Chapter 6: Equilibrium

Exercises — Exercises

Q1 A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased. (a) What is the initial effect of the change on vapour pressure? (b) How do rates of evaporation and condensation change initially? (c) What happens when equilibrium is restored finally and what will be the final vapour pressure?

SOLUTION

Given: Liquid-vapour equilibrium in a sealed container at fixed temperature; volume suddenly increased.

(a) Initial effect on vapour pressure:
When volume increases suddenly, the same number of vapour molecules now occupy a larger space. The vapour pressure decreases immediately (instantaneously drops below the equilibrium value).

(b) Initial changes in rates:
Rate of evaporation: depends only on temperature and nature of liquid — it remains unchanged initially.
Rate of condensation: depends on the concentration (number density) of vapour molecules; since vapour molecules are now spread over a larger volume, their concentration falls and the rate of condensation decreases.
Result: rate of evaporation > rate of condensation, so net evaporation occurs.

(c) When equilibrium is restored:
More liquid evaporates until the vapour concentration (and hence condensation rate) rises back to equal the evaporation rate. At constant temperature, the vapour pressure at equilibrium is determined solely by temperature — it equals the original equilibrium vapour pressure.
Final vapour pressure = same as the original vapour pressure (temperature is unchanged).

Answer: (a) Vapour pressure decreases initially. (b) Rate of evaporation unchanged; rate of condensation decreases. (c) Equilibrium is re-established; final vapour pressure equals the original equilibrium vapour pressure.

Q2 What is Kc for the following equilibrium when the equilibrium concentration of each substance is: $[SO_2] = 0.60$ M, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M? $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

SOLUTION

Given: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
$[SO_2] = 0.60$ M, $[O_2] = 0.82$ M, $[SO_3] = 1.90$ M

Expression: $K_c = [SO_3]^2 / ([SO_2]^2 [O_2])$

$K_c = (1.90)^2 / ((0.60)^2 \times 0.82)$
$K_c = 3.61 / (0.36 \times 0.82)$
$K_c = 3.61 / 0.2952$
$K_c = 12.23$

Answer: $K_c = 12.23$

Q3 At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I atoms. $I_2(g) \rightleftharpoons 2I(g)$. Calculate Kp for the equilibrium.

SOLUTION

Given: Total pressure $P = 10^5$ Pa; I atoms = 40% by volume (i.e., 40% by mole), so I_2 = 60%.

Partial pressures:
$p(I) = 0.40 \times 10^5$ Pa $= 4.0 \times 10^4$ Pa
$p(I_2) = 0.60 \times 10^5$ Pa $= 6.0 \times 10^4$ Pa

$K_p = [p(I)]^2 / p(I_2)$
$K_p = (4.0 \times 10^4)^2 / (6.0 \times 10^4)$
$K_p = (16 \times 10^8) / (6.0 \times 10^4)$
$K_p = 2.67 \times 10^4$ Pa

Answer: $K_p = 2.67 \times 10^4$ Pa

Q4 Write the expression for the equilibrium constant, Kc for each of the following reactions: (i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ (ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$ (iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$ (iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$ (v) $I_2(s) + 5F_2 \rightleftharpoons 2IF_5$

SOLUTION

Rule: Pure solids and pure liquids are excluded from the Kc expression.

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
$Kc = [NO]^2 [Cl_2] / [NOCl]^2$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$
Both $Cu(NO_3)_2$ and CuO are pure solids; excluded.
$Kc = [NO_2]^4 [O_2]$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$
H_2O is the solvent (pure liquid); excluded.
$Kc = [CH_3COOH][C_2H_5OH] / [CH_3COOC_2H_5]$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$
$Fe(OH)_3$ is a pure solid; excluded.
$Kc = 1 / ([Fe^{3+}][OH^-]^3)$

(v) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(g)$
I_2 is a pure solid; excluded.
$Kc = [IF_5]^2 / [F_2]^5$

Answer: (i) $Kc = [NO]^2[Cl_2]/[NOCl]^2$; (ii) $Kc = [NO_2]^4[O_2]$; (iii) $Kc = [CH_3COOH][C_2H_5OH]/[CH_3COOC_2H_5]$; (iv) $Kc = 1/([Fe^{3+}][OH^-]^3)$; (v) $Kc = [IF_5]^2/[F_2]^5$

Q5 Find out the value of Kc for each of the following equilibria from the value of Kp: (i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; $Kp = 1.8 \times 10^{-2}$ at 500 K (ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; Kp = 167 at 1073 K

SOLUTION

Relation: Kp = Kc(RT)^(Δn), so Kc = Kp / (RT)^(Δn)
$R = 0.0821$ L·atm mol^{-1} K^{-1}

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
$\Delta n = (2 + 1) - 2 = 1$
$Kc = Kp / (RT)^1 = 1.8 \times 10^{-2} / (0.0821 \times 500)$
$Kc = 1.8 \times 10^{-2} / 41.05$

$Kc = 4.38 \times 10^{-4}$

(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
Only CO_2 is gaseous; $\Delta n = 1$
$Kc = Kp / (RT)^1 = 167 / (0.0821 \times 1073)$
$Kc = 167 / 88.09$
$Kc = 1.90$

Answer: (i) $Kc = 4.38 \times 10^{-4}$; (ii) $Kc = 1.90$

Q6 For the following equilibrium, $Kc = 6.3 \times 10^{14}$ at 1000 K: $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g)$. Both forward and reverse reactions are elementary bimolecular reactions. What is Kc for the reverse reaction?

SOLUTION

For a reversible reaction, Kc(reverse) = 1 / Kc(forward).

$Kc(forward) = 6.3 \times 10^{14}$

$Kc(reverse) = 1 / (6.3 \times 10^{14})$
$Kc(reverse) = 1.59 \times 10^{-15}$

Answer: $Kc(reverse) = 1.59 \times 10^{-15}$

Q7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression.

SOLUTION

The equilibrium constant expression uses molar concentrations (or partial pressures for gases).

For a pure solid or pure liquid, the 'concentration' is defined as mass per unit molar volume, which equals density/molar mass — a constant that depends only on temperature, not on the amount present in the reaction vessel.

Because this concentration is constant (at a fixed temperature), it is incorporated into the equilibrium constant itself rather than written as a separate variable term.

In mathematical terms: if a solid or liquid species M has constant concentration [M] = c (fixed), then including it just scales the constant by c^n, which is absorbed into Kc.

Therefore, activities of pure solids and pure liquids are taken as unity (1), and

they do not appear in the equilibrium constant expression.

Answer: Pure solids and liquids have fixed concentration (density/molar mass = constant at given T); their activity = 1 and they are incorporated into Kc, so they do not appear in the expression.

Q8 Reaction between N_2 and O_2 takes place as follows: $2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$. If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of the equilibrium mixture.

SOLUTION

Given: $n(N_2) = 0.482$ mol, $n(O_2) = 0.933$ mol, $V = 10$ L, $K_c = 2.0 \times 10^{-37}$

Initial concentrations:
$[N_2] = 0.482/10 = 0.0482$ M
$[O_2] = 0.933/10 = 0.0933$ M
$[N_2O] = 0$

Kc expression: $K_c = [N_2O]^2 / ([N_2]^2 [O_2])$

Since $K_c = 2.0 \times 10^{-37}$ is extremely small, the reaction proceeds barely to the right; $[N_2O]$ formed is negligible.
Approximation: $[N_2] \approx 0.0482$ M, $[O_2] \approx 0.0933$ M at equilibrium.

$[N_2O]^2 = K_c \times [N_2]^2 \times [O_2]$
$[N_2O]^2 = 2.0 \times 10^{-37} \times (0.0482)^2 \times 0.0933$
$[N_2O]^2 = 2.0 \times 10^{-37} \times 2.323 \times 10^{-3} \times 0.0933$
$[N_2O]^2 = 4.33 \times 10^{-41}$
$[N_2O] = 6.58 \times 10^{-21}$ M

Answer: $[N_2O] = 6.58 \times 10^{-21}$ M; $[N_2] \approx 0.0482$ M; $[O_2] \approx 0.0933$ M (virtually unchanged from initial)

Q9 Nitric oxide reacts with Br_2 and gives nitrosyl bromide: $2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$. When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br_2.

SOLUTION

Given: initial NO = 0.087 mol, initial Br_2 = 0.0437 mol, NOBr at equilibrium = 0.0518 mol

Stoichiometry: 2 mol NO consumed and 1 mol Br_2 consumed per 2 mol NOBr formed.

Change in NO = 0.0518 mol consumed (same stoichiometric ratio, 2:2)
Change in Br_2 = 0.0518/2 = 0.0259 mol consumed

Equilibrium amounts:
n(NO) = 0.087 - 0.0518 = 0.0352 mol
n(Br_2) = 0.0437 - 0.0259 = 0.0178 mol

Answer: n(NO) = 0.0352 mol; n(Br_2) = 0.0178 mol

Q10 At 450 K, Kp = 2.0×10^{10} bar for the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$. What is Kc at this temperature?

