بسم الله الرحمن الرحيم

Midterm Exam. in

Engineering Chemistry

2^{ed} Semester, (2014-2015), 1st level, Time allowed 90 minutes (1.5 hr.)



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Answer from the following questions to obtain 20 Marks from a total of 24 Marks

مطلوب ۲۰ درجه من اجمالی ۲۶ درجة

- 1. Explain the concept of an ideal gas as described through the assumptions of the kinetic theory of gases? (2 Marks), and demonstrate how you can obtain the value of the universal gas constant Joule / K mole? (2 Marks) The concept of an ideal gas has been explained through the assumptions of the kinetic theory of gases to include:
 - 1. A gas consists of a very large number of molecules which are in a state of continual random motion.
 - 2. A molecule has a negligible size.
 - 3. The pressure of a gas is a consequence of the force on a measuring object, such as the container, of molecular collisions.
 - 4. Collisions between molecules or between a molecule and an inert surface are *perfectly elastic*, with no change in the total kinetic energy of the gas molecules.
 - 5. No forces are exerted between molecules except through collisions. Therefore between collisions, a molecule travels in a straight line at a constant speed.
 - 6. The average kinetic energy per gas molecule independent of the nature of the gas and is directly proportional to the absolute temperature. (2 Marks)

The universal gas constant (R) has different values according to the units of the other parameters. Its different values may be found as follows: Referring to Avogadro's Law, which states that:

"The volume occupied by one mole of any gas at standard temperature and pressure,(S.T.P), equals to 22.414 Lit"

 $PV = nRT \triangleright R = (PV)/(nT) = (1atm)(22.414 lit) \div (273.15K)(1g mole)$

R = 0.08208 (atm. Lit) / (K. mole) =

- = 0.08208 atm. lit (1013250 dyne/cm²/ atm).(1000 cm³/ Lit)/(K. mole) =
- = 8.314×10^7 dyne.cm / (K. mole) = 8.314×10^7 erg / (K. mole) = 8.314 J / (K. mole) (2 Marks)

2. N_2O_4 partially dissociated according to the following equation: $N_2O_4 \Leftrightarrow 2 \text{ N } O_2$ If it is found that 24 gm of a gaseous mixture containing N_2O_4 and NO_2 occupies a volume of 15000 cm³ at 363K and 97300 Pa pressure at equilibrium conditions. Calculate the percentage dissociation of N_2O_4 to NO_2 at equilibrium conditions? If the equilibrium constant is defined as $K_p = (P_{NO2})^2 \div (P_{N2O4})$, where P_{NO2} is the partial pressure of NO_2 and P_{N2O4} is the partial pressure of N_2O_4 What is the value of the equilibrium constant N_2O_4 is the partial pressure of N_2O_4 What is the value of the equilibrium constant N_2O_4 is the partial pressure of N_2O_4 What is the value of the

Basis: 1 mole of N_2O_4 in the original mixture before dissociation and let x be the fraction dissociated of N_2O_4

	N ₂ O ₄	\Leftrightarrow	2 NO ₂
Start	1		0
Chang by reaction	-x		2x
At equilibrium	1-x		2x

: Moles of N_2O_4 remaining = 1 - x, : Moles of NO_2 formed = 2 x,

 \therefore Total moles = (1-x)+2x=1+x

Mol fraction of (N_2O_4) at equilibrium = $y_{N2O4} = (1-x) \div (1+x)$,

Mol fraction of (NO_2) at equilibrium = $y_{NO2} = 2x \div (1+x)$,

Now we have 24 gm of the mixture at a pressure of 97.3 KPa = 97300/101325 = 0.9603 atm, and occupies a volume of 15 lit at a temperature of 363 K, \Rightarrow From P V=n R T \Rightarrow n= 0.48345 moles

... Average molecular weight of the gas mixture Mav= m/n =49.6432 gm/mole

But $M_{av} = y_1 M_1 + y_2 M_2$, \Rightarrow 92 $y_1 + 46$ $y_2 = 49.6432$, $y_1 + y_2 = 1$, Solving these two equations $y_1 = y_{N2O4} = 0.0792 = (1-x)/1+x) \Rightarrow x = 0.8532 \Rightarrow \%$ dissociation of $N_2 O_4 = 85.32\%$

Partial pressure of N_2O_4 at equilibrium = P_{N2O4} = P_T (y_{N2O4})=

(0.9603)(0.0792) = 0.076 atm

Partial pressure of NO_2 at equilibrium = $P_{NO_2} = P_T y_{NO_2} = P_T y_{NO$

(0.9603)(0.0792) = 0.8842 atm

Equilibrium constant $K_p = (P_{NO2})^2 \div (P_{N2O4}) = (0.8842)2 \div (0.076) = 10.29$

3. (a): Identify the main raw material resources for fertilizers industry? (2 Marks) (b): Arrange in a descending order the following compounds as efficient nitrogen fertilizers?

