Chapter 11A

Reactions involving Gases

11.1 INTRODUCTION

- Perfect gas: the absence of interatomic forces between the atoms of ideal gases($\Delta H^{M,id} = 0$)-one extreme of a range of possible situations.
- The other extreme: the situation where gases with marked chemical affinity for one another are mixed.

- As with any system @ const. T & P, the equilibrium state = minimum possible value of G^M .
- Knowledge of the variation of ΔG^M with composition → determination of the equilibrium state in any system of reactive gases.

- This determination is facilitated by the introduction of the equilibrium constant for the reaction, and the relation between this constant and the standard Gibbs free energy change, ΔG^o , for the reaction is one of the more important relationships in reaction equilibrium thermodynamics.

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

- Consider the gas reaction,

$$A_{(g)} + B_{(g)} = 2C_{(g)}$$

- To occur at const. T, P **(G′ : Gibbs free energy of the system during the reaction)**

at any instant

$$\mathbf{G'} = \mathbf{n_A \overline{G_A}} + \mathbf{n_B \overline{G_B}} + \mathbf{n_C \overline{G_C}} \qquad (11.1)$$

As this state of min. Gibbs free energy = the equilibrium state of the system at the given T & P.

→ n_A, n_B, n_C will be determined to minimize G′.

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If starting with n_A = n_B =1 mole (2 moles of gas)

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$$A_{(g)} + B_{(g)} = 2C_{(g)}$$

if the total P of system = 1atm, RT lnP=0

Eq.(11.2) simplifies to

$$G' - 2G^{\circ}_{C} = n_A(-\Delta G^{\circ}) + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1 - n_A)\ln(1 - n_A)\right] \qquad (11.3)$$

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

for the reaction at 500K and 1atm pressure.

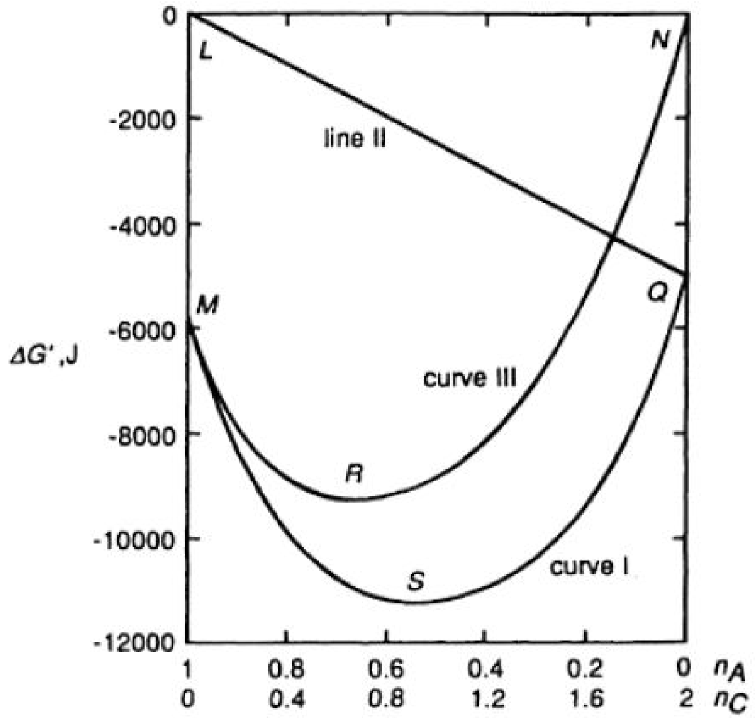

Figure 11.1 The variations of the contributions to the decrease in the Gibbs free energy due to chemical reaction (line II), the contribution to the decrease in the Gibbs free energy due to gas mixing (curve III) with the extent of the reaction $A_{(g)}+B_{(g)}=2C_{(g)}$ for which $\Delta G^\circ = -5000$ joules at 500 K.

the ordinate $\Delta G'$: the difference between ΔG° of the system containing n_A moles of A and ΔG° of the system comprising 1 mole of A and 1 mole of B before mixing of A and B occurs.