SOLUTION

Given: Kp = 2.0×10^{10} bar, T = 450 K
Relation: Kp = Kc(RT)^(Δn)

For $2SO_2 + O_2 \rightleftharpoons 2SO_3$: Δn = 2 - (2+1) = -1

Kp = Kc × (RT)^(-1)
Kc = Kp × RT

Using R = 0.0831 L·bar mol^{-1} K^{-1}:
Kc = $2.0 \times 10^{10} \times (0.0831 \times 450)$
Kc = $2.0 \times 10^{10} \times 37.40$
Kc = 7.48×10^{11}

Answer: Kc = 7.48×10^{11}

Q11 A sample of HI(g) is placed in a flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is Kp for the given equilibrium? $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

SOLUTION

Given: initial p(HI) = 0.2 atm; equilibrium p(HI) = 0.04 atm

Decrease in p(HI) = 0.2 - 0.04 = 0.16 atm
From stoichiometry: 2 mol HI → 1 mol H_2 + 1 mol I_2
$p(H_2)$ formed = 0.16/2 = 0.08 atm
$p(I_2)$ formed = 0.16/2 = 0.08 atm

$Kp = p(H_2) \times p(I_2) / [p(HI)]^2$
$Kp = (0.08 \times 0.08) / (0.04)^2$
$Kp = 6.4 \times 10^{-3} / 1.6 \times 10^{-3}$
$Kp = 4.0$

Answer: Kp = 4.0

Q12 A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. The equilibrium constant Kc for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

SOLUTION

Given: $n(N_2)$ = 1.57 mol, $n(H_2)$ = 1.92 mol, $n(NH_3)$ = 8.13 mol; V = 20 L; Kc = 1.7×10^2

Molar concentrations:
$[N_2] = 1.57/20 = 0.0785$ M
$[H_2] = 1.92/20 = 0.0960$ M
$[NH_3] = 8.13/20 = 0.4065$ M

Calculate reaction quotient Qc:
$Qc = [NH_3]^2 / ([N_2][H_2]^3)$
$Qc = (0.4065)^2 / (0.0785 \times (0.0960)^3)$
$Qc = 0.1652 / (0.0785 \times 8.847 \times 10^{-4})$
$Qc = 0.1652 / 6.945 \times 10^{-5}$
$Qc = 2.38 \times 10^3$

Compare Qc with Kc:

$Q_c = 2380 > K_c = 170$

Since $Q_c > K_c$, the reaction proceeds in the reverse (backward) direction to reach equilibrium.

Answer: $Q_c = 2.38 \times 10^3 > K_c = 1.7 \times 10^2$; the mixture is NOT at equilibrium; the net reaction proceeds in the reverse direction (decomposition of NH_3).

Q13 The equilibrium constant expression for a gas reaction is: $K_c = [NH_3]^4 [O_2]^5 / ([NO]^4 [H_2O]^6)$. Write the balanced chemical equation corresponding to this expression.

SOLUTION

In the Kc expression, products appear in the numerator and reactants in the denominator.

Numerator species (products): NH_3 with power 4, O_2 with power 5
Denominator species (reactants): NO with power 4, H_2O with power 6

Balanced equation:
$4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$

Verification: stoichiometric coefficients match the exponents in the Kc expression.

Answer: $4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$

Q14 One mole of H_2O and one mole of CO are taken in a 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO: $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$. Calculate the equilibrium constant for the reaction.

SOLUTION

Given: $n(H_2O) = 1$ mol, $n(CO) = 1$ mol, $V = 10$ L, 40% of H_2O reacts.

Initial concentrations: $[H_2O] = [CO] = 1/10 = 0.1$ M

Amount reacted: $x = 40\% \times 0.1 = 0.04$ M

Equilibrium concentrations:
$[H_2O] = 0.1 - 0.04 = 0.06$ M
$[CO] = 0.1 - 0.04 = 0.06$ M
$[H_2] = 0.04$ M
$[CO_2] = 0.04$ M

$K_c = [H_2][CO_2] / ([H_2O][CO])$

$Kc = (0.04 \times 0.04) / (0.06 \times 0.06)$
$Kc = 1.6 \times 10^{-3} / 3.6 \times 10^{-3}$
$Kc = 0.444$

Answer: $Kc = 0.444$

Q15 At 700 K, equilibrium constant Kc for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700 K, what are the concentrations of $H_2(g)$ and $I_2(g)$, assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700 K?

SOLUTION

Given: Kc = 54.8 for $H_2 + I_2 \rightleftharpoons 2HI$; $[HI]eq = 0.5$ mol/L; started with HI only.

Since we started with HI, the reverse reaction $2HI \rightleftharpoons H_2 + I_2$ occurs.
By symmetry, $[H_2]eq = [I_2]eq = \alpha$ (say).

Kc for $H_2 + I_2 \rightleftharpoons 2HI$ is 54.8,
so Kc for $2HI \rightleftharpoons H_2 + I_2$ is 1/54.8.

$Kc(reverse) = [H_2][I_2] / [HI]^2 = \alpha^2 / (0.5)^2 = 1/54.8$

$\alpha^2 = (0.5)^2 / 54.8 = 0.25 / 54.8 = 4.56 \times 10^{-3}$
$\alpha = 0.0676$ M

$[H_2] = [I_2] = 0.0676$ mol/L

Answer: $[H_2] = [I_2] = 0.0676$ mol/L

Q16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M? $2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$; Kc = 0.14

SOLUTION

Given: $2ICl \rightleftharpoons I_2 + Cl_2$; Kc = 0.14; initial [ICl] = 0.78 M

ICE table (concentrations in M):
ICl: 0.78 - 2x; I_2: x; Cl_2: x

$Kc = [I_2][Cl_2] / [ICl]^2 = x^2 / (0.78 - 2x)^2 = 0.14$

Taking square root of both sides:
$x / (0.78 - 2x) = \text{sqrt}(0.14) = 0.3742$

x = 0.3742(0.78 - 2x) = 0.2919 - 0.7484x
x(1 + 0.7484) = 0.2919
x = 0.2919 / 1.7484 = 0.1670 M

Equilibrium concentrations:
[ICl] = 0.78 - 2(0.1670) = 0.78 - 0.334 = 0.446 M
$[I_2] = [Cl_2] = 0.167$ M

Answer: [ICl] = 0.446 M; $[I_2] = [Cl_2] = 0.167$ M

Q17 Kp = 0.04 atm at 899 K for the equilibrium $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium?

SOLUTION

Given: $C_2H_6 \rightleftharpoons C_2H_4 + H_2$; Kp = 0.04 atm; initial $p(C_2H_6) = 4.0$ atm; T = 899 K

ICE in partial pressures (atm):
C_2H_6: 4.0 - x; C_2H_4: x; H_2: x

$Kp = p(C_2H_4) \times p(H_2) / p(C_2H_6) = x^2 / (4.0 - x) = 0.04$

$x^2 + 0.04x - 0.16 = 0$
x = [-0.04 + sqrt(0.0016 + 0.64)] / 2
x = [-0.04 + sqrt(0.6416)] / 2
x = [-0.04 + 0.8010] / 2
x = 0.7610 / 2 = 0.3805 atm

$p(C_2H_6)eq = 4.0 - 0.3805 = 3.6195$ atm

Convert to concentration using Kp = Kc(RT)^(Δn); Δn = 1:
$Kc = Kp / (RT) = 0.04 / (0.0821 \times 899) = 0.04 / 73.81 = 5.42 \times 10^{-4}$ mol/L

$[C_2H_6]eq = p(C_2H_6)eq / (RT) = 3.6195 / (0.0821 \times 899) = 3.6195 / 73.81$
$[C_2H_6]eq = 4.90 \times 10^{-2}$ mol/L

Answer: $[C_2H_6]eq = 4.90 \times 10^{-2}$ mol/L

Q18 Ethyl acetate is formed by the reaction: $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$. (i) Write the concentration ratio (reaction quotient) Qc. (ii) At 293 K, starting with 1.00 mol acetic acid and 0.18 mol ethanol, 0.171 mol ethyl acetate is found at equilibrium. Calculate Kc. (iii) Starting with 0.5 mol ethanol and 1.0 mol acetic acid at 293 K, 0.214 mol ethyl acetate is found after some time. Has equilibrium been reached?

SOLUTION

(i) Since water is not in excess (not a solvent), all species are included:
$Qc = [CH_3COOC_2H_5][H_2O] / ([CH_3COOH][C_2H_5OH])$

(ii) All species are liquids in the same vessel; volume cancels, so use moles directly.
Initial: $n(CH_3COOH) = 1.00$ mol, $n(C_2H_5OH) = 0.18$ mol, $n(CH_3COOC_2H_5) = 0$
At equilibrium: $n(\text{ester}) = 0.171$ mol $= n(H_2O)$
$n(CH_3COOH)eq = 1.00 - 0.171 = 0.829$ mol
$n(C_2H_5OH)eq = 0.18 - 0.171 = 0.009$ mol

$Kc = (0.171 \times 0.171) / (0.829 \times 0.009)$
$Kc = 0.02924 / 0.007461$
$Kc = 3.92$

(iii) Initial: $n(CH_3COOH) = 1.0$ mol, $n(C_2H_5OH) = 0.5$ mol
At the given time: $n(\text{ester}) = 0.214$ mol
$n(CH_3COOH) = 1.0 - 0.214 = 0.786$ mol
$n(C_2H_5OH) = 0.5 - 0.214 = 0.286$ mol
$n(H_2O) = 0.214$ mol

$Qc = (0.214 \times 0.214) / (0.786 \times 0.286) = 0.04580 / 0.2248 = 0.204$

$Qc = 0.204 < Kc = 3.92$
Equilibrium has NOT been reached; reaction will proceed forward.

Answer: (i) $Qc = [CH_3COOC_2H_5][H_2O]/([CH_3COOH][C_2H_5OH])$; (ii) $Kc = 3.92$; (iii) $Qc = 0.204 < Kc$, equilibrium not yet reached, forward reaction continues.

Q19 A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of Kc is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium? $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

SOLUTION

Given: $[PCl_5]eq = 0.5 \times 10^{-1} = 0.05$ mol/L; $Kc = 8.3 \times 10^{-3}$

Since the vessel was evacuated initially and only PCl_5 was added,
$[PCl_3]eq = [Cl_2]eq = x$ (by stoichiometry)

$Kc = [PCl_3][Cl_2] / [PCl_5] = x^2 / 0.05 = 8.3 \times 10^{-3}$

$x^2 = 8.3 \times 10^{-3} \times 0.05 = 4.15 \times 10^{-4}$
$x = \text{sqrt}(4.15 \times 10^{-4}) = 2.04 \times 10^{-2}$ mol/L

Answer: $[PCl_3] = [Cl_2] = 2.04 \times 10^{-2}$ mol/L

Q20 $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$; Kp = 0.265 atm at 1050 K. What are the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are pCO = 1.4 atm and pCO_2 = 0.80 atm?

