_N) R T$$

or $P_T V = n_T R T$

To correlate the partial pressure of any component in the gas mixture, (P_i), to the total pressure, (P_T), of the mixture, we divide its specific ideal gas equation by the ideal gas equation of the whole mixture: →

$$P_i / P_T = n_i / n_T$$

Where (n_i / n_T) is defined as the mole fraction of the component (i) and is termed as (y_i);

or → $y_i = n_i / n_T$

giving the following important relation : $P_i = P_T y_i$

(b) List two conditions under which gas can deviat from ideal behaviour and show how you can obtain van der Waals equation of state by the modification of the ideal gas equation of state?

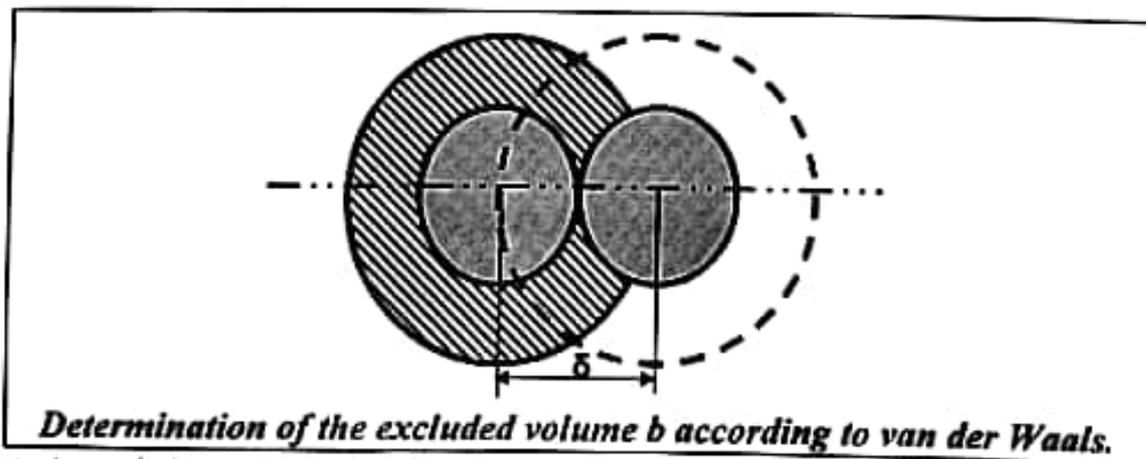
(3 Marks)

The two conditions are:-

1- high pressure

2- low temperature

If the molecules of a gas are visualized as an incompressible, rigid spheres of diameter δ , then as can be seen from the Figure an "excluded volume" of radius δ exists around each molecule and no center of another molecule can get into this volume.



If we denote Avogadro's number by N° , then the excluded volume per mole will be equal to $(4/3) \pi \delta^3 N^{\circ}$, but since two molecules are involved in a collision, the volume which is inaccessible for the free motion of molecules should be considered to be equal to half of that indicated (see figure (1.3)). Thus, the volume accessible for the free motion of the molecules is $(V - b)$. Where (V) is the molar volume of gas, (volume of one mole), and $b = (2/3) \pi \delta^3 N^{\circ}$.

The intermolecular attractive forces (which are still referred to van der Waals forces) decreases very rapidly with increasing distance between the molecules. In this particular case these forces are considered to be inversely proportional to the sixth power of the distance or to the second power of the volume occupied by

the gas. It is also assumed that the attractive forces are on the whole summed up together with the pressure that holds the gas in the given volume. Thus van der Waals equation takes the following form:

$$(P + a/V^2)(V - b) = RT$$

or for n moles of substance, it becomes:

$$(P + an^2/V^2)(V - nb) = nRT$$

The term (a/V^2) which reflects the intermolecular attraction and which is summed up with the pressure is called the internal or static pressure.

For liquids it can reach several thousands of atmospheres and for gases it may have different signs. For example, for hydrogen under ordinary conditions the internal pressure is negative, i.e. the repulsive forces operating between the hydrogen molecules exceed the forces of attraction.

(c) Compute the molecular weight of gas mixture and its density at 27 °C and 750 torr, if the mixture of gases has the following composition by weight: CO₂=0.44%, O₂=22.4%, N₂=75.36% , H₂O=1.8%?
(4Marks)

$$n_{CO_2} = 0.44/44 = 0.01 \text{ mole}, \quad n_{O_2} = 22.4/32 = 0.7 \text{ mole}, \quad n_{N_2} = 75.36/28 = 2.69 \text{ mole},$$

$$n_{H_2O} = 1.8/18 = 0.1 \text{ mole}, \quad n_T = 3.5 \text{ mole}$$

$$M_{AV} = (MY)_{CO_2} + (MY)_{N_2} + (MY)_{H_2O} + (MY)_{O_2}$$

$$= 44 \times 0.00286 + 32 \times 0.2 + 28 \times 0.766 + 18 \times 0.0286 = 28.489 \text{ gm/mole}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$P = 750/760 = 0.987 \text{ atm}$$

$$\rho = PM_{AV}/RT = (0.987 \times 28.489)/(0.082 \times 300) = 1.143 \text{ gm/litre}$$

Question No. (2):

(10 Marks)

State the three laws of thermodynamic?

