Important Questions On Chemical Equilibrium

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1. Calculate K_c for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ for which $K_p = 3.5 \times 10^{-23}$ atm at 27°C.
A. 1.42×10^{-24}
B. 1.42×10^{-28}
C. 1.42×10^{-30}
D. 1.42×10^{-39}

2. At 30°C, K_p for the dissociation reaction, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is 2.9×10^{-2} atm. If the total pressure is 1 atm, then calculate the degree of dissociation of SO_2Cl_2 (Assume $\alpha << 1$).
A. 0.29
B. 0.17
C. 0.32
D. 0.56

3. For a homogeneous gaseous reaction, $AB_2(g) \rightleftharpoons A(g) + 2B(g)$

The volume is 10 L and temperature is 300 K. Initially, the flask contains 0.4 mole of AB_2. The total pressure of the reaction mixture, after the attainment of equilibrium, is 1.2 atm. Calculate K_p.
A. 5.607×10^{-3}
B. 4.308×10^{-3}
C. 5.607×10^{-4}
D. 4.308×10^{-44}

4. Consider the homogeneous gaseous reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ carried out in a vessel at a temperature T. When 1 mole of H_2 and 3 moles of I_2 are mixed, a certain amount of HI will be formed. When 2 additional moles of H_2 are introduced, the amount of HI formed becomes doubled the earlier amount. What is the value of K_p?
A. 6
B. 2
C. 4
D. 10

5. At 25°C, for the reaction $Br_2(l) + Cl_2(g) \rightleftharpoons 2BrCl(g)$, $K_p = 2.032$. At the same temperature, the vapour pressure of $Br_2(l)$ is 0.281 atm. Pure BrCl(g) was introduced into a closed container with adjustable volume. The total pressure was kept at 1 atm and the temperature at 25°C. Calculate the fraction of BrCl originally present that has been converted into Br_2 and Cl_2 at equilibrium assuming that the gaseous species behave ideally.
A. 0.256
B. 0.357
C. 0.687
D. 0.456

6. For the reaction,

$H_2(g) + S(g) \rightleftharpoons H_2S(g)$
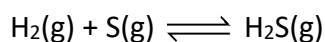
The equilibrium constant K_p is 20.2 atm^{-1} at 945°C and 9.1 atm^{-1} at 1.065°C. Calculate ΔH°.
A. -88.126 kJ/mol
B. +88.126 kJ/mol
C. -48.923 kJ/mol
D. +48.923 kJ/mol

7. The following data were obtained for the temperature-dependence of the equilibrium constant of an inhibitor binding an enzyme. Determine the value of ΔG° (in kJ/mol) for this process at 25°C.
T(°C) 16.0 21.1 25.0 31.9 37.5
K_c 7.25 5.25 4.17 2.66 2.01(× 10^7)
A. -23.5
B. +23.5
C. -43.5
D. +43.5

8. Calculate the equilibrium pressure at which graphite gets converted to diamond at 25°C, given that the densities of graphite and diamond are, respectively, 2.25 and 3.51 g cm^{-3} and are independent of pressure. ΔG°$_f$ values for graphite and diamond are zero and 2.90 kJ mol^{-1}, respectively.
A. 32000 atm
B. 25000 atm
C. 18000 atm
D. None of the above

9. Calculate the partial pressure of HCl gas above a sample of $NH_4Cl(s)$ because of its decomposition according to the reaction $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$. ΔG°$_f$ values of $NH_4Cl(s)$, $NH_3(g)$ and $HCl(g)$ are − 202.96 kJ mol^{-1}. −16.48 kJ mol^{-1} and −95.30 kJ mol^{-1}. respectively.
A. 1.02×10^{-6}
B. 2.02×10^{-8}
C. 2.02×10^{-6}
D. 1.02×10^{-8}