Ammonium nitrate, Urea, Ammonium sulfate, Ammonium chloride, Mono ammonium phosphate, Di ammonium phosphate, (4 Marks)

- (a): The major raw materials required for manufacturing fertilizers are:
- (1) Hydrogen and nitrogen for ammonia synthesis.
- (2) Phosphate rock, and potassium minerals for phosphorus and potassium.
- (3) Sulfur, which in addition to being a secondary micronutrient, it is key raw material for the fertilizer industry because of its use in production of sulfuric acid, the material most often used to solubilize phosphate rock. (2 Marks)
- (b): The efficiency of nitrogen fertilizers for application is evaluated as the % of N in the compound, therefore: (4 Marks)

% of N in Urea, [CO (NH₂)₂] = $(28 \div 60) \times 100 = 46.7 \%$

% of N in Ammonium nitrate, [NH₄NO₃] = $(28 \div 80) \times 100 = 35$

% of N in Ammonium sulfate, $(NH_4)_2SO_4 = (28 \div 128) \times 100 = 21.8 \%$

% of N in Ammonium chloride, NH₄CI = $(14 \div 53.5) \times 100 = 26\%$

% of N in Mono ammonium phosphate, $[(NH_4) H_2PO_4] = (14 \div 115) \times 100 = 12.2 \%$

% of N in Di ammonium phosphate, $[(NH_4)_2 HPO_4] = (28 \div 132) \times 100 = 21.2 \%$

The arrangement in a descending order as follows:

- 1, Urea (46.7 % N) ►
- 2. Ammonium nitrate (35 % N) ▶
- 3. Ammonium chloride, (26 % N) ▶
- 4. Ammonium sulfate, (21.8 % N) ▶
- 5. Di ammonium phosphate, (21.2 % N) ▶
- 6. Mono ammonium phosphate, (12.2 % N)

4. Explain the thermodynamic term "Entropy" and how it is implied in the second and third laws of thermodynamics? (4 Marks)

Entropy is a property of thermodynamic system like energy content, and considered as a state function. Physically, entropy measures the disorder in a system. The entropy change in a system, (ΔS), may be predicted as given in the following illustrations: <u>Phase changes:</u> Since a solid represents greater order than a liquid, and a liquid greater order than a gas. Also, mixing and raising the temperature increases the entropy of a system.

In general, any irreversible process results in an overall increase in entropy, whereas a reversible process results in no overall change in entropy.

This general statement is known as the second law of thermodynamics.

The sum of the entropy of a system plus the entropy of the surroundings is everything there is, and so we refer to the total entropy change as the entropy change of the universe, (ΔS_{univ}) . We can therefore state the second law of thermodynamics in terms of the following equations:

Reversible process: $(\Delta S_{univ}) = (\Delta S_{sytem}) + (\Delta S_{urrounding}) = 0$ Irreversible process: $(\Delta S_{univ}) = (\Delta S_{sytem}) + (\Delta S_{urrounding}) > 0$

The third law of thermodynamics 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."

5. Evaluate both the standard enthalpy and standard entropy changes the and then predict the effect of temperature on reaction spontaneity of the following reactions: (6 Marks)

a) $2NaHCO_{3(s)}$ \longrightarrow $Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

b) $CH_3CI_{(I)}+O_{2(g)} \longrightarrow CO_{2(g)} + CI_{2(g)} + HCI_{(g)}$

c) $NH_{3(g)} + HCI_{(g)} \longrightarrow NH_4CI_{(s)}$

You are given the following thermodynamic data for the standard enthalpy of formation $(\Delta H^{\circ})_f$, standard free energy of formation $(\Delta G^{\circ})_f$, and standard entropies $(S^{\circ})_f$:

Compound	State	$(\Delta H^{\circ})_f$ k cal / mole	(S°) cal / °C . mole
CO ₂	g	-94	51
O ₂	g	0	49
H ₂ O		-68	17
H ₂ O	g	-58	45
HCI	g	-22	45
Cl ₂	g	0	53
CH ₃ CI		-31	48
NaHCO₃	S	-215	37
Na ₂ CO ₃	S	-260	32
NH ₃	g	-11	46
NH ₄ CI	S	-75	23

According to second law of thermodynamics, any spontaneous change that takes place in a system must lead to the lowering of the free energy which means that (ΔG) must be negative. Thus, the Gibbs free energy change, ΔG gives us a composite of the two factor that contribute to spontaneity, ΔH and ΔS , from the relation: $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$.

Reaction	ΔH° _r k cal	ΔS°, cal/°C	ΔG° _r will be negative at:	The reaction will be spontaneous at:
(a)	18	54	High temperature	High temperature
(b)	- 85		Will be negative at all temperature	Spontaneous at all temperature
(c)	-42	-68	low temperature	Spontaneous only at low temperature