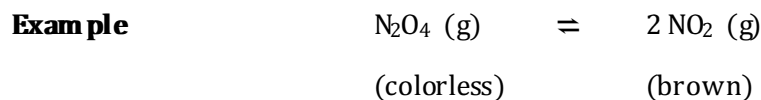


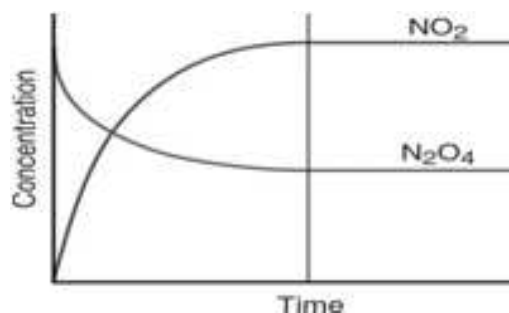
CHEMICAL EQUILIBRIUM

Chemical reactions do NOT go to completion (100% products) - even those that look like they do. A reaction will instead reach a point after which the amount of reactants and products no longer changes with time. This is due to the fact that *all reactions are reversible*.



(\rightleftharpoons means the reaction goes in both directions)

The plot shows that after a certain time, the conc's of all species do not change any more. The reaction has reached equilibrium. This is a "dynamic equilibrium", which means reactions are still occurring in both directions, but no overall change in the []'s.



Characteristics of Chemical Equilibrium

- The equilibrium is dynamic i.e. the reaction continues in both forward and reverse directions.
- The rate of forward reaction equals to the rate of reverse reaction.
- The observable properties of the system such as pressure, concentration, density remains invariant with time.
- The chemical equilibrium can be approached from either side.
- A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium.

Equilibrium Constant (K)

Law of Chemical Equilibrium

According to this law, the ratio of product of concentration of products to the product of concentration of reactants, with each concentration term is raised to the power by its coefficient in overall balanced chemical equation, is a constant quantity at a given temperature and it is called equilibrium constant.

Derivation of law of chemical equilibrium

Let us consider for the following equilibrium



then, from Law of mass action

rate of forward reaction $r_1 \propto [A]^a [B]^b$

or $r_1 = K_a [A]^a [B]^b$ and rate of reverse reaction $r_2 \propto [C]^c [D]^d$

$$r_2 = K_2 [C]^c [D]^d$$

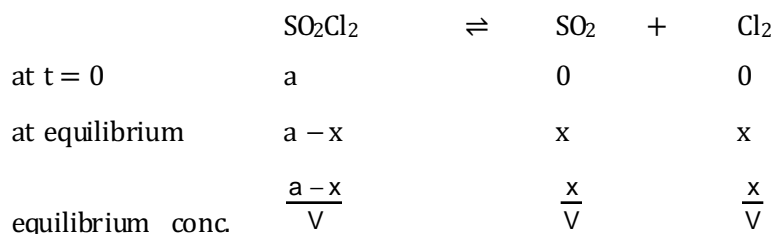
at equilibrium, $r_1 = r_2$

$$\Rightarrow K_1 [A]^a [B]^b = K_2 [C]^c [D]^d$$

$$\Rightarrow K_c = \frac{K_1}{K_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_c equilibrium constant in terms of active masses (molarity here) of reacting species.

For the reaction



(V is volume of container)

$$\text{So, } [SO_2 Cl_2] = \frac{a-x}{V}; [SO_2] = [Cl_2] = \frac{x}{V}$$

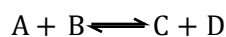
$$\text{So, } K_c = \frac{\left(\frac{x}{V}\right) \times \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT (K_c)

- (i) K_c for a particular reaction at given temperature has a constant value.
- (ii) Value of K_c always depends on nature of reactants and the temperature, but independent of presence of catalyst or, of inert material.
- (iii) Its value is always independent of the initial concentration of reactants as well as the products.
- (iv) The value of K_c indicates the proportion of products/product formed at equilibrium. Large K_c value means large proportions of product.
- (v) When the reaction is reversed, equilibrium constant for reverse reaction will also be inversed.

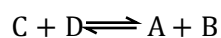
$$K'_c = \frac{1}{K_c}$$

Let us have



$$K_c = \frac{[C][D]}{[A][B]}$$

By reversing the reaction,

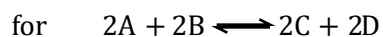


$$K'_c = \frac{[A][B]}{[C][D]} = \frac{1}{K_c}$$

(vi) If the coefficients of reactants or products are halved or, doubled then accordingly, value of K'_c will change.

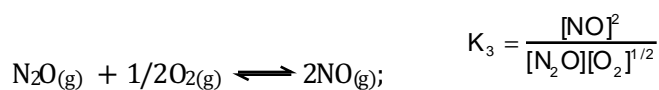
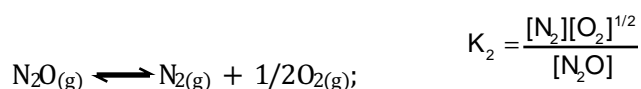
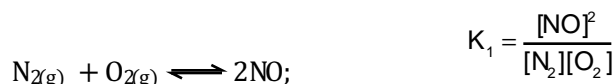


$$K_c = \frac{[C][D]}{[A][B]}$$



$$K'_c = \frac{[C]^2[D]^2}{[A]^2[B]^2} = \left\{ \frac{[C][D]}{[A][B]} \right\}^2 = K_c^2$$

(vii) When a number of equilibrium reactions are added, the equilibrium constant, for overall reaction is the product of equilibrium constants of respective reactions.



$$\frac{K_3}{K_2} = \frac{[NO]^2}{[N_2O][O_2]^{1/2}} \times \frac{[N_2O]}{[N_2][O_2]^{1/2}} = \frac{[NO]^2}{[N_2][O_2]} = K_1$$

i.e. $\frac{K_3}{K_2} = K_1$

Q: the "reaction quotient"

Q and K for any reaction

Consider $aA + bB \rightleftharpoons cC + dD$

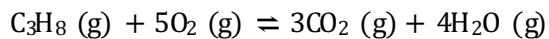
$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

a, b, c, d are stoichiometry coefficients.