10. At 450°C and 600 atm pressure, the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 4.516 × 10^{-5}. Calculate the degree of the conversion of N_2 and H_2 to NH_3 assuming that the system is a mixture of real gases. Fugacity coefficients are $\gamma_{N_2} = 1.3238$, H_2 = 1.2874 and $\gamma_{NH_3} = 0.8548$.
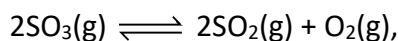A. 0.56
B. 0.43
C. 0.68
D. 0.24

ANSWER KEY

1. A	2. B	3. A	4. C	5. B	6. A
7. C	8. B	9. D	10. B		

SOLUTIONS

Solution 1. For the reaction,

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$,

$\Delta n = 2 + 1 - 1 = 1$

$\therefore K_c = \dfrac{K_p}{(RT)^{\Delta n}} = \dfrac{3.5 \times 10^{-23}}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K})} = 1.42 \times 10^{-24} \text{ mol dm}^{-3}$

Solution 2. For the given equilibrium,

$K_p = \alpha^2 P/(1 - \alpha^2)$

In the present case, $K_p = 2.9 \times 10^{-2}$ atm ; P = 1 atm

$\therefore 2.9 \times 10^{-2}$ atm $= \alpha^2 (1 \text{ atm})/(1 - \alpha^2)$.

Since, K_p in this case is very small, α would also be very small so that $\alpha^2 \ll 1$ and can be neglected in the denominator giving $K_p = \alpha^2 P$

$\therefore$ Degree of dissociation at P = 1 atm, $\alpha = (K_p)^{1/2} = (2.9 \times 10^{-2})^{1/2} = 0.17$

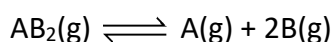Solution 3. $K_p = \dfrac{P_A P_B^2}{P_{AB_2}} = \dfrac{(x_A P)(x_B P)^2}{x_{AB_2} P} = \dfrac{x_A x_B^2 P^2}{x_{AB_2}}$

Here, $x_i x$ are the mole fractions and P is the total equilibrium pressure.

Since $x_i = n_i/n_{total}$,

$K_p = \dfrac{n_A n_B^2 P^2}{n_{AB_2} (n_{total})^2}$ ....(i)

Let y be the number of moles of A formed at equilibrium. Then,

$AB_2(g) \rightleftharpoons A(g) + 2B(g)$

0.40–y   y   2y

$n_{total} = (0.40 - y) + y + 2y = 0.40 + 2y$

Also, if the mixture behaves ideally, then,

$n_{total} = \dfrac{PV}{RT} = \dfrac{(1.20 \text{ atm}) (10 \text{ dm}^3)}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1})(300 \text{K})} = 0.487 \text{mole}$

$\therefore 0.487 = 0.40 + 2y$

y = 0.0435 mole

Hence, from Eq. (i),

$K_p = \dfrac{y(2y)^2 (1.20)^2}{(0.40 - y)(0.40 + 2y)^2} = 5.607 \times 10^{-3}$

Solution 4. Since the number of moles of reactants and products is the same, so,

$K_p = K_c = K_x$

Suppose in the first case, $n_{HI} = x$ so that $n_{H_2} = 1 - (x/2)$ and $n_{I_2} = 3 - (x/2)$

$\therefore K_p = x^2/(1 - x/2) (3 - x/2)$ ......(i)

In the second case, $n_{HI} = 2x$ so that $n_{H_2} = 3 - x$ and $n_{I_2} = 3 - x$
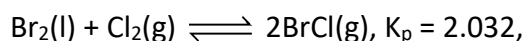
$K_p = (2x)^2/(3-x)^2$ ....(ii)

Hence, from equations (i) and (ii), $\dfrac{x^2}{\left(1-\dfrac{x}{2}\right)\left(3-\dfrac{x}{2}\right)} = \dfrac{(2x)^2}{(3-x)^2}$
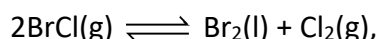
Neglecting x^2 in the denominator on both sides, cross-multiplying and simplifying,
x = 3/2. Hence, from Eq (i) or (ii),
$K_p = 4$.