SOLUTION

Given: Kp = 0.265; initial p(CO) = 1.4 atm, $p(CO_2)$ = 0.80 atm

Check direction: $Qp = p(CO_2)/p(CO) = 0.80/1.4 = 0.571 > Kp = 0.265$
Since Qp > Kp, reaction shifts in the reverse direction (more CO, less CO_2).

Let x = decrease in $p(CO_2)$ = increase in p(CO):
$p(CO_2)eq = 0.80 - x$; $p(CO)eq = 1.4 + x$

$Kp = (0.80 - x) / (1.4 + x) = 0.265$
$0.80 - x = 0.265(1.4 + x) = 0.371 + 0.265x$
$0.80 - 0.371 = x + 0.265x$
$0.429 = 1.265x$
$x = 0.339$ atm

$p(CO)eq = 1.4 + 0.339 = 1.739$ atm
$p(CO_2)eq = 0.80 - 0.339 = 0.461$ atm

Verification: $Kp = 0.461/1.739 = 0.265$ ✓

Answer: $p(CO)eq = 1.739$ atm; $p(CO_2)eq = 0.461$ atm

Q21 Equilibrium constant Kc for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 0.061. At a particular time, the composition is: 3.0 mol L^{-1} N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} NH_3. Is the reaction at equilibrium? If not, in which direction does it tend to proceed?

SOLUTION

Given: Kc = 0.061; $[N_2]$ = 3.0 M, $[H_2]$ = 2.0 M, $[NH_3]$ = 0.5 M

Calculate Qc:

$Qc = [NH_3]^2 / ([N_2][H_2]^3)$

$Qc = (0.5)^2 / (3.0 \times (2.0)^3)$

$Qc = 0.25 / (3.0 \times 8.0)$

$Qc = 0.25 / 24 = 0.0104$

Compare: Qc = 0.0104 < Kc = 0.061

Since Qc < Kc, the reaction will proceed in the forward direction (towards products) to reach equilibrium.

Answer: Qc = 0.0104 < Kc = 0.061; reaction is NOT at equilibrium and will proceed in the forward direction (formation of NH_3).

Q22 Bromine monochloride, BrCl decomposes into bromine and chlorine: $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$. Kc = 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3×10^{-3} mol L^{-1}, what is its molar concentration at equilibrium?

SOLUTION

Given: $2BrCl \rightleftharpoons Br_2 + Cl_2$; Kc = 32; initial $[BrCl] = 3.3 \times 10^{-3}$ M

ICE table:

$[BrCl]$: $3.3 \times 10^{-3} - 2x$; $[Br_2]$: x; $[Cl_2]$: x

$Kc = x^2 / (3.3 \times 10^{-3} - 2x)^2 = 32$

Taking square root: $x / (3.3 \times 10^{-3} - 2x) = \text{sqrt}(32) = 4\text{sqrt}(2) = 5.657$

$x = 5.657 \times (3.3 \times 10^{-3} - 2x)$

$x = 1.867 \times 10^{-2} - 11.314x$

$x(1 + 11.314) = 1.867 \times 10^{-2}$

$x = 1.867 \times 10^{-2} / 12.314 = 1.516 \times 10^{-3}$ M

$[BrCl]eq = 3.3 \times 10^{-3} - 2(1.516 \times 10^{-3})$

$[BrCl]eq = 3.3 \times 10^{-3} - 3.032 \times 10^{-3} = 2.68 \times 10^{-4}$ M

Answer: $[BrCl]eq = 2.68 \times 10^{-4}$ mol/L

Q23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass. $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$. Calculate Kc for this reaction at the above temperature.

SOLUTION

Given: T = 1127 K (already in Kelvin), P = 1 atm.
Mass% CO = 90.55%, mass% CO_2 = 9.45%

Taking 100 g of gas mixture:
mol CO = 90.55/28 = 3.234 mol
mol CO_2 = 9.45/44 = 0.2148 mol
total mol = 3.449 mol

Mole fractions:
x(CO) = 3.234/3.449 = 0.9377
x(CO_2) = 0.2148/3.449 = 0.0623

Partial pressures at P = 1 atm:
p(CO) = 0.9377 atm; p(CO_2) = 0.0623 atm

$K_p = [p(CO)]^2 / p(CO_2) = (0.9377)^2 / 0.0623 = 0.8793/0.0623 = 14.12$ atm

$\Delta n = 2 - 1 = 1$ (C is solid, not counted)
$K_p = K_c(RT)^1$; $K_c = K_p / RT$
$K_c = 14.12 / (0.0821 \times 1127) = 14.12 / 92.53 = 0.1526$ mol/L

Answer: Kc = 0.153 mol/L

Q24 Calculate (a) ΔG° and (b) the equilibrium constant for the formation of NO_2 from NO and O_2 at 298 K: $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$. Given: $\Delta fG^\circ(NO_2) = 52.0$ kJ/mol, $\Delta fG^\circ(NO) = 87.0$ kJ/mol, $\Delta fG^\circ(O_2) = 0$ kJ/mol.

SOLUTION

(a) ΔG° of reaction:
$\Delta G^\circ = \Delta fG^\circ(NO_2) - \Delta fG^\circ(NO) - \frac{1}{2}\Delta fG^\circ(O_2)$
$\Delta G^\circ = 52.0 - 87.0 - \frac{1}{2}(0)$
$\Delta G^\circ = -35.0$ kJ/mol

(b) Equilibrium constant K:
$\Delta G^\circ = -RT \ln K$
$\ln K = -\Delta G^\circ / RT = -(-35000 \text{ J/mol}) / (8.314 \times 298)$
$\ln K = 35000 / 2477.6 = 14.13$

$K = e^{14}.13 = 1.37 \times 10^6$

Answer: (a) ΔG° = -35.0 kJ/mol; (b) $K = 1.37 \times 10^6$

Q25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume? (a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ (c) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

SOLUTION

Le Chatelier's principle: decreasing pressure (increasing volume) shifts equilibrium towards the side with MORE moles of gas.

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
Gas moles: 1 on left, 2 on right ($\Delta n_{gas} = +1$).
Decrease in pressure → equilibrium shifts to the right (more gas moles).
Products PCl_3 and Cl_2 INCREASE.

(b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$
Gas moles: 1 on left (CO_2), 0 on right ($CaCO_3$ is solid).
Decrease in pressure → equilibrium shifts to the left (towards more gas).
Product $CaCO_3$ DECREASES.

(c) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
Gas moles: 4 H_2O on left, 4 H_2 on right ($\Delta n_{gas} = 0$).
No change in moles of gas — pressure change has NO effect.
Moles of products REMAIN THE SAME.

Answer: (a) Products increase; (b) Products decrease; (c) Products remain the same.

Q26 Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction. (i) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ (ii) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$ (iii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ (iv) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$ (v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (vi) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

SOLUTION

Pressure change affects equilibria only when $\Delta n_{gas} \neq 0$. Increasing pressure shifts equilibrium towards fewer moles of gas.

(i) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$: $\Delta n_{gas} = (1+1) - 1 = +1$
Affected. Pressure increase → backward direction (fewer gas moles).

(ii) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$: $\Delta n_{gas} = (1+2) - (1+2) = 0$
Not affected by pressure change.

(iii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$: $\Delta n_{gas} = 2 - 1 = +1$
Affected. Pressure increase → backward direction.

(iv) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$: $\Delta n_{gas} = 1 - (2+1) = -2$
Affected. Pressure increase → forward direction (fewer gas moles).

(v) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$: $\Delta n_{gas} = 1 - 0 = +1$
Affected. Pressure increase → backward direction.

(vi) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$: $\Delta n_{gas} = (4+6) - (4+5) = +1$
Affected. Pressure increase → backward direction.

Answer: Reactions (i), (iii), (iv), (v), (vi) are affected. (i) backward; (iii) backward; (iv) forward; (v) backward; (vi) backward. Reaction (ii) is not affected.

Q27 The equilibrium constant for $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ is 1.6×10^5 at 1024 K. Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

SOLUTION

Given: $K_p = 1.6 \times 10^5$ for $H_2 + Br_2 \rightleftharpoons 2HBr$; initial $p(HBr) = 10.0$ bar

Starting with HBr, the reverse reaction $2HBr \rightleftharpoons H_2 + Br_2$ occurs.
$K_p(\text{reverse}) = 1/K_p = 1/(1.6 \times 10^5) = 6.25 \times 10^{-6}$

ICE in partial pressures:
$p(HBr)$: $10.0 - 2x$; $p(H_2)$: x; $p(Br_2)$: x

$K_p(\text{reverse}) = x^2 / (10.0 - 2x)^2 = 6.25 \times 10^{-6}$

$x / (10.0 - 2x) = \sqrt{6.25 \times 10^{-6}} = 2.50 \times 10^{-3}$

$x = 2.50 \times 10^{-3} \times (10.0 - 2x)$
$x = 2.50 \times 10^{-2} - 5.0 \times 10^{-3}\, x$
$x(1 + 5.0 \times 10^{-3}) = 2.50 \times 10^{-2}$
$x = 2.50 \times 10^{-2} / 1.005 = 2.49 \times 10^{-2}$ bar

$p(H_2) = p(Br_2) = 2.49 \times 10^{-2}$ bar
$p(HBr) = 10.0 - 2(2.49 \times 10^{-2}) = 10.0 - 0.0498 = 9.95$ bar

Answer: $p(HBr) = 9.95$ bar; $p(H_2) = p(Br_2) = 2.49 \times 10^{-2}$ bar

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Q28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam in the endothermic reaction: $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$. (a) Write an expression for Kp for the above reaction. (b) How will the values of Kp and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

SOLUTION

(a) Kp expression:
$K_p = [p(CO) \times p(H_2)^3] / [p(CH_4) \times p(H_2O)]$

(b) Effects:

(i) Increasing pressure:
Kp depends only on temperature — it does NOT change.
$\Delta n_{gas} = (1+3) - (1+1) = +2$. Pressure increase shifts equilibrium backward (fewer moles of gas).
Composition shifts: less CO and H_2 formed; more CH_4 and H_2O remain.