(Q_c means Q expressed in concentrations). At equilibrium, $Q_c = K_c$

Example 1:

$C_3H_8(g) + O_2(g) \rightleftharpoons CO_2(g) + H_2O(g)$ **check:** not balanced, so we must balance it first!

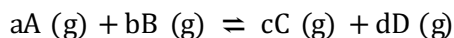


$$\therefore Q_c = \frac{[CO_2]^3 [H_2O]^4}{[C_3H_8] [O_2]^5} (= K_c \text{ if at equilibrium})$$

Magnitude of K

- $K \gg 1$ products are heavily favoured and reaction nears completion.
- $K \cong 1$ concentrations of products and reactants are approximately equal at equilibrium.
- $K \ll 1$ reactants are heavily favoured and reactants do not tend to react.

Q and K Expressed as Pressures



$$Q_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = K_p \text{ at equilibrium}$$

Q_p and K_p mean that Q and K are expressed in pressures.

Example: $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

$$Q_p \text{ (or } K_p) = \frac{p_{CO_2}^3 p_{H_2O}^4}{p_{C_3H_8} p_{O_2}^5}$$

Relationship between K_c and K_p

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \cdot (RT)^{c+d-a-b}$$

$$K_p = K_c (RT)^{\Delta n}$$

Where $\Delta n = c + d - a - b =$ change in total number of moles of gas.

∴ if there is no change in the moles of gas (i.e. $\Delta n = 0$), $K_p = K_c$

For above example: $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

$$\Delta n = 3 + 4 - 1 - 5 = 1$$

$$\therefore K_p = K_c(RT)^{\Delta n} = K_cRT$$

Predicting Reaction Directions

If Q does not equal K , reaction is not at equilibrium. Net reaction will occur until equilibrium is reached.

If $Q > K$ reaction proceeds from right-to-left to reach equilibrium

$Q < K$ reaction proceeds from left-to-right to reach equilibrium

$Q = K$ reaction at equilibrium

Sample Problem $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_c = 0.21$ at $100^\circ C$

Example: if $[N_2O_4] = 0.12 M$ and $[NO_2] = 0.55 M$, is the rxn at equil?

Answer: calculate Q_c and compare with K_c .

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.55)^2}{(0.12)} = 2.5$$

$\therefore Q_c > K_c$ ∴ the reaction shifts from the right (products) to the left (reactants) until $Q_c = K_c = 0.21$

Example: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

A 2.00 L flask is filled with 0.200 mol of HI and allowed to reach equilibrium. At equilibrium, $[HI] = 0.078 M$. Calculate K_c .

	$2HI(g)$	\rightleftharpoons	$H_2(g) +$	$I_2(g)$
[Initial]	0.100		0	0
[Equil]	$(0.100 - 2x)$		x	x

$$\text{initial } [HI] = 0.100 M$$

\therefore at equilibrium: $[HI] = 0.078M = (0.100 - 2x)$ $\therefore x = 0.011 M$

$$\therefore K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{xx}{(0.1-2x)^2} = \frac{(0.011)^2}{(0.078)^2} = 0.020$$

Example: 1.00 mol H₂ and 2.00 mol I₂ are placed in a 1.00 L vessel at 458 °C. Calculate the moles of each substance at equilibrium. K_c = 49.7

	H ₂ (g)	+	I ₂ (g)	⇌	2HI (g)
n(initial)	1.00 mol		2.00 mol		0
[initial]	1.00 M		2.00 M		0
[equil]	(1.00-x)		(2.00-x)		2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1-x)(2-x)} = \frac{4x^2}{2-3x+x^2} = 49.7$$

$$\therefore 4x^2 = 49.7x^2 - 149.1x + 99.4$$

$$45.7x^2 - 149x + 99.4 = 0$$

$$\therefore x = 2.33 \text{ M} \quad \text{OR} \quad x = 0.93 \text{ M}$$

(not possible: max [H₂] = 1.00 M) **correct x**

Finally, use x to calculate all concs:

$$[H_2] = (1.00 - 0.93) = 0.07 \text{ M} \quad [I_2] = (2.00 - 0.93) = 1.07 \text{ M}$$

$$[HI] = 2(0.93) = 1.86 \text{ M}$$

$$n(H_2) = 0.07 \text{ mol} \quad n(I_2) = 1.07 \text{ mol} \quad n(HI) = 1.86 \text{ mol}$$

Example: I₂ (g) ⇌ 2I (g) at 500 K.