The pt. L (n_A =1, n_B =1 before mixing): at $\Delta G'$=0, and the pt. Q (n_C =2) is located at $\Delta G'$=-5000 J.

The pt. M: the decrease in G due to mixing of 1 mole of A and 1 mole of B before any chemical reaction, i.e., from Eq. (8.20),

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

from Eq. (8.20),

$$\Delta G(L \rightarrow M) = \sum_i n_i RT \ln\left(\frac{p_i}{P_i}\right) \qquad = RT\left[n_A \ln\left(\frac{p_A}{P_A}\right) + n_B \ln\left(\frac{p_B}{P_B}\right)\right]$$

But $n_A = n_B$, and

$$P_A = P_B = P_{\text{mixture}} = 1$$

in which case

$$p_A = p_B = \frac{1}{2}$$

Thus $$\Delta G(L \rightarrow M) = 8.3144 \times 500 \times 2 \times \overset{(1/2)}{\ln} = -5763 \text{ J}$$

or $$G' + 5000 = 1 \times 5000 - 5763 \text{ J}$$

and hence $$G' = -5763 \text{ J}$$

and so $$\Delta G' = G' - (G_A^\circ + G_B^\circ) = -5763 \text{ J}$$

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

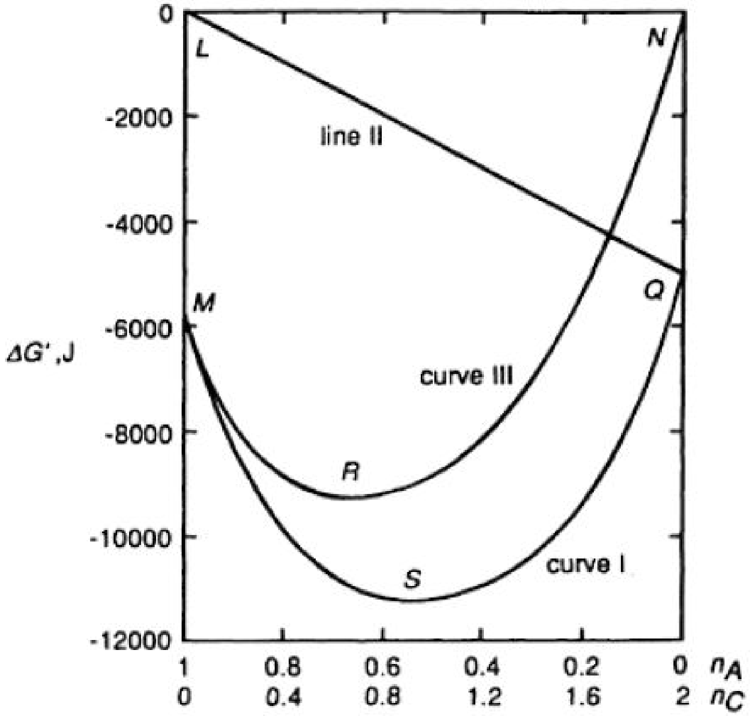

Figure 11.1 The variations of the contributions to the decrease in the Gibbs free energy due to chemical reaction (line II), the contribution to the decrease in the Gibbs free energy due to gas mixing (curve III) with the extent of the reaction $A_{(g)}+B_{(g)}=_{2C(g)}$ for which $\Delta G^\circ = -5000$ joules at 500 K.

Curve I : the sum of line II (the first term of Eq. (11.3)
↔Decrease in G due to chemical reaction

Curve III : (the second term on the right-hand side of Eq. (11.3)—the decrease in G due to gas mixing).