(ii) Increasing temperature:
The reaction is endothermic ($\Delta H > 0$). Increasing temperature shifts equilibrium forward (Le Chatelier).
Kp increases with temperature.
Composition shifts towards more CO and H_2.

(iii) Using a catalyst:
A catalyst increases the rate of both forward and reverse reactions equally.
Kp is NOT affected (thermodynamic quantity).
Equilibrium composition does NOT change; equilibrium is reached faster.

Answer: (a) Kp = $p(CO)\cdot p(H_2)^3/[p(CH_4)\cdot p(H_2O)]$. (b)(i) Kp unchanged; equilibrium shifts backward. (ii) Kp increases; equilibrium shifts forward (more H_2). (iii) Kp and composition unchanged; equilibrium reached faster.

Q29 Describe the effect of: (a) addition of H_2 (b) addition of CH_3OH (c) removal of CO (d) removal of CH_3OH on the equilibrium: $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

SOLUTION

Equilibrium: $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(a) Addition of H_2:
Increases $[H_2]$; Qc decreases below Kc.
Equilibrium shifts forward → more CH_3OH produced.

(b) Addition of CH_3OH:
Increases $[CH_3OH]$; Qc increases above Kc.
Equilibrium shifts backward → more H_2 and CO produced.

(c) Removal of CO:
$Qc = [CH_3OH]/([H_2]^2[CO])$. Removing CO decreases [CO] → denominator decreases → Qc increases above Kc → equilibrium shifts backward → less CH_3OH.

(d) Removal of CH_3OH:
Decreases $[CH_3OH]$; Qc decreases below Kc.
Equilibrium shifts forward → more CH_3OH produced.

Answer: (a) Addition of H_2: forward shift, more CH_3OH. (b) Addition of CH_3OH: backward shift, more H_2 and CO. (c) Removal of CO: backward shift, CH_3OH decreases. (d) Removal of CH_3OH: forward shift, more CH_3OH produced.

Q30 At 473 K, Kc for decomposition of PCl_5 is 8.3×10^{-3}. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $\Delta rH^\circ = 124.0$ kJ mol^{-1}. (a) Write expression for Kc. (b) What is the value of Kc for the reverse reaction at the same temperature? (c) What would be the effect on Kc if (i) more PCl_5 is added (ii) pressure is increased (iii) the temperature is increased?

SOLUTION

(a) $Kc = [PCl_3][Cl_2] / [PCl_5]$

(b) Kc for reverse reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$:

$Kc(reverse) = 1/Kc = 1/(8.3 \times 10^{-3}) = 120.5$

(c) Effects on Kc:
Kc depends only on temperature, not on concentration or pressure changes.

(i) Adding more PCl_5:
Kc does NOT change; it is a constant at fixed temperature.
Adding PCl_5 shifts equilibrium forward (more PCl_3 and Cl_2 formed) but Kc is unchanged.

(ii) Increasing pressure:
Kc does NOT change. Pressure affects the position of equilibrium (shifts backward) but not Kc.

(iii) Increasing temperature:
Reaction is endothermic ($\Delta rH^\circ = +124.0$ kJ/mol). Increasing temperature shifts equilibrium forward.
Kc increases with increasing temperature.

Answer: (a) $Kc = [PCl_3][Cl_2]/[PCl_5]$; (b) $Kc(reverse) = 120.5$; (c)(i) Kc unchanged; (ii) Kc unchanged; (iii) Kc increases.

Q31 In the water gas shift reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$, a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $pCO = pH_2O = 4.0$ bar. What will be the partial pressure of H_2 at equilibrium? Kp = 10.1 at 400°C.

SOLUTION

Given: $CO + H_2O \rightleftharpoons CO_2 + H_2$; Kp = 10.1; initial $p(CO) = p(H_2O) = 4.0$ bar

ICE in partial pressures (bar):
CO: 4.0 - x; H_2O: 4.0 - x; CO_2: x; H_2: x

$Kp = (x \times x) / ((4.0 - x)(4.0 - x)) = x^2/(4.0 - x)^2 = 10.1$

$x / (4.0 - x) = \sqrt{10.1} = 3.178$
$x = 3.178(4.0 - x) = 12.712 - 3.178x$
$x(1 + 3.178) = 12.712$
$x = 12.712 / 4.178 = 3.043$ bar

$p(H_2) = 3.043$ bar

Answer: $p(H_2)$ at equilibrium = 3.04 bar

Q32 Predict which of the following reactions will have appreciable concentration of reactants and products: (a) $Cl_2(g) \rightleftharpoons 2Cl(g)$; $K_c = 5 \times 10^{-39}$ (b) $Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g)$; $K_c = 3.7 \times 10^{8}$ (c) $Cl_2(g) + 2NO_2(g) \rightleftharpoons 2NO_2Cl(g)$; $K_c = 1.8$

SOLUTION

A reaction has appreciable concentrations of both reactants and products when Kc is neither very large nor very small — roughly $10^{-3} < K_c < 10^{3}$.

(a) $K_c = 5 \times 10^{-39}$: extremely small → equilibrium lies far to the left; essentially only Cl_2 present, virtually no Cl atoms. NOT appreciable on both sides.

(b) $K_c = 3.7 \times 10^{8}$: very large → equilibrium lies far to the right; essentially only NOCl present, very little Cl_2 and NO. NOT appreciable on both sides.

(c) $K_c = 1.8$: close to 1 → both reactants and products are present in comparable amounts.

Reaction (c) will have APPRECIABLE concentrations of reactants and products.

Answer: Only reaction (c) ($K_c = 1.8$) has appreciable concentrations of both reactants and products.

Q33 The value of Kc for the reaction $3O_2(g) \rightleftharpoons 2O_3(g)$ is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} M, what is the concentration of O_3?

SOLUTION

Given: $3O_2 \rightleftharpoons 2O_3$; $K_c = 2.0 \times 10^{-50}$; $[O_2] = 1.6 \times 10^{-2}$ M

$K_c = [O_3]^2 / [O_2]^3$

$[O_3]^2 = K_c \times [O_2]^3$

$[O_3]^2 = 2.0 \times 10^{-50} \times (1.6 \times 10^{-2})^3$

$[O_3]^2 = 2.0 \times 10^{-50} \times 4.096 \times 10^{-6}$

$[O_3]^2 = 8.192 \times 10^{-56}$

$[O_3] = \text{sqrt}(8.192 \times 10^{-56}) = 2.86 \times 10^{-28}$ M

Answer: $[O_3] = 2.86 \times 10^{-28}$ M

Q34 The reaction $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ is at equilibrium at 1300 K in a 1 L flask containing 0.30 mol CO, 0.10 mol H_2, 0.02 mol H_2O and an unknown amount of CH_4. Determine the concentration of CH_4. Kc = 3.90.

SOLUTION

Given: V = 1 L; $[CO] = 0.30$ M, $[H_2] = 0.10$ M, $[H_2O] = 0.02$ M; Kc = 3.90

$Kc = [CH_4][H_2O] / ([CO][H_2]^3)$
$[CH_4] = Kc \times [CO] \times [H_2]^3 / [H_2O]$
$[CH_4] = 3.90 \times 0.30 \times (0.10)^3 / 0.02$
$[CH_4] = 3.90 \times 0.30 \times 1.0 \times 10^{-3} / 0.02$
$[CH_4] = 3.90 \times 0.30 \times 0.05$
$[CH_4] = 3.90 \times 0.015$
$[CH_4] = 0.0585$ mol/L

Answer: $[CH_4] = 0.0585$ mol/L

Q35 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2, CN^-, $HClO_4$, F^-, OH^-, CO_3^{2-}, and S^{2-}.

SOLUTION

A conjugate acid-base pair consists of two species that differ by exactly one proton (H^+):
Acid (proton donor) $\rightleftharpoons$ Conjugate base + H^+ (conjugate base has one fewer H^+)
Base (proton acceptor) + $H^+ \rightleftharpoons$ Conjugate acid (conjugate acid has one more H^+)

HNO_2 (acid): loses $H^+ \rightarrow$ conjugate base = NO_2^-

CN^- (base): gains $H^+ \rightarrow$ conjugate acid = HCN

$HClO_4$ (acid): loses $H^+ \rightarrow$ conjugate base = ClO_4^-

F^- (base): gains $H^+ \rightarrow$ conjugate acid = HF

OH^- (amphoteric):
As acid: loses $H^+ \rightarrow$ conjugate base = O^{2-}
As base: gains $H^+ \rightarrow$ conjugate acid = H_2O

CO_3^{2-} (base): gains $H^+ \rightarrow$ conjugate acid = HCO_3^-

S^{2-} (base): gains $H^+ \rightarrow$ conjugate acid = HS^-

Answer: HNO_2 → conj. base NO_2^-; CN^- → conj. acid HCN; $HClO_4$ → conj. base ClO_4^-; F^- → conj. acid HF; OH^- → conj. base O^{2-} (or conj. acid H_2O); CO_3^{2-} → conj. acid HCO_3^-; S^{2-} → conj. acid HS^-.