Initial conc of I₂ is 0.45 M. What is [I] at equilibrium? K_c = 5.6 × 10⁻¹²

	I ₂ (g)	⇌	2I (g)
[initial]	0.45 M		0
[equil]	(0.45-x)		2x

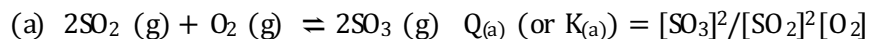
$$K = 5.6 \times 10^{-12} = \frac{(2x)^2}{(0.45-x)} \approx \frac{(2x)^2}{0.45} \text{ because } x \ll 0.45, \text{ since } K \text{ is very small}$$

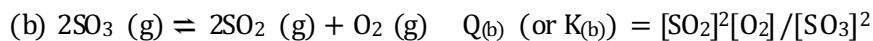
$$\text{Solving: } x = 7.9 \times 10^{-7} \quad \text{Therefore, } [I] = 2x = 1.6 \times 10^{-6} \text{ M}$$

If

How K changes with reactions

1) Opposite reactions





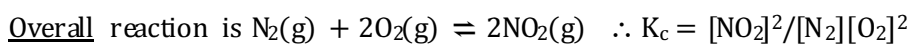
$$K_{(a)} = 1/K_{(b)}$$

2) Reaction consisting of more than one step.

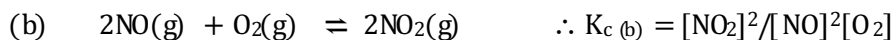
The overall K (what we normally work with) are related to the K of individual steps by the relationships

$$K_{\text{overall}} = K_1 \times K_2 \times K_3 \times \dots$$

Example:



But this reaction has two steps;

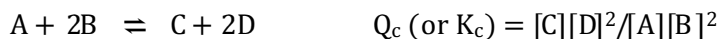


$$\therefore K_{c(a)} \times K_{c(b)} = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = K_{c(\text{overall})}$$

3) Coefficients multiplied by a common factor.

Q and K refer to a balanced reaction as written

\therefore Q and K change if the equation is multiplied by some number.

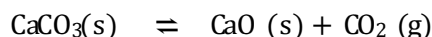


$$\therefore Q_{c'} = \sqrt{Q_c}$$



$$\therefore Q_{c''} = Q_c^2$$

4) Reactions involving pure liquids and solids (heterogeneous equilibria).



Concs of solids or liquids are constant \therefore in such a heterogeneous reaction, only the substances whose concs can change are included.

$$\therefore Q_c = [CO_2] \quad \text{strange as it seems, this is correct!}$$

(**Note** the amount of a solid or liquid can change, but not its conc)

Example: In an experiment it was found that when 20.55 moles of hydrogen were heated with 31.89 moles of iodine at 440°C, the equilibrium mixture contained 2.06 moles of hydrogen, 13.40 moles of iodine and 36.98 moles of HI. Calculate the equilibrium constant for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$.

Solution: In the problem, initial moles of H_2 and I_2 are given. The moles of H_2 , I_2 and HI are also given at equilibrium, so the initial moles are not needed in the problem to calculate K_c . Let the volume of the container be 'V' litre.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{36.98}{V}\right)^2}{\left(\frac{2.06}{V}\right)\left(\frac{13.40}{V}\right)} = \frac{(36.93)^2}{(2.06)(13.40)} = 49.54$$

Le Chatelier's Principle

If a system at equilibrium is disturbed, it will adjust in a way that reduces the effect of the disturbance, and returns to equilibrium.

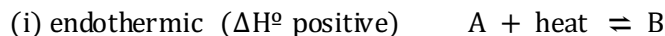
(A) Change in Temperature (Note: this DOES change K)

Remember: $K = k_{\text{fwd}}/k_{\text{rev}}$ \therefore Since k 's change with T , so does K

Rule:

- (i) endothermic reactions (ΔH° positive); as $T \uparrow$, reaction $L \rightarrow R$, $K \uparrow$
endothermic reactions (ΔH° positive); as $T \downarrow$, reaction $R \rightarrow L$, $K \downarrow$
- (ii) exothermic reactions, (ΔH° negative); as $T \downarrow$, reaction $L \rightarrow R$, $K \uparrow$
exothermic reactions, (ΔH° negative); as $T \uparrow$, reaction $R \rightarrow L$, $K \downarrow$

Proof: think of heat as a component of the reaction



As $T \uparrow$, heat \uparrow \therefore reaction shifts $L \rightarrow R$



As $T \uparrow$, heat \uparrow \therefore reaction shifts $R \rightarrow L$

The van't Hoff Equation.

This equation tells us mathematically how the K value is affected by changes in the temperature (T).

$$\ln \left(\frac{K_2}{K_1} \right) = - \frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

This tells us how the K changes in going from temperature T_1 to T_2 , the K changing from K_1 to K_2 .

Note:

- (i) the change in K with T depends only on the $\Delta H^\circ (= \Delta H^\circ_{\text{rxn}})$
- (ii) the van't Hoff equation looks similar to the Arrhenius equation for the change in the rate constant k of a reaction as the T is changed.

(B) Change in Concentration or Pressure of Reactant or Product

(Note: this DOES NOT change K_c or K_p)

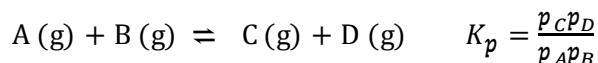


If [C] or [D] are increased (for example, by dissolving more C or D in a solution), the equilibrium is disturbed. The change in [C] or [D] causes $Q \neq K$, and the reaction adjusts to return to equilibrium. How? Since there is now too much [C] or [D], the reaction proceeds right-to-left until it is back to equilibrium.

if [D] \uparrow $Q > K$ \therefore rxn proceeds right-to-left \therefore [D] \downarrow [C] \downarrow [A] \uparrow [B] \uparrow

if [D] \downarrow $Q < K$ \therefore rxn proceeds left-to-right \therefore [A] \downarrow [B] \downarrow [C] \uparrow [D] \uparrow

Changing the partial pressure (p) of a gas affects the reaction in the same way as changing conc.



