MAHARASHTRA STATE BOARD OF TECHNICAL EDUCATION
(Autonomous)
(ISO/IEC - 27001 - 2005 Certified)

WINTER-19 EXAMINATION

Model Answer

Subject title: Chemical Engineering Thermodynamics

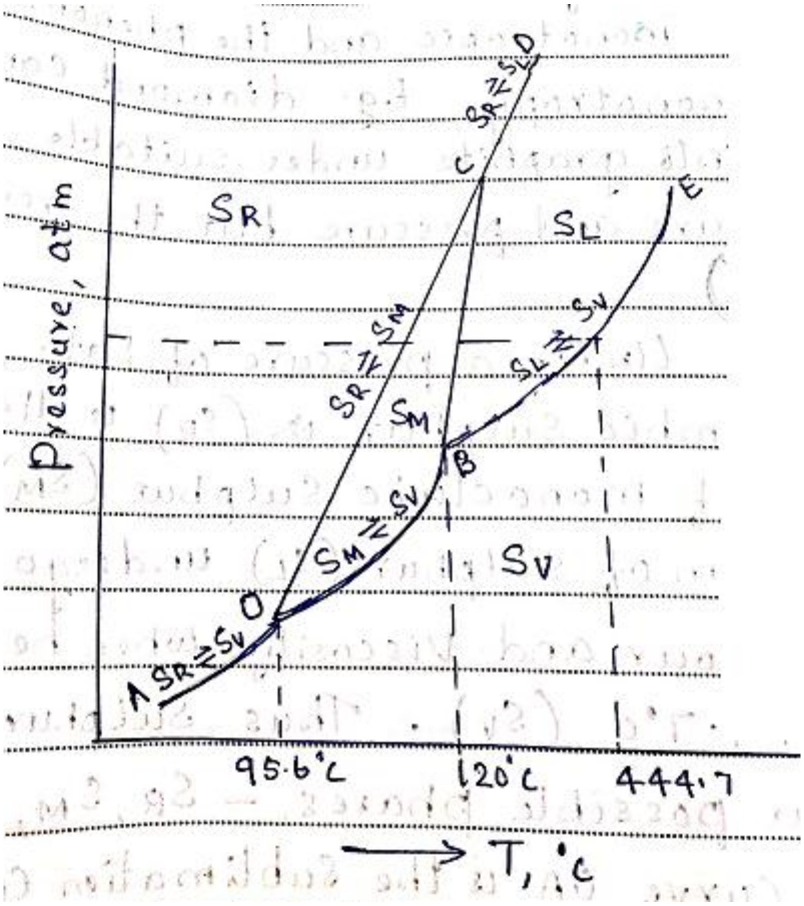
Subject code 22406

Important Instructions to examiners:

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

Q No.		Answer	Marking scheme
1		**Attempt any five**	**10**
1	a	**Open system:** Systems which can exchange both mass and energy across the boundaries are known as open system. **Closed system:** Systems that can exchange energy with the surroundings but which cannot transfer mass across the boundaries are known as closed system.	1 1
1	b	**Extensive property:** If the property of the system depend on the quantity of matter present in the system , then it is known as extensive property. Eg Volume, mass. **Intensive property:** If the property of the system does not depend on the quantity of matter present in the system, then it is known as intensive property. Eg. Temperature, Pressure.	½ ½ ½ ½
1	c	**First law of thermodynamics:** The law States that although energy assumes many forms, the total quantity of energy is constant and when energy disappears in one form, it appears simultaneously in other forms.	2
1	d	**Expression for C_p** $C_p = (\partial H / \partial T)_P$ **Expression for C_v**	1 1