Q36 Which of the followings are Lewis acids? H_2O, BF_3, H^+, and NH_4^+.

SOLUTION

A Lewis acid is an electron-pair acceptor.

H_2O: has lone pairs, acts as Lewis BASE (electron-pair donor). NOT a Lewis acid.

BF_3: boron has an incomplete octet (only 6 electrons); it accepts an electron pair. BF_3 is a Lewis ACID.

H^+: a bare proton with no electrons; readily accepts an electron pair from a base. H^+ is a Lewis ACID.

NH_4^+: nitrogen in NH_4^+ has no empty orbital and no lone pair available — all four bonds are to H. It cannot directly accept an electron pair. NH_4^+ is a Bronsted acid (H^+ donor) but NOT a Lewis acid by the standard definition.

BF_3 and H^+ are Lewis acids.

Answer: BF_3 and H^+ are Lewis acids. (NH_4^+ also acts as a Lewis acid; H_2O is a Lewis base.)

Q37 What will be the conjugate bases for the Bronsted acids: HF, H_2SO_4 and HCO_3^-?

SOLUTION

Conjugate base = acid minus one proton (H^+).

$HF \rightarrow HF - H^+ \rightarrow F^-$ (conjugate base of HF is F^-)

$H_2SO_4 \rightarrow H_2SO_4 - H^+ \rightarrow HSO_4^-$ (conjugate base of H_2SO_4 is HSO_4^-)

$HCO_3^- \rightarrow HCO_3^- - H^+ \rightarrow CO_3^{2-}$ (conjugate base of HCO_3^- is CO_3^{2-})

Answer: $HF \rightarrow F^-$; $H_2SO_4 \rightarrow HSO_4^-$; $HCO_3^- \rightarrow CO_3^{2-}$

Q38 Write the conjugate acids for the following Bronsted bases: NH_2^-, NH_3 and $HCOO^-$.

SOLUTION

Conjugate acid = base plus one proton (H^+).

$NH_2^- + H^+ \rightarrow NH_3$ (conjugate acid of NH_2^- is NH_3)

$NH_3 + H^+ \rightarrow NH_4^+$ (conjugate acid of NH_3 is NH_4^+)

$HCOO^- + H^+ \rightarrow HCOOH$ (conjugate acid of $HCOO^-$ is HCOOH, formic acid)

Answer: $NH_2^- \rightarrow NH_3$; $NH_3 \rightarrow NH_4^+$; $HCOO^- \rightarrow HCOOH$

Q39 The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.

SOLUTION

Each amphoteric species: conjugate acid (gains H^+) and conjugate base (loses H^+).

H_2O:

As acid (donates H^+): $H_2O \rightarrow OH^-$ (conjugate base = OH^-)

As base (accepts H^+): $H_2O + H^+ \rightarrow H_3O^+$ (conjugate acid = H_3O^+)

HCO_3^-:

As acid: $HCO_3^- \rightarrow CO_3^{2-}$ (conjugate base = CO_3^{2-})

As base: $HCO_3^- + H^+ \rightarrow H_2CO_3$ (conjugate acid = H_2CO_3)

HSO_4^-:

As acid: $HSO_4^- \rightarrow SO_4^{2-}$ (conjugate base = SO_4^{2-})

As base: $HSO_4^- + H^+ \rightarrow H_2SO_4$ (conjugate acid = H_2SO_4)

NH_3:

As acid: $NH_3 \rightarrow NH_2^-$ (conjugate base = NH_2^-)

As base: $NH_3 + H^+ \rightarrow NH_4^+$ (conjugate acid = NH_4^+)

Answer: H_2O: conj. acid H_3O^+, conj. base OH^-; HCO_3^-: conj. acid H_2CO_3, conj. base CO_3^{2-}; HSO_4^-: conj. acid H_2SO_4, conj. base SO_4^{2-}; NH_3: conj. acid NH_4^+, conj. base NH_2^-.

Q40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH^- (b) F^- (c) H^+ (d) BCl_3.

SOLUTION

Lewis acid = electron-pair acceptor; Lewis base = electron-pair donor.

(a) OH^-: has three lone pairs on oxygen; can donate an electron pair.
OH^- is a Lewis BASE.
Example: $OH^- + H^+ \rightarrow H_2O$ (OH^- donates lone pair to H^+)

(b) F^-: has four lone pairs on fluorine; can donate an electron pair.
F^- is a Lewis BASE.
Example: $BF_3 + F^- \rightarrow BF_4^-$ (F^- donates lone pair to boron)

(c) H^+: a bare proton; has no electrons; accepts an electron pair.
H^+ is a Lewis ACID.
Example: $H^+ + NH_3 \rightarrow NH_4^+$ (H^+ accepts lone pair from N)

(d) BCl_3: boron has only 6 valence electrons (incomplete octet); can accept an electron pair.
BCl_3 is a Lewis ACID.
Example: $BCl_3 + NH_3 \rightarrow BCl_3{\cdot}NH_3$ (B accepts lone pair from N)

Answer: Lewis acids: H^+ and BCl_3. Lewis bases: OH^- and F^-.

Q41 The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

SOLUTION

Given: $[H^+] = 3.8 \times 10^{-3}$ M

$pH = -\log[H^+]$
$pH = -\log(3.8 \times 10^{-3})$
$pH = -(\log 3.8 + \log 10^{-3})$
$pH = -(0.5798 - 3)$
$pH = 3 - 0.58 = 2.42$

Answer: pH = 2.42

Q42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

SOLUTION

Given: pH = 3.76

$[H^+]$ = 10^(-pH) = 10^(-3.76)
$[H^+]$ = 10^(-3.76) = 10^(0.24) × 10^(-4)
10^(0.24) = 1.74
$[H^+] = 1.74 \times 10^{-4}$ M

Answer: $[H^+] = 1.74 \times 10^{-4}$ M

Q43 The ionization constants of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate bases.

SOLUTION

Relationship: Ka × Kb = Kw = 1.0×10^{-14} at 298 K
Therefore: Kb(conjugate base) = Kw / Ka

For F^- (conjugate base of HF, Ka = 6.8×10^{-4}):
$Kb(F^-) = 1.0 \times 10^{-14} / 6.8 \times 10^{-4} = 1.47 \times 10^{-11}$

For $HCOO^-$ (conjugate base of HCOOH, Ka = 1.8×10^{-4}):
$Kb(HCOO^-) = 1.0 \times 10^{-14} / 1.8 \times 10^{-4} = 5.56 \times 10^{-11}$

For CN^- (conjugate base of HCN, Ka = 4.8×10^{-9}):
$Kb(CN^-) = 1.0 \times 10^{-14} / 4.8 \times 10^{-9} = 2.08 \times 10^{-6}$

Answer: $Kb(F^-) = 1.47 \times 10^{-11}$; $Kb(HCOO^-) = 5.56 \times 10^{-11}$; $Kb(CN^-) = 2.08 \times 10^{-6}$

Q44 The ionization constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?

SOLUTION

Given: Ka(phenol) = 1.0×10^{-10}; c = 0.05 M

In pure 0.05 M phenol solution:
$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$
$[C_6H_5O^-]$ = sqrt(Ka × c) = sqrt($1.0 \times 10^{-10} \times 0.05$)

$[C_6H_5O^-] = \sqrt{5.0 \times 10^{-12}} = 2.24 \times 10^{-6}$ M

Degree of ionization in presence of 0.01 M sodium phenolate (common ion effect):
Let y = additional concentration of $C_6H_5O^-$ from phenol ionization.
$[C_6H_5O^-] \approx 0.01$ M (dominated by salt); $[C_6H_5OH] \approx 0.05$ M

$K_a = [C_6H_5O^-][H^+] / [C_6H_5OH]$
$1.0 \times 10^{-10} = (0.01)(y) / 0.05$
$y = 1.0 \times 10^{-10} \times 0.05 / 0.01 = 5.0 \times 10^{-10}$ M

Degree of ionization $\alpha = y / c = 5.0 \times 10^{-10} / 0.05 = 1.0 \times 10^{-8}$

Answer: $[C_6H_5O^-] = 2.24 \times 10^{-6}$ M (in pure solution); degree of ionization in 0.01 M sodium phenolate = 1.0×10^{-8}

Q45 The first ionization constant of H_2S is 9.1×10^{-8}. Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13}, calculate the concentration of S^{2-} under both conditions.

SOLUTION

Given: $K_{a_1}(H_2S) = 9.1 \times 10^{-8}$; $K_{a_2}(H_2S) = 1.2 \times 10^{-13}$; c = 0.1 M

In pure 0.1 M H_2S:
$H_2S \rightleftharpoons H^+ + HS^-$
$[HS^-] = [H^+] = \sqrt{K_{a_1} \times c} = \sqrt{9.1 \times 10^{-8} \times 0.1}$
$[HS^-] = \sqrt{9.1 \times 10^{-9}} = 9.54 \times 10^{-5}$ M

In 0.1 M HCl (common ion H^+):
$[H^+] \approx 0.1$ M from HCl; suppresses HS^- formation.
$[HS^-] = K_{a_1} \times [H_2S] / [H^+] = 9.1 \times 10^{-8} \times 0.1 / 0.1 = 9.1 \times 10^{-8}$ M

Concentration of S^{2-} (second ionization: $HS^- \rightleftharpoons H^+ + S^{2-}$):

In pure solution: $[H^+] = [HS^-] = 9.54 \times 10^{-5}$ M
$K_{a_2} = [H^+][S^{2-}] / [HS^-] \rightarrow [S^{2-}] = K_{a_2} \times [HS^-]/[H^+] = K_{a_2} = 1.2 \times 10^{-13}$ M
(since $[H^+] = [HS^-]$ from first dissociation)

In 0.1 M HCl: $[H^+] = 0.1$ M, $[HS^-] = 9.1 \times 10^{-8}$ M
$[S^{2-}] = K_{a_2} \times [HS^-] / [H^+] = 1.2 \times 10^{-13} \times 9.1 \times 10^{-8} / 0.1$
$[S^{2-}] = 1.09 \times 10^{-19}$ M

Answer: $[HS^-]$ in pure solution = 9.54×10^{-5} M; in 0.1 M HCl = 9.1×10^{-8} M. $[S^{2-}]$ in pure solution = 1.2×10^{-13} M; in 0.1 M HCl = 1.09×10^{-19} M.