Add more D to the flask: p_D increases \therefore rxn proceeds right-to-left

The reaction does what is necessary to recover from the disturbance, and re-establish equilibrium.

To help us understand and remember this, let's make up an example with convenient numbers. Consider the reaction:



Consider this reaction when [A] = 4M, [B] = 40M and [C] = 10M

$$\therefore Q_c = [B][C]/[A] = (40)(10)/4 = 100 \quad \text{Since } Q_c = K_c, \text{ the reaction is at equilibrium.}$$

Now, let's add more C to make new [C] = 20M, i.e., we double [C].

$$\text{New } Q_c = (40)(20)/4 = 200 \neq K_c$$

\therefore Reaction no longer at equilibrium. $Q_c > K_c$ \therefore shifts to the left until it returns to equilibrium \therefore more A forms, [A] \uparrow , [B] \downarrow and [C] \downarrow

When [A] = 4.00M [B] = 40.00M [C] = 20.00M $Q_c = 200 \neq K_c$

[A] = 5.00M [B] = 39.00M [C] = 19.00M $Q_c = 148 \neq K_c$

[A] = 5.50M [B] = 38.50M [C] = 18.50M $Q_c = 130 \neq K_c$

[A] = 6.00M [B] = 38.00M [C] = 18.00M $Q_c = 114 \neq K_c$

$$[A] = 6.30M \quad [B] = 37.70M \quad [C] = 17.70M \quad Q_c = 106 \neq K_c$$

$$[A] = 6.50M \quad [B] = 37.50M \quad [C] = 17.50M \quad Q_c = 101 \neq K_c$$

$$[A] = 6.55M \quad [B] = 37.45M \quad [C] = 17.45M \quad Q_c = 100 = K_c$$

\therefore reaction at equilibrium again. New $[A] = 6.55 M$, new $[B] = 37.45 M$, new $[C] = 17.55M$

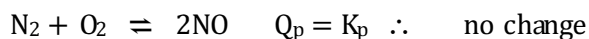
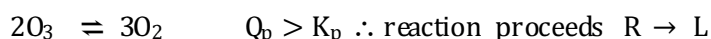
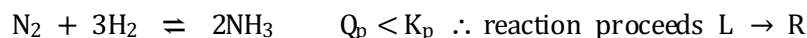
$$Q_c = [B][C]/[A] = (37.45)(17.55)/(6.55) = 100 = K_c$$

(C) Change in Volume **(Note: this DOES NOT change K_p)**

Question: If a reaction involving gases is at equilibrium and the volume of the vessel is changed, what happens to the equilibrium?

Answer: the total pressure (P) is changed, and reaction will respond in the direction that opposes this, if it can. Let's summarize results - see textbook for details.

e.g. consider volume decreased ($\therefore P$ increased) in the following:



However, addition of an inert gas (one not involved in the reaction) to the flask to increase total pressure (P) does NOT change the reaction in any way, because the individual partial pressures (p) of the gases involved in the reaction stay the same, and therefore $Q_p = K_p$ still.

(D) Addition of a Catalyst **(Note: this DOES NOT change K)**

Catalysts speed up the rates of reactions, but do not affect the equilibrium constant (K_c or K_p). Therefore, a catalyst will speed up the rate at which a reaction reaches equilibrium, but it will NOT affect the equilibrium position.

Note: the rates of reactions are affected by the activation energy barrier that must be overcome for the reaction to occur. We say the rates of reaction involve "KINETICS". The equilibrium constant (K) is not affected by activation energy barriers: it depends

instead on thermodynamic quantities (such as ΔH° , and others --- . We say the equilibrium constant involves "THERMODYNAMICS".

"KINETICS" controls reaction rates

"THERMODYNAMICS" controls equilibrium position

Thus, a reaction $A \rightarrow B$ might be very slow (i.e. slow kinetics) but it might still lie far to the side of product B (i.e. large K).

Finally: let us repeat one more time - the ONLY change that will alter the value of K is to change the temperature T. The other changes can affect the relative concentrations or pressures of the reactants and products, but they do NOT change the value of K.

PROBLEMS FOR EXERCISE:

1. Phosphorous pentachloride dissociates on heating:

$\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$.If $K_c = 3.26 \times 10^{-2}$ at 191°C , what is K_p at this temperature?

Ans.: $K_p = 1.24$

2. The value of K_c for the following reaction at 900°C is 0.28. $\text{S}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$ What is K_p at this temperature?

Ans.: $K_p = 3.0 \times 10^{-5}$

3. Consider the following reaction at 1000°C : $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ At equilibrium, the following concentrations are measured: $[\text{CO}] = 0.0613$ M, $[\text{H}_2] = 0.1839$ M, $[\text{CH}_4] = 0.0387$, $[\text{H}_2\text{O}] = 0.0387$ M. Calculate the value of K_c for this reaction. Calculate the value of K_p ?

Ans.: $K_c = 3.93$, $K_p = 3.60 \times 10^{-4}$

4. A 5.00 L vessel contained 0.0185 mol of phosphorus trichloride, 0.0158 mol of phosphorus pentachloride, and 0.0870 mol chlorine at 503 K in an equilibrium mixture. Calculate the value of K_c at this temperature. $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$

Ans.: $K_c = 49.1$

5. Carbon dioxide decomposes at elevated temperatures to carbon monoxide and oxygen: $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$ At 3000 K, 2.00 mol of CO_2 is placed

into a 1.00 L container and allowed to come to equilibrium. At equilibrium, 0.90 mol CO_2 remains. What is the value for K_c at this temperature?