(3 Marks)

First law of thermodynamics contains the existence of a finite quantity of energy in the universe. The energy can be changed from one form into another and transferred from one part of the universe to another, but it can be neither created nor destroyed. Another statement of the first law is as follows:

"THE ENERGY OF UNIVERSE IS CONSTANT" mathematically it may be written as:

$$(\Delta E)_{universe} = 0 \quad \text{or} \quad (\Delta E)_{system} + (\Delta E)_{surrounding} = 0$$

The second law of thermodynamics contains that when all the entropy changes in the universe that result from a natural process are added together, the sum is greater than zero. The statement of the second law is: "THE ENTROPY OF THE UNIVERSE IS INCREASING"

Mathematically it is expressed as: $(\Delta S)_{universe} > 0$

The third law of thermodynamics gives us an absolute reference point from which we can make determinations of the absolute value of S. This law states that "The entropy of an element or a compound present in the form of a perfectly ordered crystal is zero at the absolute zero of temperature.

(b) Derive the relationship between CP and Cv for Real gases?

(3 Marks)

$$C = dQ/dT \quad \dots\dots\dots (1)$$

$$C_p = dQ_p/dT = dH/dT \quad \dots\dots\dots (2)$$

$$C_v = dQ_v/dT = dE/dT \quad \dots\dots\dots (3)$$

$$H = E + PV$$

From the Real gas equation, for one mole, $PV = ZRT$

$\therefore H = E + ZRT$ Differentiating both sides with respect to T

$$\therefore dH/dT = dE/dT + ZR \quad \dots\dots\dots (4)$$

Combining equations (2), (3) and (4) we get $C_p - C_v = ZR$

(c) Referring to the information in the table at 25°C:

(4 Marks)

- (1) Calculate ΔS°_r at 25°C for the reaction:
 $\text{CO(g)} + 2\text{H}_2\text{(g)} = \text{CH}_3\text{OH(l)}$
 (2) Calculate ΔS° for CO(g) at 25°C.
 (3) Discuss the effect of temperature on the spontaneity of the above reaction

Compound	ΔH°_f kcal/mole	ΔG°_f kcal/mole	cal/mole
$\text{H}_2\text{(g)}$	0.00	0.00	31.212
CO(g)	-26.415	-32.808	-----
$\text{CH}_3\text{OH(l)}$	-57.036	-39.747	30.26

$$\Delta G^\circ_r = \sum \text{prod } \Delta G^\circ_f - \sum \text{react } \Delta G^\circ_f = [(-39.747) - [(-32.808) + (0)]] = -6.939 \text{ kcal/mol}$$

$$\Delta H^\circ_r = \sum \text{Prod } H^\circ_f - \sum \text{React } H^\circ_f = [(-57.036)] - [-26.415] = -30.621 \text{ kcal/K}$$

Applying equation (2.31) $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

$$\therefore \Delta S^\circ_r = (\Delta H^\circ_r - \Delta G^\circ) / T = -23.682 / 298 = -0.07947 \text{ kcal/mol K} = -79.47 \text{ cal/mol K}$$

$$\Delta S^\circ = \sum \text{Prod } S^\circ - \sum \text{React } S^\circ$$

$$-79.47 = [(30.256)] - [2(31.212) + S^\circ_{\text{CO}}]$$

$$S^\circ_{\text{CO}} = 47.302 \text{ cal/mole K}$$

The reaction is spontaneous at low temperature because the reaction is exothermic and unnatural

Question No. (3):

(10 Marks)

(a) What is meant by colligative properties of solutions? (2 Marks)

Dilute solutions have many properties that are determined by concentration alone, without reference to the particular nature of the dissolved materials, these properties are called the colligative properties of solutions, which include:

- * Vapor pressure lowering. $P_A = P^\circ_A x_A$, $P_B = P^\circ_B x_B$
- * Freezing point lowering. $\Delta T_f = T^\circ_f - T_f = K_f(\mu)$, $K_f = R(T^\circ_f)^2 M^\circ / (1000)(\Delta H_{\text{fus}})$
- * Boiling point elevation. $\Delta T_b = T_b - T^\circ_b = K_b(\mu)$, $K_b = R(T^\circ_b)^2 M^\circ / (1000)(\Delta H_{\text{vap}})$
- * Osmotic pressure. $\pi = MRT = \rho g h$