Solution 5. Since for the reaction,

$Br_2(l) + Cl_2(g) \rightleftharpoons 2BrCl(g)$, $K_p = 2.032$,

Therefore, for the reverse reaction that is,

$2BrCl(g) \rightleftharpoons Br_2(l) + Cl_2(g)$,

$K_p = 1/K_p = 1/2.032 = 0.4921$

$p_{BrCl} + p_{Br_2} + p_{Cl_2} = 1\,atm$

$\therefore\ p_{BrCl} + p_{Cl_2} = 1\,atm - p_{Br_2} = (1-0.281)\,atm = 0.719\,atm$

Let n_0 be the number of moles of BrCl initially present and α be its degree of dissociation.
Then, at equilibrium,

$n_{BrCl} = n_0/(1-\alpha)$

$n_{Cl_2} = n_0 \times 1/2\,(\alpha)\ [\because BrCl \rightarrow ½Cl_2]$

$n_{BrCl} + n_{Cl_2} = n_0(1-\alpha/2)$

$\therefore\ p_{BrCl} = \left\{\dfrac{n_0(1-\alpha)}{n_0(1-\alpha/2)}\right\}(0.719\,atm)$

$p_{Cl_2} = \left\{\dfrac{1/2\alpha \times n_0}{n_0(1-\alpha/2)}\right\}(0.719\,atm)$

$K'_p = \dfrac{p_{Cl_2}}{(p_{BrCl})^2} = \dfrac{\alpha/2(1-\alpha/2)}{(1-\alpha)^2 \times 0.719} = 0.4921$

This gives the quadratic equation $0.604\,\alpha^2 - 1.208\alpha + 0.354 = 0$ whose solution yields α = 0.357.

Solution 6. According to the integrated Van't Hoff equation,

$\ln\left(\dfrac{K_{p2}}{K_{p1}}\right) = \dfrac{\Delta H^\circ}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

Or,

$\Delta H^\circ = R \ln\left(\dfrac{K_{p2}}{K_{p1}}\right)\left(\dfrac{T_1 T_2}{T_2 - T_1}\right) = (8.314\,J\,K^{-1}\,mol^{-1})\ln(9.21/20.2)\left[\dfrac{(1218\,K)(1338\,K)}{1338\,K - 1218\,K}\right]$

$= -88126.3\,J\,mol^{-1} = -88.126\,kJ\,mol^{-1}$

Solution 7. Let us rewrite the data in the following form:
T(K) 289 294.1 298 304.9 310.5
1/T×100 3.46 3.40 3.36 3.28 3.22
$K_c/10^7$ 7.25 5.25 4.17 2.66 2.01

ln K_c 18.10 17.78 17.55 17.10 16.81

A plot of ln K_c versus 1/T will give a straight line whose slope comes out to be 5.40×10^3.

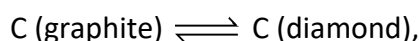At 25°C, $K_c = 4.17 \times 10^7$, hence,

$\Delta G° = - RT \ln K_c = -(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$ (298 K) ln 4.17×10^7

$= - 43.5 \text{ kJ mol}^{-1}$

Solution 8. This example is an application of the thermodynamic relation

$[\partial(\Delta G) / \partial P]_T = \Delta V$ ....(i)

For the reaction,

C (graphite) $\rightleftharpoons$ C (diamond),

$\Delta G° = \Delta G°_f(\text{diamond}) - \Delta G°_f(\text{graphite}) = 2.90 \text{ kJ} - 0 = 2.90 \text{ kJ mol}^{-1}$

$= (2.90 \text{ kJ mol}^{-1}) \times \dfrac{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})}{8.314 \times 10^{-3} \text{ kJ mol}^{-1}} = 28.6 \text{ dm}^3 \text{ atm mol}^{-1}$

The respective volumes of diamond and graphite are obtained from their densities, recalling that the atomic mass of carbon is 12 g mol^{-1}.