Ans.: $K_c = 0.82$

6. Consider the following reaction at 1000°C : $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ The original concentrations of CO and H_2 were 0.2000 M and 0.3000 M, respectively. At equilibrium, the concentration of CH_4 was measured to be 0.0478 M. Calculate the values of K_c and K_p .

Ans.: $K_c = 3.91$, $K_p = 3.60 \times 10^{-4}$

7. Consider the following reaction at 1000°C : $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ When 4.00 mol of HI was placed into the 5.0 L reaction vessel at 458°C , the equilibrium mixture was found to contain 0.422 mol I_2 . Calculate the value of K_c for the decomposition of HI.

Ans.: $K_c = 1.79 \times 10^{-2}$

8. Hydrogen sulfide, a colorless gas with a foul odor, dissociates on heating: $2\text{H}_2\text{S}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{S}_2(\text{g})$ When 0.100 mol H_2S was put into a 10.0 L vessel and heated to 1132°C , it gave an equilibrium mixture containing 0.0285 mol H_2 . Calculate the value of K_c at this temperature.

Ans.: $K_c = 1.35 \times 10^{-6}$ M

9. The following reaction has an equilibrium constant K_c of 3.07×10^{-4} at 24°C : $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$ For each of the following compositions, decide whether the reaction is at equilibrium. If not, decide which direction the reaction should go.

a) $[\text{NOBr}] = 0.0610$ M, $[\text{NO}] = 0.0151$ M, $[\text{Br}_2] = 0.0108$ M

b) $[\text{NOBr}] = 0.115$ M, $[\text{NO}] = 0.0169$ M, $[\text{Br}_2] = 0.0142$ M

c) $[\text{NOBr}] = 0.181$ M, $[\text{NO}] = 0.0123$ M, $[\text{Br}_2] = 0.0201$ M

Ans.: a.) goes left; b.) equilibrium; c.) goes right

10. Nitrogen and oxygen form nitric oxide: $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ If an equilibrium mixture at 25°C contains 0.040 mol/L N_2 and 0.010 mol/L O_2 , what is the concentration of NO in this mixture? $K_c = 1 \times 10^{-30}$ at this temperature.

Ans.: 2×10^{-17} M

11. An equilibrium mixture at 1200 K contains 0.30 mol CO, 0.10 mol H_2 and 0.020 mol H_2O , plus an unknown amount of CH_4 in each liter. What is the concentration of CH_4

in this mixture if $K_c = 3.92$? The reaction is: $\text{CO(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_4\text{(g)} + \text{H}_2\text{O(g)}$

Ans.: 0.059 M

12. The reaction: $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ is used to increase the ratio of hydrogen in synthesis gas (mixtures of CO and H_2). Suppose you start with 1.00 mol each of carbon monoxide and water in a 50.0 L vessel. What is the concentration of each substance in the equilibrium mixture at 1000°C given that $K_c = 0.58$ at this temperature?

Ans.: $[\text{CO}] = [\text{H}_2\text{O}] = 0.0114 \text{ M}$,

$[\text{CO}_2] = [\text{H}_2] = 0.0086 \text{ M}$

13. Hydrogen iodide decomposes to hydrogen gas and iodine gas: $2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ At 800 K, K_c for this reaction is 0.016. If 0.50 mol HI is placed into a 5.0 L flask, what will be the composition of the mixture at equilibrium?

Ans.: $[\text{HI}] = 0.080 \text{ M}$, $[\text{H}_2] = [\text{I}_2] = 0.010 \text{ M}$

14. N_2O_4 decomposes to NO_2 according to the reaction: $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$ At 100°C , $K_c = 0.36$. If a 1.00 L flask initially contains 0.100 mol N_2O_4 , what will be the concentrations of N_2O_4 and NO_2 at equilibrium?

Ans.: $[\text{N}_2\text{O}_4] = 0.040 \text{ M}$, $[\text{NO}_2] = 0.12 \text{ M}$

15. Hydrogen and iodine react according to the equation: $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightleftharpoons 2\text{HI(g)}$ Suppose 1.00 mol H_2 and 2.00 mol I_2 are placed into a 1.00 L vessel. How many moles of each substance are in the equilibrium mixture at 458°C if $K_c = 49.7$ at this temperature?

Ans.: 1.86 mol HI, 0.07 mol H_2 , 1.07 mol I_2

16. Iodine and bromine react to give iodine monobromide: $\text{I}_2\text{(g)} + \text{Br}_2\text{(g)} \rightleftharpoons 2\text{IBr(g)}$.What is the equilibrium composition of a mixture at 150°C that initially contained 0.0015 mol each of iodine and bromine in a 5.0 L vessel if $K_c = 1.2 \times 10^2$ at this temperature?

Ans.: $[\text{IBr}] = 5.1 \times 10^{-4} \text{ M}$,

$[\text{Br}_2] = [\text{I}_2] = 4.7 \times 10^{-5} \text{ M}$

17. Predict the effect of the following concentration changes on the reaction below.



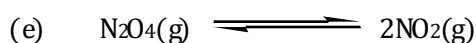
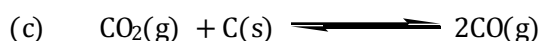
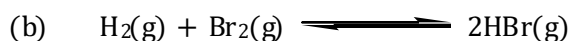
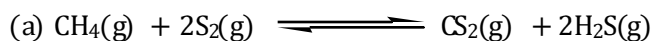
(a) Some $\text{CH}_4\text{(g)}$ is removed.