(b) Ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$ is used as anti-coolant in vehicle's engine cooler (رديتير السيارات), specially in cold climates. If the temperature reached to -10°C , what weight of ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$ must be added to 100 gm of water to prevent the formation of ice? (4 Marks)

$$\Delta T_f = K_f(\mu)$$

$$\Delta T_f = T^\circ_f - T_f = 10^\circ\text{C}$$

$$K_f = R(T^\circ_f)^2 M^\circ / (1000)(\Delta H_{\text{fus}}) = 1.86$$

$$\mu = \Delta T_f / K_f = 10 / 1.86 = 5.376$$

$$\mu = n_B / m_A$$

$$n_B = 5.376 \times 0.1 = 0.5376$$

$$m_B = 0.5376 \times 62 = 33.33 \text{ gm}$$

(c) What is the density at 17°C of aqueous solution containing 0.75 gm of sucrose, $(\text{C}_{12}\text{H}_{22}\text{O}_{11})$, per 2 litre of a solution developed a rise of 26.4 cm at osmotic equilibrium? (4 Marks)

$$\pi = \rho g h = MRT = nRT/V$$

where: $h = 26.4 \text{ cm}$ $\rho = \text{----- gm/cm}^3$ $g = 980.0 \text{ cm/sec}^2$

$$R = 0.08206 \text{ atm. lit/ K. mole} \quad T = 25 + 273 = 298 \text{ K}$$

$$\pi = nRT/V = (2.193 \times 10^{-3})(0.082)(298)/2 = 0.026 \text{ atm}$$

$$1 \text{ atm.} = 76 \times 980 \times 13.6 = 1013250 \text{ dyne/cm}^2$$

$$\therefore 0.026 \text{ atm} = 26420.05 \text{ dyne/cm}^2 \quad \pi = \rho g h$$

$$\therefore \rho = \pi / g h$$

$$\therefore \rho = (26420.05) / (26.4)(980) = 1.021 \text{ gm/cm}^3$$

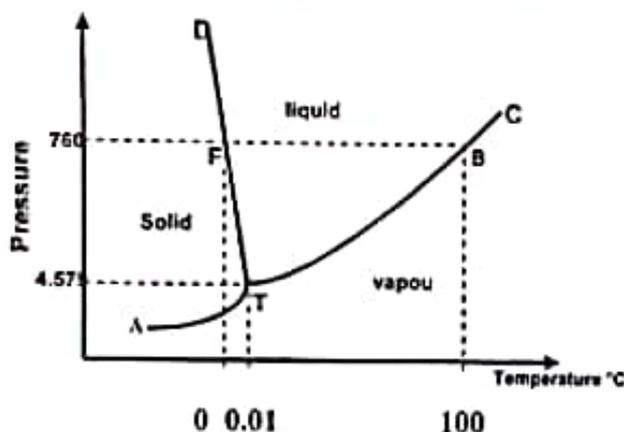
Question No. (4):

(10 Mar)

(a) Explain the main features of the phase diagram of water? Define the triple point of water on its diagram? (4 Marks)

A given substance may exist in various states depending on the specific conditions which prevail. The behavior of the substance may be summarized on a graph, called a *phase diagram*. As an illustrative example, the phase diagram of water is explained as follows:

- * Any point in the plane indicates the pressure and temperature of the given phase, (state).
- * Curve (TC) represents the equilibrium between liquid water and water vapor.
- * Curve (TD) shows how the melting point of ice changes with pressure. Only along this curve, can solid and liquid exist together in equilibrium.
- * Curve (AT) is the vapor-pressure curve for ice. Only along this curve can solid and vapor exist together in equilibrium. (This curve represents the sublimation equilibrium of solid water).
- * The temperature at point (T), the intersection of the solid and liquid vapor-pressure curves, is the melting temperature of ice at a pressure equal to its vapor pressure. This point is called *triple point* of water, which, indicates the temperature and pressure at which pure solid, liquid and vapor can be exist in equilibrium.



Phase Diagram of Water, (not drawn to scale).

- * Point (F) is the normal freezing point of water.
- * Point (B) is the normal boiling point of water.
- * Point (C) is the critical point of water.
- * It should be noted that the curve (TD) has a negative slope. With increasing pressure, the melting point of ice is shifted toward lower temperatures. This property of water makes ice skating possible; under the pressure of the skate blade, the ice melts and the skate glides along on a thin layer of water. This behavior of water is unique; the melting points of most substances increase with increasing pressure.