$\therefore \quad \Delta V = V_{\text{diamond}} - V_{\text{graphite}} = \dfrac{12g \text{ mol}^{-1}}{3.51 \times 10^3 \text{ g dm}^{-3}} - \dfrac{12g \text{ mol}^{-1}}{2.25 \times 10^3 \text{ g dm}^{-3}}$

$= 1.91 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$ ....(iii)

From Eq. (i),

d(ΔG) = ΔV/dP, which on integration gives

$\int_1^2 d(\Delta G) = \int_{P_1}^{P_2} \Delta V dp$

Let $P_1 = 1$ atm and $P_2 = P$ Then,

$\Delta G_2 - \Delta G_1 = \Delta V(P_2 - P_1) = \Delta V(P - 1)$

$0 - 28.6 \text{ dm}^3 \text{ atm mol}^{-1} = - 1.91 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} (P - 1)$

$P - 1 = \dfrac{28.6 \text{ dm}^3 \text{ atm mol}^{-1}}{1.91 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}} = 1.497 \times 10^4 \text{ atm}$

$\therefore$ The equilibrium pressure, P = $2.497 \times 10^4 \approx 25,000$ atm

Solution 9. For the given reaction,

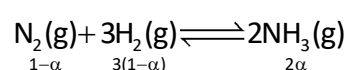$\Delta G° = [(-16.48) + (- 95.30) - (-95.30) - (-202.96)] = 91.18 \text{ kJ mol}^{-1}$

$\therefore K_p = \exp (-\Delta G°/RT)$

$= \exp [-91.18 \text{ kJ mol}^{-1}/(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$ (298 K) $= 1.04 \times 10^{-16}$

$K_p = p_{NH_3} \times p_{HCl} = p_{HCl}^2$

$\therefore p_{HCl} = K_p^{1/2} = 1.02 \times 10^{-8}$ atm

Solution 10. Let α be the degree of conversion. Then, at equilibrium,

$\underset{1-\alpha}{N_2(g)} + \underset{3(1-\alpha)}{3H_2(g)} \rightleftharpoons \underset{2\alpha}{2NH_3(g)}$

$K_{thermo} = \dfrac{(f_{NH_3})^2}{f_{N_2}(f_{H_2})^3} = \dfrac{(p_{NH_3})^2}{p_{N_2}(p_{H_2})^3} \times \dfrac{(\gamma_{NH_3})^2}{\gamma_{N_2}(\gamma_{H_2})^3} = K_p K_\gamma$

At equilibrium, the total number of moles,

$= (1 - \alpha) + 3(1 - \alpha) + 2\alpha = 2(2 - \alpha)$

$$\therefore \ p_{N_2} = \frac{(1-\alpha)P}{2(2-\alpha)}; \ p_{H_2} = \frac{3(1-\alpha)P}{2(2-\alpha)}; p_{NH_3} = \frac{2\alpha P}{2(2-\alpha)}$$

Here, P = 600 atm.

$$\therefore \ 4.516 \times 10^{-5} = \frac{4\alpha^2 (600)^2}{4(2-\alpha)^2} \times \frac{2(2-\alpha)}{(1-\alpha)600} \times \frac{8(2-\alpha)^3}{27(1-\alpha)^3 (600)^3} \times \frac{(0.8548)^2}{(1.3238)(1.2874)^3}$$

This equation, on rearranging, gives a quadratic equation in α which on solving gives two values of α viz, 1.56 and 0.43. The first value is not acceptable since the conversion to NH_3 cannot be more than 1 (i.e., more than 100%). Thus, α = 0.43, i.e., the degree of conversion of N_2 and H_2 to NH_3 is 0.43.