(b) Some $\text{S}_2\text{(g)}$ is added.

- (c) Some CS₂(g) is added.
- (d) Some H₂S(g) is removed.
- (e) Some argon gas is added.

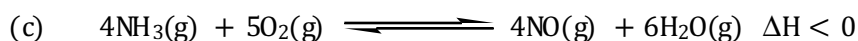
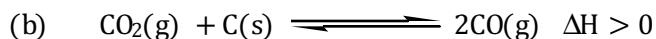
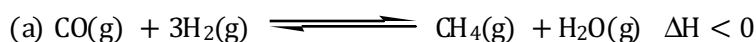
Ans.: a.) goes left; b.) goes right; c.) goes left;
d.) goes right ;e.) no effect

18 Predict the effect of increasing pressure (decreasing volume) on each of the following reactions.



Ans.: a.) no effect; b.) no effect; c.) goes left;
d.) goes right ; e.) goes left

19 Predict the effect of increasing temperature on each of the following reactions. What effect does this change have on K_c?



Ans.: a.) goes left, K_c decreases;
b.) goes right, K_c increases;
c.) goes left, K_c decreases;
d.) goes right, K_c increases

20 A reaction has a ΔG° value of -40 kJ/mol at 25°C. What is the K_{eq} for this reaction?

Ans: K_{eq} = 1.02 x 10⁷

Level-I

1. N_2O_4 gas is 25% dissociated at 37°C and 1 atm. pressure. Calculate

(i) K_p of the reaction (ii) the percentage dissociation at 0.1 atm and 37°C .

2. 0.15 mole of CO is taken in a flask of 2.5 L at 705 K to perform the reaction $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$. Hydrogen is introduced in the reaction mixture till the total pressure of the system was 8.5 atmosphere at equilibrium and 0.08 moles of methanol were formed. Calculate the values of K_p and K_c of the reaction.

3. A compound $\text{AB}_2(g)$ dissociates at temperature T according to the reaction $2\text{AB}_2(g) \rightleftharpoons 2\text{AB}(g) + \text{B}_2(g)$. Deduce the expression $X = \left[\frac{2K_p}{P} \right]^{\frac{1}{3}}$, where x is the degree of dissociation and P is the total pressure

4. For the reaction $\text{Ag}(\text{CN})_2^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$, the equilibrium constant at 25°C is 4.0×10^{-19} . Calculate the $[\text{Ag}^+]$ in a solution which has 0.10 M KCN and 0.03 M AgNO_3 .

5. Carbonyl chloride gas dissociates according to the equation $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$. When the gas was heated to a temperature of 724 K and at a pressure of 1.0 atm., the density of gas mixture at equilibrium was found to be 1.162 g L^{-1} . Calculate the degree of dissociation and K_p of the reaction.

6. When 0.578 g of N_2O_4 was introduced into a one-litre flask at 308 K, the equilibrium pressure was 0.238 atm. Calculate the degree of dissociation and K_p of the reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$.

7. A sample of air having N_2 and O_2 was heated to 2500 K until the equilibrium $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ was established. K_c of the reaction was 2.18×10^{-3} and mole percent of NO at equilibrium was 1.8. Estimate the initial composition of air in mole fractions of N_2 and O_2 .

8. For the reaction $\text{N}_2\text{O}_5(g) \rightleftharpoons 2\text{NO}_2(g) + 0.5 \text{O}_2(g)$, calculate the mole fraction of $\text{N}_2\text{O}_5(g)$ which decomposed at a constant volume and temperature, if the initial pressure was 600 mm Hg and pressure at any time was 960 mm Hg. Assume ideal behaviour for gases.

9. A mixture of NO gas at 0.373 atm. pressure and Cl_2 gas at 0.310 atm pressure was kept in a flask at 500 K temperature. The gases reacted as $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$. The total pressure at equilibrium was 0.544 atm. Calculate the equilibrium constant of the reaction.

- 10.** CaCO_3 dissociates in a container of volume 0.654 L at 1000 K. The equilibrium constant for the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 3.9×10^{-2} atm. at this temperature. Calculate the mass of CaO present at equilibrium.
- 11.** K_c for the dissociates of $\text{PCl}_5(\text{g})$ is equal to 4.15×10^{-12} at 250°C . If the reaction takes place in a two-litre flask initially having 0.01 moles of PCl_5 , what will be the total pressure of all gases at 250°C when equilibrium is achieved.
- 12.** For the equilibrium $\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Ag}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$, the equilibrium constants are 3.98×10^{-4} and 1.41×10^{-2} respectively at 350 K and 400 K. Calculate ΔH° of the reaction.
- 13.** Acetic acid was evaporated in a container of volume 21.45 cm^3 at 437 K and an external pressure of 764.3 Torr. The container was then sealed. The mass of acid present in the sealed container was 0.0519 g Calculate the equilibrium constant of dimerisation of the acid.
- 14.** The equilibrium constant for the reaction $\text{cis-2-butene} \rightleftharpoons \text{trans-2-butene}$ is 2.07 at 400 K temperature. Calculate the standard reaction Gibbs function.