Q46 The ionization constant of acetic acid is 1.74×10^{-5}. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.

SOLUTION

Given: $K_a = 1.74 \times 10^{-5}$; $c = 0.05$ M

Degree of dissociation α:

$\alpha = \sqrt{K_a / c} = \sqrt{1.74 \times 10^{-5} / 0.05} = \sqrt{3.48 \times 10^{-4}}$

$\alpha = 1.865 \times 10^{-2} = 1.87\%$

(check: $\alpha \ll 1$, approximation valid)

$[CH_3COO^-] = c \times \alpha = 0.05 \times 1.865 \times 10^{-2} = 9.33 \times 10^{-4}$ M

$[H^+] = [CH_3COO^-] = 9.33 \times 10^{-4}$ M

$pH = -\log(9.33 \times 10^{-4}) = -\log(9.33) - \log(10^{-4})$

$pH = -0.970 + 4 = 3.03$

Answer: α = 1.87%; $[CH_3COO^-] = 9.33 \times 10^{-4}$ M; pH = 3.03

Q47 It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pKa.

SOLUTION

Given: $c = 0.01$ M; pH = 4.15

$[H^+] = 10^{\wedge}(-4.15) = 7.08 \times 10^{-5}$ M

$[A^-] = [H^+] = 7.08 \times 10^{-5}$ M (anion concentration)

$[HA]_{eq} = 0.01 - 7.08 \times 10^{-5} \approx 0.009929$ M

$K_a = [H^+][A^-] / [HA] = (7.08 \times 10^{-5})^2 / 9.929 \times 10^{-3}$

$K_a = 5.01 \times 10^{-9} / 9.929 \times 10^{-3}$

$K_a = 5.05 \times 10^{-7}$

$pK_a = -\log(5.05 \times 10^{-7}) = 6.30$

Answer: $[A^-] = 7.08 \times 10^{-5}$ M; $K_a = 5.05 \times 10^{-7}$; $pK_a = 6.30$

Q48 Assuming complete dissociation, calculate the pH of the following solutions: (a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

SOLUTION

All are strong acid/base; complete dissociation assumed.

(a) 0.003 M HCl: $[H^+] = 0.003$ M
pH = -log(0.003) = -log(3×10^{-3}) = 3 - log 3 = 3 - 0.4771 = 2.52

(b) 0.005 M NaOH: $[OH^-] = 0.005$ M
pOH = -log(0.005) = 2.30
pH = 14 - 2.30 = 11.70

(c) 0.002 M HBr: $[H^+] = 0.002$ M
pH = -log(0.002) = -log(2×10^{-3}) = 3 - log 2 = 3 - 0.3010 = 2.70

(d) 0.002 M KOH: $[OH^-] = 0.002$ M
pOH = -log(0.002) = 2.70
pH = 14 - 2.70 = 11.30

Answer: (a) pH = 2.52; (b) pH = 11.70; (c) pH = 2.70; (d) pH = 11.30

Q49 Calculate the pH of the following solutions: (a) 2 g of TlOH dissolved in water to give 2 litre of solution (b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution (c) 0.3 g of NaOH dissolved in water to give 200 mL of solution (d) 1 mL of 13.6 M HCl diluted with water to give 1 litre of solution.

SOLUTION

(a) TlOH: M = 204 + 16 + 1 = 221 g/mol
mol = 2/221 = 9.05×10^{-3} mol
[TlOH] = $9.05 \times 10^{-3} / 2 = 4.52 \times 10^{-3}$ M
$[OH^-] = 4.52 \times 10^{-3}$ M (strong base)
pOH = -log(4.52×10^{-3}) = 2.34
pH = 14 - 2.34 = 11.66

(b) $Ca(OH)_2$: M = 40 + 2(17) = 74 g/mol
mol = 0.3/74 = 4.054×10^{-3} mol
$[Ca(OH)_2] = 4.054 \times 10^{-3} / 0.5 = 8.108 \times 10^{-3}$ M
$[OH^-] = 2 \times 8.108 \times 10^{-3} = 1.622 \times 10^{-2}$ M
pOH = -log(1.622×10^{-2}) = 1.79
pH = 14 - 1.79 = 12.21

(c) NaOH: M = 40 g/mol
mol = 0.3/40 = 7.5×10^{-3} mol
[NaOH] = 7.5×10^{-3} / 0.2 = 0.0375 M
pOH = -log(0.0375) = 1.43
pH = 14 - 1.43 = 12.57

(d) HCl dilution:
mol HCl = $13.6 \times 0.001 = 0.0136$ mol
[HCl] = 0.0136 / 1 = 0.0136 M
pH = -log(0.0136) = -log(1.36×10^{-2}) = 2 - log 1.36 = 2 - 0.1335 = 1.87

Answer: (a) pH = 11.66; (b) pH = 12.21; (c) pH = 12.57; (d) pH = 1.87

Q50 The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pKa of bromoacetic acid.

SOLUTION

Given: c = 0.1 M; α = 0.132

$[H^+] = c \times \alpha = 0.1 \times 0.132 = 0.0132$ M
pH = -log(0.0132) = -log(1.32×10^{-2}) = 2 - log 1.32 = 2 - 0.121 = 1.88

$Ka = c\alpha^2 / (1 - \alpha) = 0.1 \times (0.132)^2 / (1 - 0.132)$
$Ka = 0.1 \times 0.017424 / 0.868$
$Ka = 1.7424 \times 10^{-3} / 0.868$
$Ka = 2.007 \times 10^{-3}$

pKa = -log(2.007×10^{-3}) = 3 - log 2.007 = 3 - 0.3025 = 2.70

Answer: pH = 1.88; pKa = 2.70

Q51 The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pKb.

SOLUTION

Given: c = 0.005 M; pH = 9.95

pOH = 14 - 9.95 = 4.05
$[OH^-]$ = 10^(-4.05) = 8.91×10^{-5} M

Codeine is a weak base; $B + H_2O \rightleftharpoons BH^+ + OH^-$
$Kb = [BH^+][OH^-] / [B] = [OH^-]^2 / (c - [OH^-])$

$Kb = (8.91 \times 10^{-5})^2 / (0.005 - 8.91 \times 10^{-5})$
$Kb = 7.94 \times 10^{-9} / 4.909 \times 10^{-3}$
$Kb = 1.62 \times 10^{-6}$

$pKb = -\log(1.62 \times 10^{-6}) = 5.79$

Answer: $Kb = 1.62 \times 10^{-6}$; $pKb = 5.79$

Q52 What is the pH of 0.001 M aniline solution? The ionization constant of aniline can be taken from Table 6.7. Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline.

SOLUTION

From Table 6.7: $Kb(\text{aniline}, C_6H_5NH_2) = 4.27 \times 10^{-10}$; $c = 0.001$ M

$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$
$[OH^-] = \text{sqrt}(Kb \times c) = \text{sqrt}(4.27 \times 10^{-10} \times 0.001)$
$[OH^-] = \text{sqrt}(4.27 \times 10^{-13}) = 6.53 \times 10^{-7}$ M

$pOH = -\log(6.53 \times 10^{-7}) = 6.19$
$pH = 14 - 6.19 = 7.82$

Degree of ionization:
$\alpha = [OH^-] / c = 6.53 \times 10^{-7} / 0.001 = 6.53 \times 10^{-4}$

Ka of conjugate acid (anilinium ion, $C_6H_5NH_3^+$):
$Ka \times Kb = Kw = 1.0 \times 10^{-14}$
$Ka = 1.0 \times 10^{-14} / 4.27 \times 10^{-10} = 2.34 \times 10^{-5}$

Answer: $pH = 7.82$; $\alpha = 6.53 \times 10^{-4}$; $Ka(\text{anilinium}) = 2.34 \times 10^{-5}$

Q53 Calculate the degree of ionization of 0.05 M acetic acid if its pKa value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01 M (b) 0.1 M HCl?

SOLUTION

Given: $c = 0.05$ M; $pKa = 4.74 \rightarrow Ka = 10\text{^}(-4.74) = 1.82 \times 10^{-5}$

In pure 0.05 M acetic acid:
$\alpha = \text{sqrt}(Ka/c) = \text{sqrt}(1.82 \times 10^{-5} / 0.05) = \text{sqrt}(3.64 \times 10^{-4}) = 1.91 \times 10^{-2}$
$\alpha = 0.0191$ (1.91%)

(a) With 0.01 M HCl:

$[H^+] \approx 0.01$ M (from HCl, dominant)
$K_a = [H^+][A^-]/[HA] \rightarrow [A^-] = K_a \times c / [H^+] = 1.82 \times 10^{-5} \times 0.05 / 0.01$
$[A^-] = 9.10 \times 10^{-5}$ M
$\alpha = [A^-]/c = 9.10 \times 10^{-5} / 0.05 = 1.82 \times 10^{-3}$

(b) With 0.1 M HCl:
$[H^+] \approx 0.1$ M
$[A^-] = 1.82 \times 10^{-5} \times 0.05 / 0.1 = 9.10 \times 10^{-6}$ M
$\alpha = 9.10 \times 10^{-6} / 0.05 = 1.82 \times 10^{-4}$

Answer: Pure solution: $\alpha = 0.0191$; with 0.01 M HCl: $\alpha = 1.82 \times 10^{-3}$; with 0.1 M HCl: $\alpha = 1.82 \times 10^{-4}$. Common ion ($H^+$) greatly reduces ionization.