		$C_v = (\partial U / \partial T)_V$	
1	e	**Internal energy (U):** It is the energy stored in the system by virtue of the configuration and motion of the molecules constituting the system.	2
1	f	**Degree of freedom:** The number of intensive parameters that can be varied independently is called the degree of freedom	2
1	g	**Standard entropy:** Entropy of 1 mole of a substance at 1 atm and 25^0C is known as standard entropy.	2
2		**Attempt any three**	**12**
2	a	**Definition:** **System:** It is the part of the universe which is set apart for the process to takes place. **Surroundings:** The part of the universe outside the system and separated from the system by boundaries is called surroundings. **Boundary:** Boundary is a closed surface surrounding (enclosing) a system through which mass and energy may enter or leave	1.5 1.5 1
2	b	**Zeroth law of thermodynamics:** It states that if body A is in thermal equilibrium with body B and B is in thermal equilibrium with body C, then C is also in thermal equilibrium with A. It is the basis of temperature measurement **Mathematical statement:** If A= B and B =C then C=A (A,B, C are in thermal equilibrium with each	2 2

		other ie they are having the same or common temperature.)	
2	c	**Phase diagram of sulphur system:**  Triple point O (S_R-S_M-S_V) B (S_M-S_L-S_V) C (S_R-S_M-S_L) AO – Sublimation curve of rhombic sulphur OB - Sublimation curve of monoclinic sulphur BE – Vaporization curve of liquid sulphur	4

		OC – Transition curve BC – Fusion curve for monoclinic sulphur CD - Fusion curve for rhombic sulphur	
2	d	n = 3moles $T_1 = 27^0C = 300$ K $T_2 = 727^0C = 1000$ K $P_1 = 0.2$ atm $P_2 = 2$ atm Cp = 7 cal / mol K $\Delta S = nC_p \ln\frac{T_2}{T_1} + nR \ln\frac{P_1}{P_2} = 3*7*\ln(1000/300) + 3*1.987*\ln(0.2/2)$ **= 11.557 cal**	3 1
3		**Attempt any three**	**12**
3	a	**Definition:** **Isothermal process** It is the process in which temperature is maintained constant. ii) **Adiabatic process** In an adiabatic process, there is no heat interaction between the system and the surroundings. iii) **Isochoric process** Isochoric process also constant volume process in a thermodynamic process is the process in which the volume of closed system remains constant. vi) **Isobaric process** It is the process in which the pressure remains constant.	1 1 1 1
3	b	**Definition:** **Enthalpy:** **It is the total heat content of a system.** H = U + PV	2

		Heat capacity The heat capacity of a substance is the quantity of heat to be supplied to effect a temperature rise of one degree. **Specific heat** The specific heat is the amount of heat per unit mass required to raise the temperature by one degree.	1 1
3	c	**Third law of thermodynamics:** The law states that absolute entropy is zero for a perfect crystalline substance at absolute zero temperatures. In comparison with internal energy and enthalpy, which are calculated relative to an arbitrary reference state, entropy is a reference property and is absolute, as are pressure, volume and temperature. Third law of thermodynamics can be utilized to calculate the absolute entropy of substances at a given temperature by assigning the value zero for entropy of the crystalline form of the substance at absolute zero. This is done by measuring the heat capacity at different temperatures and the latent heats of phase transition that the substance must have undergone to arrive at the present state from the initial state of absolute zero of temperature. For example, let the melting point of the substance be *Tf* and the boiling point be *Tb*. The entropy at *T*, where *T* is above the boiling point may be evaluated as $S = \int_0^{T_f} \frac{C_{PS} dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{PL} dT}{T} + \frac{\Delta H_V}{T_b} + \int_{T_b}^{T} \frac{C_{PG} dT}{T}$ where C_{PS}, C_{PL} and C_{PG} are the specific heats of solid, liquid and gas respectively and ΔH_f and ΔH_V are the latent heats of fusion and vaporization respectively.	4
3	d	$T_1 = 90$K $T_2 = 320$ K (i) Volume is constant	