Level-2

- 15.** The equilibrium constant K_p of the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ is 900 atm^{-1} at a temperature of 800 K. A mixture containing SO_3 and O_2 at initial partial pressures of 1 atm. and 2 atm. respectively is heated at a constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.
- 16.** Ammonium hydrogen sulphide (NH_4HS) solid when kept in an evacuated flask at a certain temperature dissociates into H_2S gas and NH_3 gas and the total gas pressure was 500 Torr. Calculate the value of K_p for the dissociation reaction. If an additional amount of ammonia is introduced in the mixture without changing the temperature until the partial pressure of ammonia becomes 700 Torr, what is the partial pressure of H_2S and total gas pressure in the flask?
- 17.** CaCO_3 solid dissociates to give CaO and CO_2 gas at 298 K. What will be the pressure of CO_2 at equilibrium state of the reaction?; Given $\Delta G_f^\circ(\text{CaCO}_3\text{s}) = -1129 \text{ KJ mol}^{-1}$; $\Delta G_f^\circ(\text{CaOs}) = -604.2 \text{ KJ mol}^{-1}$ and $\Delta G_f^\circ(\text{CO}_2\text{g}) = -395 \text{ KJ mol}^{-1}$
- 18.** Br_2 gas and NO gas were reacted at 300 K to produce NO Br gas. At equilibrium, the total pressure was 110.5 Torr. If the initial pressure of NO was 98.4 Torr and Br_2 was 41.3 Torr, calculate the value of equilibrium constant and the standard free energy change of the reaction at 300 K.

19. A saturated solution of iodine in water has 0.330 g of iodine per litre. Larger amounts of iodine can be dissolved with the help of KI and the following reaction takes place $KI + I_2 \rightleftharpoons KI_3$. When 0.100 M KI solution dissolves 12.5 g of iodine per litre, most of it is converted to KI_3 . If the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant of the above reaction.

20. At 817°C K_p for the reaction between CO_2 and excess of hot graphite to form $\text{CO}(g)$ is 10. $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g)$

(a) What are the partial pressures of $\text{CO}(g)$ and $\text{CO}_2(g)$ at equilibrium at 817°C and a total pressure of 4 atm.?

(b) At what total pressure will the gas mixture have 6% CO_2 by volume?

21. ΔH° of $\text{Zn}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{ZnO}(s) + \text{H}_2(g)$ is + 224 kJ mol⁻¹ from 920 K to 1280 K. ΔG° is +33 kJ mol⁻¹ at 1280 K. Assuming that both quantities remain constant, estimate the temperature at which the equilibrium constant becomes greater than 1.0.

22. The equilibrium constant for the reaction $\text{H}_3\text{BO}_3 + \text{glycerine} \rightleftharpoons \text{H}_3\text{BO}_3\text{-glycerine}$ is 0.75. How much glycerine should be added per litre to 0.20 M H_3BO_3 so that 60% of the H_3BO_3 is converted to $\text{H}_3\text{BO}_3\text{-glycerine}$ complex?

23. A 0.01 M solution of a weak acid HA has an osmotic pressure of 0.293 atm at 25°C . A 0.01 M solution of another weak acid HB has an osmotic pressure of 0.345 atm under the same conditions. Which acid has a larger equilibrium constant for ionisation?

24. In a vessel with a volume of one litre, the following gases are at equilibrium at 400°C and the equilibrium concentrations of the same are given below:

$[\text{N}_2] = 1.00\text{ M}$; $[\text{H}_2] = 0.50\text{ M}$; $[\text{NH}_3] = 0.25\text{ M}$.

How many moles of H_2 must be removed from the vessel to increase the concentration of nitrogen to 1.1 M?

Answer:

1. $K_p = 0.267$ atm. and 63% dissociation at 0.1 atm pressure and 37°C

2. $K_c = 150.85$ (mol L⁻¹)⁻² and $K_p = 0.04513$ atm⁻²

4. 7.5×10^{-18} M

5. $\mu = 0.433$ and $K_p = 0.231$

6. $\mu = 0.5$ and $K_p = 0.319$

7. $\text{N}_2 = 0.79$ and $\text{O}_2 = 0.21$

8. 0.407

9. 50.08 atm⁻¹

10. 0.0174 g

11. 0.408 atm.

12. 83.06 KJ

13. $K = 0.704$

14. $\Delta G^\circ = -242 \text{ KJ mole}^{-1}$

15. $P_{\text{SO}_2} = 0.023 \text{ atm}$, $P_{\text{O}_2} = 2.0115 \text{ atm}$,
 $P_{\text{SO}_3} = 0.977 \text{ atm}$.

16. $K_p = 62$, 500 Torr, $P_{\text{H}_2\text{S}} = 89.3 \text{ Torr}$,
 $P_{\text{total}} = 789.3 \text{ Torr}$

17. $1.776 \times 10^{-23} \text{ atm}$

18. $K_p = 132.41 \text{ atm}^{-1}$ and $\Delta G = -12.188$
 KJ mol^{-1}

19. $K = 707.0$

20. $P_{\text{CO}} = 3.062 \text{ atm}$ and $P_{\text{CO}_2} = 0.938$
 atm . $P = 0.679 \text{ atm}$