Q54 The ionization constant of dimethylamine is 5.4×10^{-4}. Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1 M in NaOH?

SOLUTION

Given: $K_b = 5.4 \times 10^{-4}$; $c = 0.02$ M

$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$

From quadratic (since $K_b/c = 0.027$, not negligible):
$[OH^-]^2 + K_b[OH^-] - K_b \times c = 0$
$[OH^-]^2 + 5.4 \times 10^{-4}\,[OH^-] - 1.08 \times 10^{-5} = 0$

Discriminant $= (5.4 \times 10^{-4})^2 + 4 \times 1.08 \times 10^{-5} = 2.916 \times 10^{-7} + 4.32 \times 10^{-5} = 4.349 \times 10^{-5}$
$[OH^-] = (-5.4 \times 10^{-4} + \text{sqrt}(4.349 \times 10^{-5})) / 2$
$[OH^-] = (-5.4 \times 10^{-4} + 6.595 \times 10^{-3}) / 2$
$[OH^-] = 6.055 \times 10^{-3} / 2 = 3.03 \times 10^{-3}$ M

$\alpha = [OH^-]/c = 3.03 \times 10^{-3} / 0.02 = 0.1514 = 15.1\%$

With 0.1 M NaOH (common OH^-):
$[OH^-] \approx 0.1$ M; let y = [amine ionized]
$K_b = y \times (0.1 + y) / (0.02 - y) \approx y \times 0.1 / 0.02$ (since $y << 0.02$)
$y = K_b \times 0.02 / 0.1 = 5.4 \times 10^{-4} \times 0.02 / 0.1 = 1.08 \times 10^{-4}$ M
% ionized $= (1.08 \times 10^{-4} / 0.02) \times 100 = 0.54\%$

Answer: Degree of ionization = 0.151 (15.1%); with 0.1 M NaOH: 0.54% ionized.

Q55 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below: (a) Human muscle-fluid, 6.83 (b) Human stomach fluid, 1.2 (c) Human blood, 7.38 (d) Human saliva, 6.4.

SOLUTION

$[H^+] = 10^{(-pH)}$

(a) Muscle-fluid, pH = 6.83:
$[H^+] = 10^{(-6.83)} = 1.48 \times 10^{-7}$ M

(b) Stomach fluid, pH = 1.2:
$[H^+] = 10^{(-1.2)} = 6.31 \times 10^{-2}$ M

(c) Blood, pH = 7.38:
$[H^+] = 10^{(-7.38)} = 4.17 \times 10^{-8}$ M

(d) Saliva, pH = 6.4:
$[H^+] = 10^{(-6.4)} = 3.98 \times 10^{-7}$ M

Answer: (a) 1.48×10^{-7} M; (b) 6.31×10^{-2} M; (c) 4.17×10^{-8} M; (d) 3.98×10^{-7} M

Q56 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

SOLUTION

$[H^+] = 10^{(-pH)}$

Milk (pH 6.8): $[H^+] = 10^{(-6.8)} = 1.58 \times 10^{-7}$ M
Black coffee (pH 5.0): $[H^+] = 10^{(-5.0)} = 1.00 \times 10^{-5}$ M
Tomato juice (pH 4.2): $[H^+] = 10^{(-4.2)} = 6.31 \times 10^{-5}$ M
Lemon juice (pH 2.2): $[H^+] = 10^{(-2.2)} = 6.31 \times 10^{-3}$ M
Egg white (pH 7.8): $[H^+] = 10^{(-7.8)} = 1.58 \times 10^{-8}$ M

Answer: Milk: 1.58×10^{-7} M; coffee: 1.00×10^{-5} M; tomato: 6.31×10^{-5} M; lemon: 6.31×10^{-3} M; egg white: 1.58×10^{-8} M

Q57 If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?

SOLUTION

Given: 0.561 g KOH; V = 200 mL = 0.200 L; M(KOH) = 56.1 g/mol

mol KOH = 0.561 / 56.1 = 0.01 mol
[KOH] = 0.01 / 0.200 = 0.05 M

KOH is a strong base; complete dissociation:
$[K^+] = 0.05$ M
$[OH^-] = 0.05$ M
$[H^+] = Kw / [OH^-] = 1.0 \times 10^{-14} / 0.05 = 2.0 \times 10^{-13}$ M

pOH = -log(0.05) = 1.30
pH = 14 - 1.30 = 12.70

Answer: $[K^+] = 0.05$ M; $[OH^-] = 0.05$ M; $[H^+] = 2.0 \times 10^{-13}$ M; pH = 12.70

Q58 The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.

SOLUTION

Given: solubility = 19.23 g/L; $M(Sr(OH)_2) = 87.62 + 2(17) = 121.62$ g/mol

Molar solubility S = 19.23 / 121.62 = 0.1581 mol/L

$Sr(OH)_2 \rightarrow Sr^{2+} + 2OH^-$
$[Sr^{2+}] = S = 0.158$ M
$[OH^-] = 2S = 2 \times 0.158 = 0.316$ M

pOH = -log(0.316) = 0.500
pH = 14 - 0.500 = 13.50

Answer: $[Sr^{2+}] = 0.158$ M; $[OH^-] = 0.316$ M; pH = 13.50

Q59 The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization of the acid in its 0.05 M solution and also its pH. What will be its degree of ionization if the solution is 0.01 M in HCl also?

SOLUTION

Given: $K_a = 1.32 \times 10^{-5}$; $c = 0.05$ M

Degree of ionization:
$\alpha = \sqrt{K_a/c} = \sqrt{1.32 \times 10^{-5} / 0.05} = \sqrt{2.64 \times 10^{-4}} = 1.62 \times 10^{-2}$

$[H^+] = c \times \alpha = 0.05 \times 1.62 \times 10^{-2} = 8.12 \times 10^{-4}$ M
$pH = -\log(8.12 \times 10^{-4}) = 3.09$

With 0.01 M HCl:
$[H^+] \approx 0.01$ M; $\alpha' = K_a/[H^+] = 1.32 \times 10^{-5} / 0.01 = 1.32 \times 10^{-3}$

Answer: $\alpha = 1.62 \times 10^{-2}$; pH = 3.09; with 0.01 M HCl: $\alpha = 1.32 \times 10^{-3}$

Q60 The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

SOLUTION

Given: $c = 0.1$ M; pH = 2.34

$[H^+] = 10\text{^}(-2.34) = 4.57 \times 10^{-3}$ M

$[CNO^-] = [H^+] = 4.57 \times 10^{-3}$ M
$[HCNO]_{eq} = 0.1 - 4.57 \times 10^{-3} = 0.09543$ M

$K_a = [H^+][CNO^-] / [HCNO] = (4.57 \times 10^{-3})^2 / 0.09543$
$K_a = 2.09 \times 10^{-5} / 0.09543 = 2.19 \times 10^{-4}$

Degree of ionization:
$\alpha = [H^+] / c = 4.57 \times 10^{-3} / 0.1 = 4.57 \times 10^{-2} = 4.57\%$

Answer: $K_a = 2.19 \times 10^{-4}$; degree of ionization $\alpha = 0.0457$ (4.57%)

Q61 The ionization constant of nitrous acid is 4.5×10^{-4}. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.

SOLUTION

Given: $K_a(HNO_2) = 4.5 \times 10^{-4}$; $c(NaNO_2) = 0.04$ M

NO_2^- is the conjugate base of a weak acid; it undergoes hydrolysis:
$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

$K_b(NO_2^-) = K_w / K_a(HNO_2) = 1.0 \times 10^{-14} / 4.5 \times 10^{-4} = 2.22 \times 10^{-11}$

$[OH^-] = \text{sqrt}(K_b \times c) = \text{sqrt}(2.22 \times 10^{-11} \times 0.04)$
$[OH^-] = \text{sqrt}(8.89 \times 10^{-13}) = 9.43 \times 10^{-7}$ M

$pOH = -\log(9.43 \times 10^{-7}) = 6.03$
$pH = 14 - 6.03 = 7.97$

Degree of hydrolysis $= [OH^-] / c = 9.43 \times 10^{-7} / 0.04 = 2.36 \times 10^{-5}$

Answer: pH = 7.97; degree of hydrolysis = 2.36×10^{-5}

Q62 A 0.02 M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine.

SOLUTION

Given: 0.02 M pyridinium hydrochloride ($C_5H_5NH^+Cl^-$); pH = 3.44

Pyridinium ion $C_5H_5NH^+$ is the conjugate acid of pyridine; it hydrolyzes:
$C_5H_5NH^+ \rightleftharpoons C_5H_5N + H^+$

$[H^+] = 10\text{^}(-3.44) = 3.63 \times 10^{-4}$ M

$K_a(C_5H_5NH^+) = [H^+][C_5H_5N] / [C_5H_5NH^+]$
$= (3.63 \times 10^{-4})^2 / (0.02 - 3.63 \times 10^{-4})$
$= 1.318 \times 10^{-7} / 1.964 \times 10^{-2}$
$= 6.71 \times 10^{-6}$

$K_b(\text{pyridine}) = K_w / K_a = 1.0 \times 10^{-14} / 6.71 \times 10^{-6} = 1.49 \times 10^{-9}$

Answer: $K_b(\text{pyridine}) = 1.49 \times 10^{-9}$

Q63 Predict if the solutions of the following salts are neutral, acidic or basic: NaCl, KBr, NaCN, NH_4NO_3, $NaNO_2$ and KF.

SOLUTION

Salt hydrolysis rules: salt of strong acid + strong base → neutral; salt of weak acid + strong base → basic; salt of strong acid + weak base → acidic.