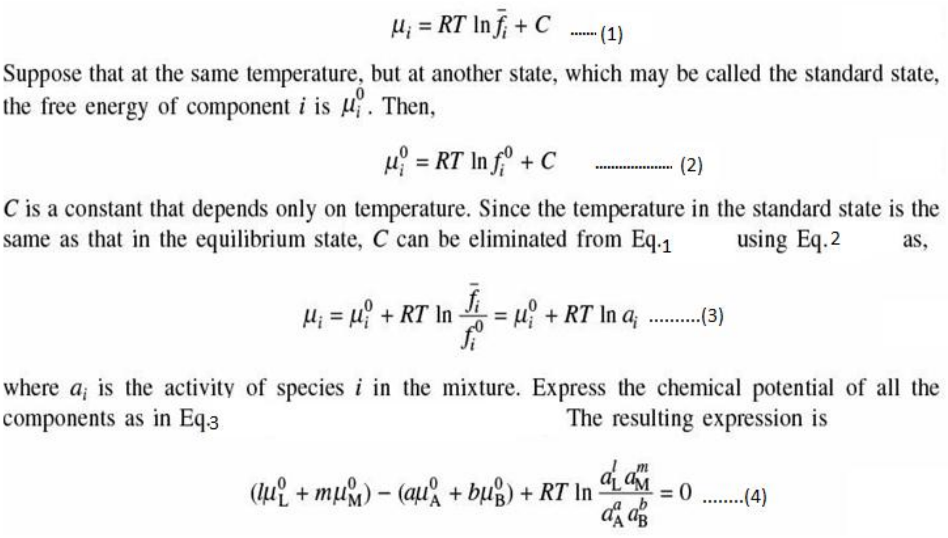
		$\Delta S = nC_v \ln\frac{T_2}{T_1} = 2*1.5*8.314*\ln(320/90) =$ **31.639J/ K =7.53 cal /K** (ii) Pressure is kept constant $\Delta S = nC_p \ln\frac{T_2}{T_1}$ $C_v = 1.5R$ $C_p - C_v = R$ ie $C_p = R + C_v = R + 1.5R = 2.5R$ $\Delta S = nC_p \ln\frac{T_2}{T_1} = 2*2.5*8.314*\ln(320/90)$ = **52.73J/K =12.603 Cal/ K**	2 2
4		**Attempt any three**	**12**
4	a	**Relation between ΔG and K** Consider the reaction $aA + bB \rightarrow rR + sS$ ΔG reaction = ΔG product - ΔG reactant. $= (r\mu_R + s\mu_S) - (a\mu_A + b\mu_B)$. At equilibrium there is no Gibb's free energy change, $\Delta G = 0$ $(r\mu_R + s\mu_S) - (a\mu_A + b\mu_B) = 0$ $(r\mu_R + s\mu_S) = (a\mu_A + b\mu_B)$ But $\mu_i = \mu_i^0 + RT\ln p_i$ Therefore $r(\mu_R^0 + RT\ln p_R) + s(\mu_S^0 + RT\ln p_S) = a(\mu_A^0 + RT\ln p_A) + b(\mu_B^0 + RT\ln p_B)$ $RT\ln\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = (a\mu_A^0 + b\mu_B^0) - (r\mu_R^0 + s\mu_S^0)$ $= -(\Delta G$ product $- \Delta G$ reactant$)$ $= -\Delta G$ reaction. $\ln\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = \frac{-\Delta G \text{ reaction}}{RT}$ But $\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = K_p$ Therefore $\Delta G = -RT\ln K$	2 2

OR

The criterion of equilibrium, can be written for the general chemical reaction represented by Eq. as

$$(l\mathrm{m}_L + m\mathrm{m}_M) - (a\mathrm{m}_A + b\mathrm{m}_B) = 0$$

The chemical potential of a component in the equilibrium state of the reaction mixture is related to its fugacity in that state as given below



$$\mu_i = RT \ln \bar{f}_i + C \quad \text{......}(1)$$

Suppose that at the same temperature, but at another state, which may be called the standard state, the free energy of component i is μ_i^0. Then,

$$\mu_i^0 = RT \ln f_i^0 + C \quad \text{..................}(2)$$

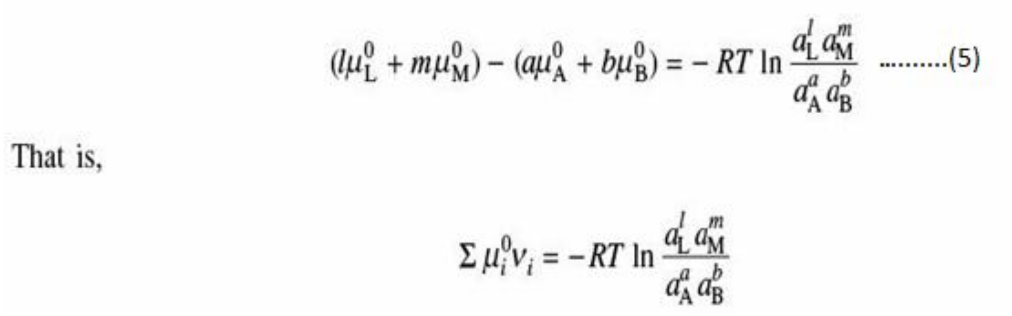
C is a constant that depends only on temperature. Since the temperature in the standard state is the same as that in the equilibrium state, C can be eliminated from Eq.1 using Eq.2 as,