21. $T_2 = 1501.2 \text{ K}$

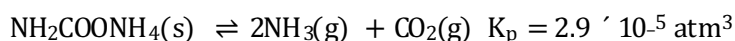
22. 2.0 moles

23. $\text{HA}_K = 5 \times 10^{-4}$ and $\text{HB}_K = 3 \times 10^{-3}$

24. 0.0156 mole

More Questions

- At a certain temperature, 1.00 mole of $\text{PCl}_3(\text{g})$ and 2.00 mole of $\text{Cl}_2(\text{g})$ were placed in a 3-litre container. At equilibrium, only 0.7 mole of PCl_3 remained. Calculate the value of K for the reaction. (0.757)
- Determine the equilibrium concentration of each of the species that react according to the equation $\text{A} + \text{B} \rightleftharpoons \text{C} + 2\text{D}$ (value of $K = 1.8 \times 10^{-6}$), when 1.0 mole of C and 1.0 mole of D are placed in a one-litre vessel and allowed to come to equilibrium. $[\text{D}] = 9.5 \times 10^{-4}$ mol/Litre, $[\text{C}] = [\text{B}] = [\text{A}] = 0.50$ mol L^{-1}
- When 46.0 g of iodine and 1.0 g of H_2 are heated to equilibrium at 470°C , the equilibrium mixture contains 1.9 g of iodine. Compute the equilibrium constant. How many moles of each gas are present in the equilibrium mixture? $[\text{I}_2] = 0.0075$, $[\text{H}_2] = 0.326$, $[\text{HI}] = 0.348$, $K = 50$
- K_p for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ is 0.66 atm. at 46°C . What will be the percent dissociation of N_2O_4 at this temperature and a total pressure of 380 Torr? (49.8)
- One mole of N_2 and 3.0 moles of PCl_5 were placed in a 100-litre vessel and heated to 227°C . The equilibrium pressure was 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of PCl_5 and K_p of the reaction at 227°C . (0.333, $K_p = 0.205$ atm.)
- H_2 gas is introduced for the reaction $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$ in a five-litre flask at 327°C containing 0.2 mole of CO gas. H_2 gas was introduced till the pressure became 4.92 atm. At this point, 0.1 mole of CH_3OH (g) was formed. Calculate the values of K_p and K_c for the reaction. (27.78, 0.115)
- The equilibrium constant for the reaction $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ is 0.3 atm. at a temperature of 1000K. One mole of SO_2 and two moles of O_2 are placed in a vessel maintained at a pressure of 4.0 atm. Evaluate the amount of SO_3 present at equilibrium. (0.742 moles)
- The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 348 K is 1.84 g dm^{-3} . Calculate the equilibrium constant of the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. (5.206 atm)
- When 3.06 g of solid NH_4HS is introduced in a two-litre evacuated flask at 27°C , 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. Calculate K_p and K_c for the reaction at 27°C . 8.1×10^{-5} , 4.9×10^{-2}
- The decomposition of ammonium carbamate at 30°C is represented as



What is the total pressure of gas in equilibrium with $\text{NH}_2\text{COONH}_4$ (s) at 30°C ? (0.0582 atm.)

- K_p for the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is 1.16 atm. at 800°C . If 20.0 g of CaCO_3 was kept in a 10-litre container and heated to 800°C , what percentage of CaCO_3 will remain unreacted at the equilibrium? (34%)

12. Under what conditions will the following reactions go in the forward direction?
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + 23 \text{ k cal}$
 - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) + 45 \text{ k cal}$
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) - 43.2 \text{ k cal}$
 - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) + 27.8 \text{ k cal}$
 - $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g}) + X \text{ k cal}$
 - $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) - X \text{ k cal}$
 - $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) - 14 \text{ k cal}$
13. The equilibrium constant K_p for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is $1.6 \times 10^{-4} \text{ atm}^{-2}$ at 400°C . What will be the equilibrium constant at 500°C if heat of the reaction in this temperature range is -25.14 k cal ? ($1.46 \times 10^{-5} \text{ atm}^{-2}$)
14. $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$; $\Delta H = \text{negative}$
What are the conditions of temperature and pressure favorable for this reaction?
15. For the equilibrium $\text{NH}_4\text{I}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HI}(\text{g})$ $\Delta H = +ve$
What will be the effect on the equilibrium constant on increasing the temperature?
16. K_p for the reaction $2\text{BaO}_2(\text{s}) \rightleftharpoons 2\text{BaO}(\text{s}) + \text{O}_2(\text{g})$ is $1.6 \times 10^{-4} \text{ atm}$, at 400°C . Heat of reaction is -25.14 kcal . What will be the no. of moles of O_2 gas produced at 500°C temperature, if it is carried in 2 litre reaction vessel? (4.6×10^{-7})
17. Equilibrium constant K_p for the reaction $\frac{3}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{N}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ are 0.0266 and 0.0129 at 310°C and 400°C respectively. Calculate the heat of formation of gaseous ammonia (-12140 cal)
18. A system is in equilibrium as $\text{PCl}_5 + \text{Heat} \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ Why does the temperature of the system decreases, when PCl_3 are being removed from the equilibrium mixture at constant volume?
19. N_2O_4 is 25% dissociated at 27°C and 1 atm pressure.
Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and 27°C . (.266, 93.27%)
20. When PCl_5 is heated it dissociates into PCl_3 and Cl_2 . The density of the gas mixture at 200°C and at 250°C is 70.2 and 57.9 respectively. Find the degree of dissociation at 200°C and 250°C (.485, .8)
21. The degree of dissociation of PCl_5 is 60%, then find out the observed molar mass of the mixture. (129.06)
22. Vapour density of N_2O_4 which dissociates according to the equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ is 25.67 at 100°C and a pressure of 1 atm. Calculate the degree of dissociation and K_p for the reaction. (0.792, 6.73 atm)
23. How much PCl_5 must be added to a one litre vessel at 250°C in order to obtain a concentration of 0.1 mole of Cl_2 ? K_c for $\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$ is 0.0414 mol/litre (.3415 mole)