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

- The position of the minimum in curve I is fixed by the criterion that, at the minimum

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

$$2G_C^\circ - G_A^\circ - G_B^\circ = -RT \ln \frac{p_C^2}{p_A p_B}$$

$$\Delta G^\circ = -RT \ln \left(\frac{p_C^2}{p_A p_B} \right) \qquad (11.6)$$

From the Gibbs-Duhem equation, Eq. (9.19),

$$n_A d\overline{G}_A + n_B d\overline{G}_B + n_C d\overline{G}_C = 0.$$

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

As ΔG° = f(T), thus K_p = f(T). For the example used in Fig. 11.1,

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = \frac{5000}{8.3144 \times 500} = 1.203$$

Therefore

$$K_p = 3.329$$

Now

$$K_p = \frac{p_C^2}{p_A p_B} = \frac{X_C^2 P^2}{X_A P X_B P} = \frac{X_C^2}{X_A X_B} = \frac{(1 - n_A)^2}{n_A^2/4} = 3.329$$

and hence

$$n_A = 0.523 \quad \text{(the other solution, } n_A = 11.4\text{, is nonphysical)}$$

i.e., reaction equilibrium occurs with n_A=n_B=0.523 and n_C=0.954.

11.2 REACTION EQUILIBRIUM IN A GAS MIXTURE AND THE EQUILIBRIUM CONSTANT

- If ΔG° =0, no chemical reaction contribution to $\Delta G'$, and $\Delta G'$ with n_A varies according to curve III the criterion for reaction equilibrium would be maximization of the randomness of the system, at the composition R. From Eq. (11.8), if ΔG°=0, then K_p=1, and thus

$$1 = \frac{4(1-n_A)^2}{n_A^2} \quad \text{and} \quad n_A = \frac{2}{3}$$

- It is important to note that the minimum in curve I in Fig. 11.1, in representing the equilibrium state of the system at P=1 atm and 500 K, is the only point on curve I which has any significance within the scope of classical thermodynamics. The point S is the only state on the curve I which lies on the equilibrium surface in P-T-composition space for the fixed values of P=1 atm and T=500 K. Any change in P and/or T moves the equilibrium composition over the equilibrium surface in P-T-composition space.

11.3 THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

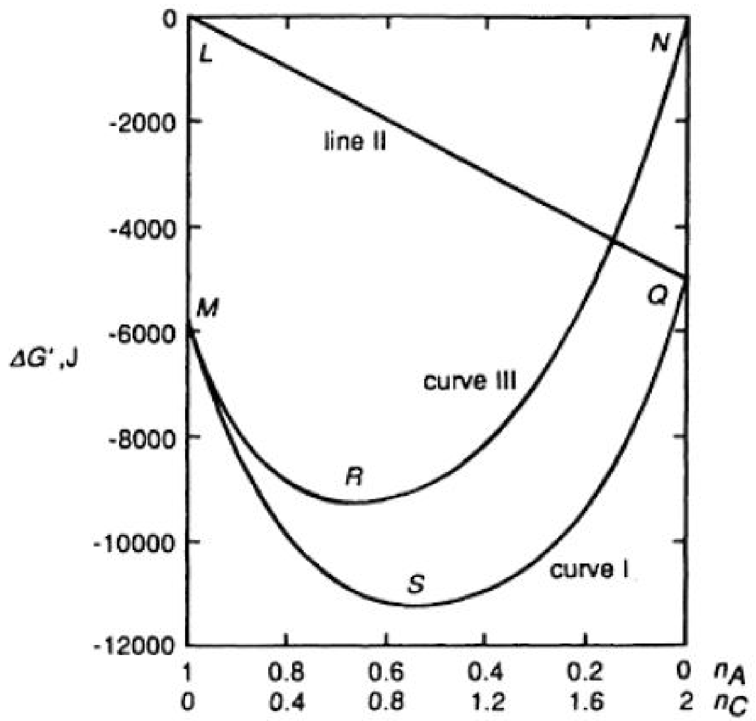

Figure 11.1 The variations of the contributions to the decrease in the Gibbs free energy due to chemical reaction (line II), the contribution to the decrease in the Gibbs free energy due to gas mixing (curve III) with the extent of the reaction $A_{(g)}+B_{(g)}=2C_{(g)}$ for which $\Delta G^\circ = -5000$ joules at 500 K.

- The position of the minimum in curve I : determined by the difference between the lengths of *LM* and *NQ*.

- The effect of T on the comp. for the minimum in curve I (and hence on the value of K_p) depends on the relative effects of T on the lengths of *LM* and *NQ*.