$$\mu_i = \mu_i^0 + RT \ln \frac{\bar{f}_i}{f_i^0} = \mu_i^0 + RT \ln a_i \quad \text{..........}(3)$$

where a_i is the activity of species i in the mixture. Express the chemical potential of all the components as in Eq.3 The resulting expression is

$$(l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) + RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} = 0 \quad \text{........}(4)$$

Equation can be put into the following form:



$$(l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b} \quad \text{..........}(5)$$

That is,

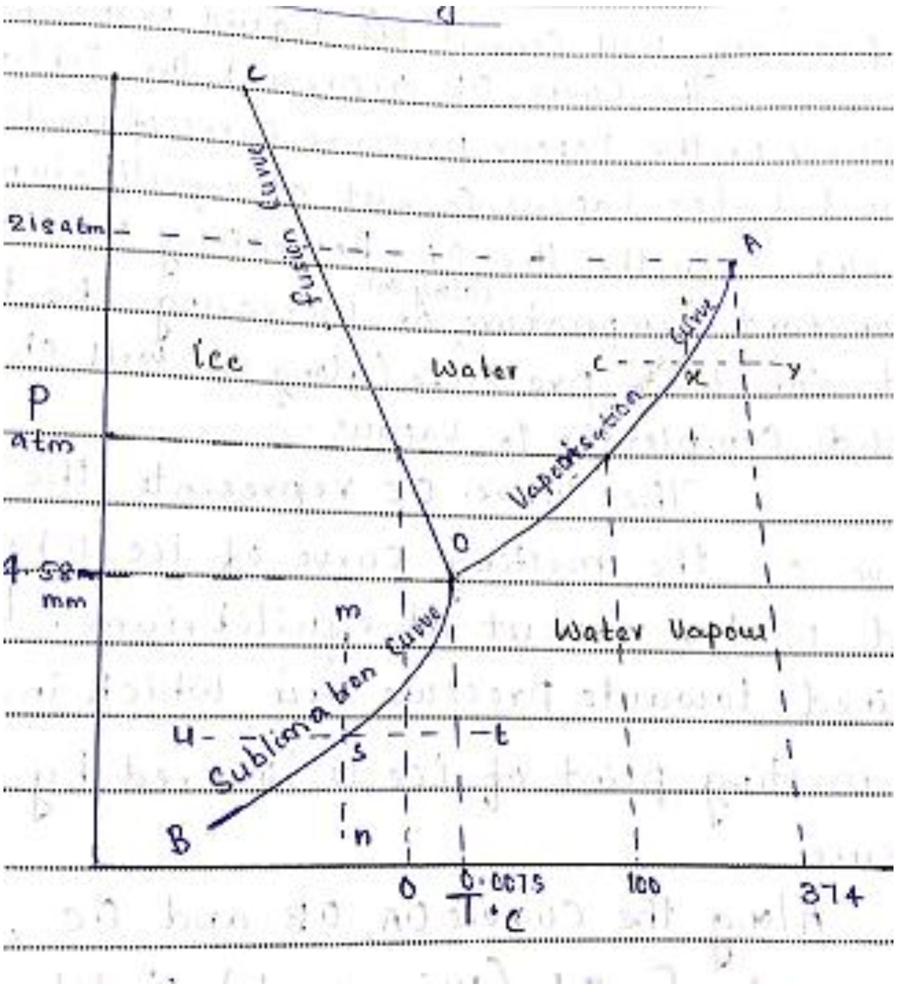
$$\Sigma \mu_i^0 \nu_i = -RT \ln \frac{a_L^l a_M^m}{a_A^a a_B^b}$$