Phase diagram, is readily interpreted in terms of a generalization known as the *phase rule*. The rule states that: *the number of phases, p, plus the number of variables, (also called degrees of freedom), f, exceeds the number of components, c, by 2.* This rule may be written algebraically as:

$$p + f = c + 2$$

* There is no but one component, H_2O , at the triple point (point T), where three phases are in equilibrium ; $p = 3$. Therefore, applying the phase rule, $\Rightarrow p + f = c + 2 \quad 3 + f = 1 + 2 \quad \therefore f = 0$

The system is *invariant*; there is only one temperature and one vapor pressure at which the three phases can exist simultaneously at equilibrium

(b) Study the effect of pressure on the melting point of water, starting from a pressure of 1 to 101 atm with an incremental change of 20 atm, where the density of liquid water at $0^\circ C$ is given as 0.99 gm/cm^3 and that for ice at $0^\circ C$ is 0.92 gm/cm^3 . (6 Marks)

$$\Delta T = [(\Delta V) / (\Delta S)] (\Delta P)$$

Where (ΔV) is the change in molar volume of the substance. Consider one mole of water, its volume would be: $V_l = 18/\rho_l = 18/0.9998 = 18.0036 \text{ cm}^3/\text{mole}$

$$V_s = 18/\rho_s = 18/0.9168 = 19.6335 \text{ cm}^3/\text{mole}$$

$$\Delta V = V_l - V_s = 18.0036 - 19.6335 = -1.6299 \text{ cm}^3/\text{mole} = -1.6299 \times 10^{-3} \text{ liter/mole}$$

(ΔS) is obtained from equation (2.31),

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

Where, at equilibrium conditions, $\Delta G = 0$ and ΔH would be the enthalpy of fusion, (ΔH_{fus}), which is obtained from Appendix (11); (for water), $\Delta H_{\text{fus}} = 1436.42 \text{ cal / mole}$

$$\Delta H_{\text{fus}} - T(\Delta S) = 0$$

$$\therefore \Delta S = 1436.42/273 = 5.2616 \text{ cal / K.mole}$$

$$\Delta S = (5.2616 \times 0.08206) / 1.98 = 0.2181 \text{ (atm.liter) / (K.mole)}$$

normal freezing point of water is 273 °K at 1 atm.

$$\Delta T = (1.6299 \times 10^{-3} / -0.2181)(\Delta P)$$

$$\Delta T = (-7.473 \times 10^{-3})(\Delta P)$$

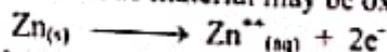
P atm	1	21	41	61	81	101
T °C	0	-0.149	-0.298	-0.445	-0.596	-0.745

Question No. (5): (10 Marks)

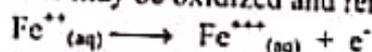
(a) Give different five examples of anodic reactions and different four examples of cathodic reactions? (3 Marks)

(i) **Anode reactions**

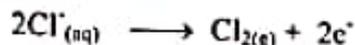
(a) The electrode material may be oxidized to positive ions:



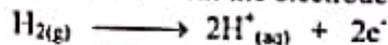
(b) Solutes may be oxidized and remain in solution:



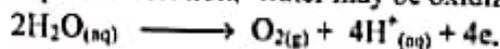
(c) Negatively charged ions may be oxidized and form neutral molecules which escape from solution:



(d) A gas in contact with the electrode may be oxidized to positively charged ions:

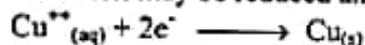


(e) In an aqueous solution, water may be oxidized to molecular oxygen:

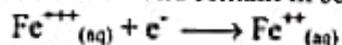


(ii) **Cathode Reactions**

(a) Positive ions in solution may be reduced and deposited on the electrode:



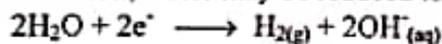
(b) Solutes may be reduced and remain in solution:



(c) A gas may be reduced to a negative ion:



(d) In an aqueous solution; water may be reduced to molecular hydrogen:



(b) Based on the relation between electrode potentials and free energy change, derive the Nernst equation? (2 Marks)

$$\Delta G_r = -nFE_{\text{cell}}$$

Where:

ΔG_r = Free energy change of reaction (calories/mole).

n = Number of moles of electrons transferred, as indicated in the balanced chemical equation.

F = Faraday constant, which has a value of 23061 cal/ mole-electron or (96500 coulombs/ mole electron)

E_{cell} = Potential of cell (volts).

If the cell reaction occurs under standard state conditions, would be expressed as:

$$\Delta G_r^{\circ} = -nFE_{\text{cell}}^{\circ}$$

Substituting for ΔG_r° gives:

$$-nFE_{\text{cell}}^{\circ} = - (RT) \ln (K_{\text{eq}})$$

$$E_{\text{cell}}^{\circ} = (RT/nF) \ln (K_{\text{eq}})$$

it is shown that the free energy change for a chemical reaction under non standard state conditions is given by the relationship:

$$\Delta G_r = \Delta G_r^{\circ} + (RT) \ln (Q)$$