- For given reactants, the length of *LM* increases linearly with T, and the variation of the length *NQ* with T is determined by the sign and magnitude of ΔS° for the reaction according to

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_P = -\Delta S^\circ$$

11.3 THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

- The variation of K_p with T is from the Gibbs-Helmholtz equation, Eq. (5.37a),

- the effect of T on K_p : determined by the sign and magnitude of ΔH° for the reaction.

- If $\Delta H^\circ > 0$, i.e., endothermic, then K_p increases with increasing T,
  If $\Delta H^\circ < 0$, i.e., exothermic, then K_p decreases with increasing T.

11.3 THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

- For

$$\mathbf{Cl_2{=}2Cl}$$

- $\Delta H^\circ > 0$, i.e., endothermic,
  $K_p = p_{Cl}^2 / p_{Cl_2}$, increases with more heat (high T)
  i.e., the equilibrium shifts in that direction which involves the absorption of heat.

- For

$$\mathbf{2Cl{=}Cl_2}$$

- $\Delta H^\circ < 0$, $K_p = p_{Cl}^2 / p_{Cl_2}$ decreases with increasing T,
  i.e., the equilibrium shifts in that direction which involves the absorption of heat.

In both cases an increase in T increases p_{Cl} and decreases p_{Cl_2}.

- For $\Delta H^\circ \neq f(T)$, then ln K_p varies linearly with 1/T.

11.4 THE EFFECT OF PRESSURE ON THE EQUILIBRIUM CONSTANT

- Kp ≠ f(P_{total}), as defined by Eq. (11.7)

- Example $Cl_2 = 2Cl$

- If P increased, $2Cl \rightarrow Cl_2$, if P decreased, $Cl_2 \rightarrow 2Cl$

11.4 THE EFFECT OF PRESSURE ON THE EQUILIBRIUM CONSTANT

$$K_p = \frac{p_{\mathrm{Cl}}^2}{p_{\mathrm{Cl}_2}} \quad \text{which is independent of pressure}$$

11.4 THE EFFECT OF PRESSURE ON THE EQUILIBRIUM CONSTANT

- The magnitude of the effect of a change in pressure on the value of K_x depends on the magnitude of the change in the number of moles present in the system, occurring as a result of the chemical reaction.
- For the general reaction

$$aA + bB = cC + dD \qquad K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{X_C^c X_D^d}{X_A^a X_B^b} \frac{P^c P^d}{P^a P^b} = K_x P^{(c+d-a-b)}$$

- which shows that K_x is independent of the total pressure only if c+d-a-b=0.

Example: A + B = 2C, no change in the # of moles before and after reaction.