		The left-hand side gives the standard free energy change ΔG^0, the free energy change accompanying the reaction when each of the reactants and the products is in its standard state. Using the definition of the equilibrium constant, $\Delta G^0 = - RT \ln K$	
4	b	**Second law of thermodynamics :** The second law of thermodynamics is just the generalization of our experiences with spontaneous processes and can be stated in a number of ways: 1. Heat cannot by itself pass from a cold to a hot body. 2. All spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy. 3. Every system, when left to itself, will on the average, change toward a system of maximum probability. 4. Kelvin–Planck statement. It is impossible to construct an engine that, operating continuously (in a cycle), will produce no effect other than the transfer of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work.	4
4	c	**Clausius inequality.** It states that in a cyclic operation, the sum of the dQ/T terms around a complete cycle is less than or equal to zero depending on whether the process is irreversible or reversible. $\oint \frac{dQ}{T} \leq 0$	2

		$\oint \frac{dQ}{T} < 0$ for irreversible process $\oint \frac{dQ}{T}$ equals zero for reversible process	1 1
4	d	As per Gibb's Phase rule, F=C-P+2 C=1, P=3, F=1-3+2 F=0	2 1 1
4	e	**Relation between K_p and K_y :** Consider the reaction aA + bB→ rR + sS $K_p = (p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b)$ But $p_A = P \cdot y_A$ Where p_A - partial pressure of A, P- total pressure y_A – mole fraction of A. $K_p = (p_R^r \cdot p_S^s) / (p_A^a \cdot p_B^b)$ $= \{(Py_R)^r \cdot (Py_S)^s\} / \{(Py_A)^a \cdot (Py_B)^b\}$ $= (y_R^r \cdot y_S^s) / (y_A^a \cdot y_B^b) \cdot P^{(r+s+\ldots)-(a+b+\ldots))}$ $K_p = K_y \cdot P^{\Delta n}$ where $K_y = (y_R^r \cdot y_S^s) / (y_A^a \cdot y_B^b)$ and $\Delta n = (r + s + \ldots)-(a + b + \ldots))$is the difference in the number of moles of product and reactant	1 2 1
5		**Attempt any two**	**12**
5	a	**Cp – Cv = R (proof)** Cp = dH / dT and Cv = dU / dT $Cp - Cv = \frac{dH}{dT} - \frac{dU}{dT} = \frac{dH-dU}{dT}$ …..(1)	2

		H = U+PV dH = dU + d(PV) dH – dU = d(PV) …………..(2) Substituting(2) in (1) Cp – Cv $= \frac{d(PV)}{dT}$ …..(3) For ideal gas PV = RT Equation (3) becomes Cp – Cv $= \frac{d(RT)}{dT}$ $=R\frac{d(T)}{dT}$ = R Therefore Cp – Cv = R	2 2
5	b	**Gibb's Phase rule:** The phase rule states that number of degree of freedom of the system is related to the number of components and number of phases by the equation F = C – P + 2 for any system at equilibrium at a definite temperature and pressure. Where C is the number of components, P is the number of phases in thermodynamic equilibrium with each other and F is the number of degrees of freedom or variance of the system. **Component** is the smallest number of independent variable constituents, taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation, **Phase** is any homogeneous, physically distinct and mechanically separable portion of a system which is separated from other such parts of the system by definite boundary surfaces. The number of intensive parameters that can be varied independently is called **the degree of freedom**	3 3

5	c	**Van't Hoff equation:** Consider the reaction aA + bB→rR+sS $\Delta G^0 = -RT\ln K$….. (1) $\Delta G^0 = (r\mu R + s\,\mu s) - (a\,\mu A + b\,\mu B)$……(2) From 1 and 2 $-RT\ln K = (r\mu R + s\,\mu s) - (a\,\mu A + b\,\mu B)$ Differentiating with respect to T at constant pressure $d/dT \ln k = -(1/R)\,((r\,\partial/\partial T\,\mu R/T + s\,\partial/\partial T\,\mu s/T) - (a\,\partial/\partial T\,\mu A/T + b\,\partial/\partial T\,\mu b/T))$ Gibb's Helmholtz equation is a $\partial/\partial T\,(\mu i/T) = -Hi/RT^2$ ie $d/dT \ln k = (1/RT^2)\,\{[rH_R + sH_s] - [aH_A + bH_B]\}$ $= (1/RT^2)(\Sigma H^0_{product} - \Sigma H^0_{reactant})$ $\mathbf{d/dT \ln k = \Delta H^0/RT^2}$ is the Van't Hoff equation where ΔH^0 is molal enthalpy	2 2 2
6		**Attempt any TWO of the following**	**12**
6	a	**Phase diagram for water system:** Water can exist in 3 possible phases, hence there can be 3 forms of equilibrium namely liquid ↔ vapour, solid ↔vapour, solid↔ liquid. Each equilibrium involves 2 phases. The curve OA represents the vapour pressure curve where liquid water and its vapour coexist at equilibrium. Curve OA extends only up to the critical temperature of water (374^{0}C) since above this temperature liquid water cannot exist. Consider a point x on the line OA .Increasing the pressure at constant temperature (line xb) or decreasing the temperature at constant pressure (line xc) will convert the vapour un to liquid. The curve OB represents the sublimation curve where ice and water vapour coexist at equilibrium. Consider point s on the line OB. Decreasing the pressure at constant temperature(along line sn) or increasing the temperature	3