11.4 THE EFFECT OF PRESSURE ON THE EQUILIBRIUM CONSTANT

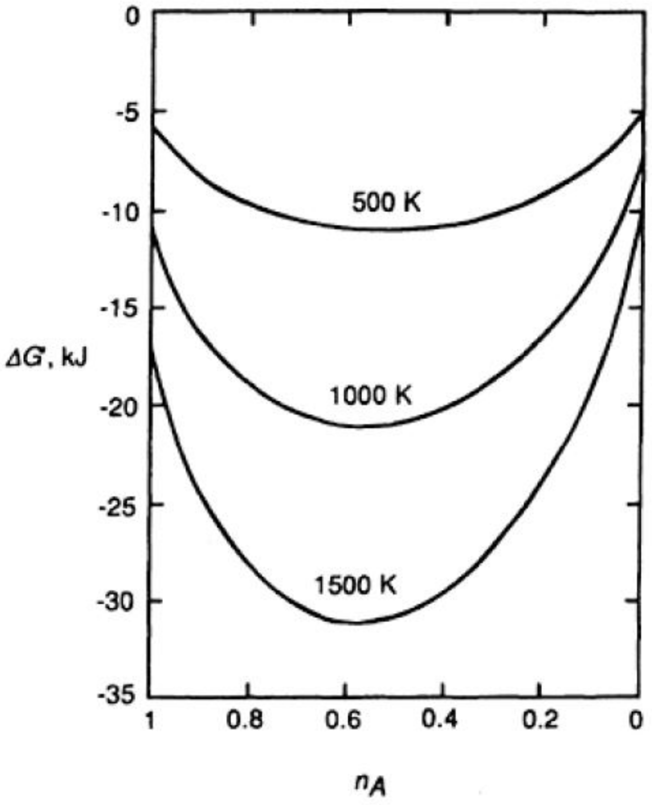

Figure 11.3 The effect of temperature on the equilibrium state of the reaction $A_{(g)}+B_{(g)}=2C_{(g)}$ for which $\Delta G°=-2500-5T$ joules.

11.5 REACTION EQUILIBRIUM AS A COMPROMISE BETWEEN ENTHALPY AND ENTROPY

- The Gibbs free energy of a system is defined as

$$G=H-TS$$

- Low values of G are obtained with low H and large S.

  equilibrium occurs as the result of a compromise between H and S.

  Similar discussions ~ concerning chemical reaction equilibria.

- The reaction Cl_2=2Cl is with $\Delta H^{\circ}>0$ (ΔH° is the thermal energy required to break Avogadro's number of Cl–Cl bonds) and has a positive value of $\Delta S^{\circ} > 0$ (2 moles of chlorine atoms are produced from 1 mole of chlorine molecules).

- This compromise between the enthalpy and the entropy is analogous to the compromise between the contributions of the chemical reaction and the mixing of gases to the decrease in $\Delta G'$ shown in Fig. 11.1.

11.5 REACTION EQUILIBRIUM AS A COMPROMISE BETWEEN ENTHALPY AND ENTROPY

- For the reaction A+B=2C, Eq. (11.3) can be written as

$$\begin{aligned} G' - 2G^{\circ}_{C} &= n_A(-\Delta H^{\circ}) + n_A(T\Delta S^{\circ}) + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right) + (1 - n_A)\ln(1 - n_A)\right] \\ &= [n_A(-\Delta H^{\circ})] + T\left\{n_A\Delta S^{\circ} + 2R\left[n_A \ln\left(\frac{n_A}{2}\right) + (1 - n_A)\ln(1 - n_A\right]\right\} \end{aligned} \quad (11.11)$$

- The term in the first brackets = H contribution to the change in the Gibbs free energy,

  and the second term on the right-hand side = S contribution, with $n_A\Delta S^{\circ}$ being the entropy change caused by the chemical reaction and $2R[n_A ln\left(\frac{n_A}{2}\right) + (1 - n_A)\ln(1 - n_A)]$ being the entropy change caused by gas mixing.

- In the previous example ΔG°equaled -5000 joules at 500 K. Let it be that $\Delta \mathrm{H}^{\circ}$=-2500 joules and ΔS°=5 J/K, in which case Fig. 11.2 can be drawn from Fig. 11.1.

11.5 REACTION EQUILIBRIUM AS A COMPROMISE BETWEEN ENTHALPY AND ENTROPY

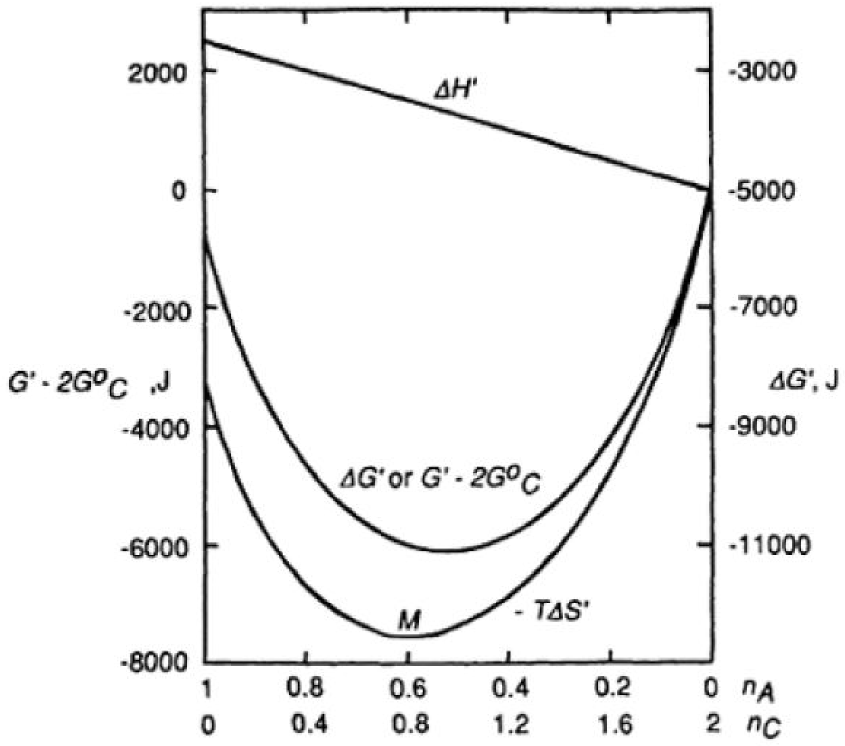

Figure 11.2 The variations at 500 K of AH', $-T\Delta S'$, and $\Delta G'$ with the extent of reaction $A(g)+B(g)=2C(g)$ for which $\Delta G^{\circ}=-2500-5T$.

the Δ H' line : the first term on the right-hand side of Eq. (11.11) and the $\mathrm{T}\Delta S'$line is the second term.

The sum of these two gives $\mathrm{G}' - 2\mathrm{G}^{\circ}_{\mathrm{C}}$.T
The scale on the right-hand edge : $\Delta\mathrm{G}'$ where the reference zero of Gibbs free energy is chosen $\mathrm{G}^{\circ}_{\mathrm{A}} + \mathrm{G}^{\circ}_{\mathrm{B}} = 0$ such that $\mathrm{G}' = \mathrm{G}'$(i.e., the joules).

On this scale the G' curve in Fig. 11.2 is identical with curve I in Fig. 11.1.

The minimum in the $\Delta G'$: determined as the compromise between the min. value of H' at n_A =0 and the max. value of $\mathrm{T}\Delta S'$ at n_A=0.597 (the point M in Fig. 11.2).

11.5 REACTION EQUILIBRIUM AS A COMPROMISE BETWEEN ENTHALPY AND ENTROPY

- If the temperature is increased then the $\mathrm{T}\Delta S'$ term becomes relatively more important, and, hence, the equilibrium value of n_A increases (the minimum in the $\Delta \mathrm{G}'$ curve shifts to the left). Thus, K_p decreases with increasing temperature in accordance with Eq. (11.9) ($\Delta \mathrm{H}^{\circ}$ is negative).
- The effect of temperature on the $\Delta \mathrm{G}'$ curve is illustrated in Fig. 11.3, in which curves are drawn for the reaction A+B=2C at 500, 1000, and 1500 K. It is assumed that $\Delta \mathrm{C_p}$ for the reaction is zero, in which case $\Delta \mathrm{H}^{\circ}$ and ΔS° are independent of temperature. As $\Delta \mathrm{G}^{\circ} = \Delta \mathrm{H}^{\circ} - \mathrm{T}\Delta S^{\circ}$, then

$$\Delta G^{\circ}_{500} = -2500 - (500 \times 5) = -5000 \text{ J} \qquad K_{p,500} = 3.329$$
$$\Delta G^{\circ}_{1000} = -2500 - (1000 \times 5) = -7500 \text{ J} \qquad K_{p,1000} = 2.465$$
$$\Delta G^{\circ}_{1500} = -2500 - (1500 \times 5) = -10{,}000 \text{ J} \qquad K_{p,1500} = 2.229$$

- The equilibrium values of nA at 500, 1000, and 1500 K are thus, respectively, 0.523, 0.560, and 0.572.
- Although K_p is constant at constant temperature, note that an infinite set of partial pressures of reactants and products correspond to the fixed value of K_p If the reaction involves three species, then arbitrary choice of the partial pressures of two of the species uniquely fixes the equilibrium partial pressure of the third.