		at constant pressure (along line st) will change the solid completely in to vapour. The curve OC represents the fusion curve or melting curve of ice where ice and water coexist at equilibrium. Line OC is inclined towards pressure axis which indicates that the melting point of ice is lowered by increase of pressure. The curve OA,OB and OC meet at a common point O called the triple point where all the 3 phases coexist at equilibrium. 	3

<table>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>6</td><td>b</td><td>**Vander Waals equation of state:**
An equation of state is an equation which relates the variables of state (T, P, V, and n). It's particularly useful when we want to know the effect of a change in one of the variables of state, The ideal gas law is only an approximation to the actual behavior of gases. At high densities, that is at high pressures and low temperatures, the behavior of actual or real gases deviate from that predicted by the ideal gas law. An equation of state taking account the volume occupied by the molecules and the attractive forces between them is the Vander Waals equation.
Vander Waals equation is $\left(P + \frac{a}{V^2}\right)$ (V-b) = RT
Where a and b are constants.
a = $\frac{27R^2 T_C^2}{64P_C}$
and b = $\frac{RT_C}{8P_C}$
where T_c and P_c are critical temperature and critical pressure respectively.</td><td>2
2
2</td></tr>
<tr><td>6</td><td>c</td><td>Reaction is $N_2 + 3 H_2 \leftrightarrow 2NH_3$
P = 30 atm
Let there be 1 mole of N_2 and 3 moles of H_2 initially.
Let x mole of NH_3 be produced at equilibrium
<table>
<tr><th></th><th>N_2</th><th>H_2</th><th>NH_3</th><th>Total moles</th></tr>
<tr><td>Moles present initially</td><td>1</td><td>3</td><td>0</td><td></td></tr>
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Moles reacted / produced at equilibrium	$\frac{x}{2}$	$\frac{3x}{2}$	x		
Moles present at equilibrium	$1-\frac{x}{2}$	$3-\frac{3x}{2}$	x	4 - x	3
Mole fraction = individual moles / Total moles	$\frac{1-\frac{x}{2}}{4-x}$	$\frac{3-\frac{3x}{2}}{4-x}$	$\frac{x}{4-x}$		
Partial pressure = Total pressure * mole fraction	$30*\frac{1-\frac{x}{2}}{4-x}$	$30*\frac{3-\frac{3x}{2}}{4-x}$	$30*\frac{x}{4-x}$		

% of NH_3 at equilibrium = 10%

$\frac{x}{4-x} = 0.1$ x = 0.3636

1

Partial pressure of N_2 = $30*\frac{1-\frac{x}{2}}{4-x} = 30*\frac{(1-0.3636/2)}{(4-0.3636)} = 6.75$ atm

Partial pressure of H_2 = $30*\frac{3-\frac{3x}{2}}{4-x} = 30*\frac{\left(3-\left(3*\frac{0.3636}{2}\right)\right)}{(4-0.3636)} = 20.25$ atm

Partial pressure of NH_3 = $30*\frac{x}{4-x} = 30*\frac{0.3636}{(4-0.3636)} = 2.996$ atm

2

$Kp = \frac{(P_{NH3})^2}{(P_{H2})^3 * P_{N2}} = \frac{2.996^2}{6.75 * 20.25^3}$ = **$1.6014 * 10^{-4}$ atm^{-2}**