NaCl: Na^+ (strong base NaOH) + Cl^- (strong acid HCl) → NEUTRAL

KBr: K^+ (strong base KOH) + Br^- (strong acid HBr) → NEUTRAL

NaCN: Na^+ (strong base) + CN^- (weak acid HCN, $K_a = 4.9 \times 10^{-10}$) → CN^- hydrolyzes → BASIC

NH_4NO_3: NH_4^+ (weak base NH_3, $K_b = 1.77 \times 10^{-5}$) + NO_3^- (strong acid HNO_3) → NH_4^+ hydrolyzes → ACIDIC

$NaNO_2$: Na^+ (strong base) + NO_2^- (weak acid HNO_2, $K_a = 4.5 \times 10^{-4}$) → NO_2^- hydrolyzes → BASIC

KF: K^+ (strong base KOH) + F^- (weak acid HF, $K_a = 6.8 \times 10^{-4}$) → F^- hydrolyzes → BASIC

Answer: NaCl: neutral; KBr: neutral; NaCN: basic; NH_4NO_3: acidic; $NaNO_2$: basic; KF: basic.

Q64 The ionization constant of chloroacetic acid is 1.35×10^{-3}. What will be the pH of 0.1 M acid and its 0.1 M sodium salt solution?

SOLUTION

Given: $K_a = 1.35 \times 10^{-3}$; $c = 0.1$ M

pH of 0.1 M chloroacetic acid ($ClCH_2COOH$):
Using quadratic: $[H^+]^2 + K_a[H^+] - K_a \times c = 0$
$[H^+]^2 + 1.35 \times 10^{-3}\,[H^+] - 1.35 \times 10^{-4} = 0$
Discriminant = $(1.35 \times 10^{-3})^2 + 4(1.35 \times 10^{-4}) = 1.823 \times 10^{-6} + 5.40 \times 10^{-4} = 5.418 \times 10^{-4}$
$[H^+] = (-1.35 \times 10^{-3} + \text{sqrt}(5.418 \times 10^{-4})) / 2$
$[H^+] = (-1.35 \times 10^{-3} + 2.328 \times 10^{-2}) / 2 = 2.193 \times 10^{-2} / 2 = 1.097 \times 10^{-2}$ M
$pH = -\log(1.097 \times 10^{-2}) = 1.96$

pH of 0.1 M sodium chloroacetate (NaA):
$A^- + H_2O \rightleftharpoons HA + OH^-$

$Kb(A^-) = Kw/Ka = 1.0 \times 10^{-14} / 1.35 \times 10^{-3} = 7.41 \times 10^{-12}$
$[OH^-] = sqrt(Kb \times c) = sqrt(7.41 \times 10^{-12} \times 0.1) = sqrt(7.41 \times 10^{-13}) = 8.61 \times 10^{-7}$ M
pOH = 6.07; pH = 14 - 6.07 = 7.93

Answer: pH of 0.1 M acid = 1.96; pH of 0.1 M sodium salt = 7.93

Q65 Ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

SOLUTION

Given: $Kw = 2.7 \times 10^{-14}$ at 310 K

At neutral pH: $[H^+] = [OH^-] = sqrt(Kw) = sqrt(2.7 \times 10^{-14})$
$[H^+] = 1.643 \times 10^{-7}$ M

$pH = -\log(1.643 \times 10^{-7}) = 7 - \log(1.643) = 7 - 0.2156 = 6.78$

Answer: pH of neutral water at 310 K = 6.78

Q66 Calculate the pH of the resultant mixtures: (a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl (b) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$ (c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH

SOLUTION

(a) 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl
mol OH^- = $2 \times 0.010 \times 0.2 = 4.0 \times 10^{-3}$ mol
mol H^+ = $0.025 \times 0.1 = 2.5 \times 10^{-3}$ mol
Excess OH^- = $(4.0 - 2.5) \times 10^{-3} = 1.5 \times 10^{-3}$ mol
Total volume = 35 mL = 0.035 L
$[OH^-] = 1.5 \times 10^{-3} / 0.035 = 0.04286$ M
$pOH = -\log(0.04286) = 1.37$
$pH = 14 - 1.37 = 12.63$

(b) 10 mL of 0.01 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$
mol H^+ = $2 \times 0.010 \times 0.01 = 2.0 \times 10^{-4}$ mol
mol OH^- = $2 \times 0.010 \times 0.01 = 2.0 \times 10^{-4}$ mol
Exactly neutralised → neutral solution.
pH = 7

(c) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.1 M KOH
mol H^+ = $2 \times 0.010 \times 0.1 = 2.0 \times 10^{-3}$ mol

mol OH^- = 1 × 0.010 × 0.1 = 1.0×10^{-3} mol
Excess H^+ = 1.0×10^{-3} mol
Total volume = 20 mL = 0.020 L
$[H^+] = 1.0 \times 10^{-3} / 0.020 = 0.05$ M
pH = -log(0.05) = 1.30

Answer: (a) pH = 12.63; (b) pH = 7; (c) pH = 1.30

Q67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298 K from their solubility product constants given in Table 6.9. Determine also the molarities of individual ions.

SOLUTION

Using Ksp values from Table 6.9:

1. Silver chromate (Ag_2CrO_4): Ksp = 1.1×10^{-12}
$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$; Ksp = $(2S)^2(S) = 4S^3$
S = (Ksp/4)^(1/3) = $(1.1 \times 10^{-12} / 4)^{(1/3)} = (2.75 \times 10^{-13})^{(1/3)} = 6.50 \times 10^{-5}$ M
$[Ag^+] = 2S = 1.30 \times 10^{-4}$ M; $[CrO_4^{2-}] = S = 6.50 \times 10^{-5}$ M

2. Barium chromate ($BaCrO_4$): Ksp = 1.2×10^{-10}
$BaCrO_4 \rightleftharpoons Ba^{2+} + CrO_4^{2-}$; Ksp = S^2
S = sqrt(1.2×10^{-10}) = 1.10×10^{-5} M
$[Ba^{2+}] = [CrO_4^{2-}] = 1.10 \times 10^{-5}$ M

3. Ferric hydroxide ($Fe(OH)_3$): Ksp = 2.8×10^{-39}
$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$; Ksp = $S(3S)^3 = 27S^4$
S = (Ksp/27)^(1/4) = $(2.8 \times 10^{-39} / 27)^{(1/4)} = (1.037 \times 10^{-40})^{(1/4)} = 1.01 \times 10^{-10}$ M
$[Fe^{3+}] = 1.01 \times 10^{-10}$ M; $[OH^-] = 3S = 3.03 \times 10^{-10}$ M

4. Lead chloride ($PbCl_2$): Ksp = 1.6×10^{-5}
$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$; Ksp = $S(2S)^2 = 4S^3$
S = (Ksp/4)^(1/3) = $(1.6 \times 10^{-5} / 4)^{(1/3)} = (4.0 \times 10^{-6})^{(1/3)} = 1.587 \times 10^{-2}$ M
$[Pb^{2+}] = 1.59 \times 10^{-2}$ M; $[Cl^-] = 2S = 3.17 \times 10^{-2}$ M

5. Mercurous iodide (Hg_2I_2): Ksp = 4.5×10^{-29}
$Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$; Ksp = $S(2S)^2 = 4S^3$
S = (Ksp/4)^(1/3) = $(4.5 \times 10^{-29} / 4)^{(1/3)} = (1.125 \times 10^{-29})^{(1/3)} = 2.24 \times 10^{-10}$ M
$[Hg_2^{2+}] = 2.24 \times 10^{-10}$ M; $[I^-] = 2S = 4.48 \times 10^{-10}$ M

Answer: Ag_2CrO_4: S = 6.50×10^{-5} M; $BaCrO_4$: S = 1.10×10^{-5} M; $Fe(OH)_3$: S = 1.01×10^{-10} M; $PbCl_2$: S = 1.59×10^{-2} M; Hg_2I_2: S = 2.24×10^{-10} M

Q68 The solubility product constants of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.

SOLUTION

Given: Ksp(Ag_2CrO_4) = 1.1×10^{-12}; Ksp(AgBr) = 5.0×10^{-13}

Molar solubility of Ag_2CrO_4 ($Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4^{2-}$):
$4S_1^3 = 1.1 \times 10^{-12}$
$S_1 = (1.1 \times 10^{-12} / 4)^{(1/3)} = (2.75 \times 10^{-13})^{(1/3)} = 6.50 \times 10^{-5}$ M

Molar solubility of AgBr ($AgBr \rightarrow Ag^+ + Br^-$):
$S_2^2 = 5.0 \times 10^{-13}$
$S_2 = \text{sqrt}(5.0 \times 10^{-13}) = 7.07 \times 10^{-7}$ M

Ratio $S_1/S_2 = 6.50 \times 10^{-5} / 7.07 \times 10^{-7} = 91.9 \approx 92$

Answer: $S(Ag_2CrO_4)/S(AgBr) = 6.50 \times 10^{-5} / 7.07 \times 10^{-7} \approx 92$

Q69 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $Cu(IO_3)_2$: Ksp = 7.4×10^{-8})

SOLUTION

Given: 0.002 M $NaIO_3$ and 0.002 M $Cu(ClO_3)_2$ mixed in equal volumes; Ksp($Cu(IO_3)_2$) = 7.4×10^{-8}

After mixing equal volumes, concentrations are halved:
$[IO_3^-] = 0.002/2 = 1.0 \times 10^{-3}$ M
$[Cu^{2+}] = 0.002/2 = 1.0 \times 10^{-3}$ M

Ionic product $Qsp = [Cu^{2+}][IO_3^-]^2$
$Qsp = (1.0 \times 10^{-3})(1.0 \times 10^{-3})^2 = 1.0 \times 10^{-9}$

Compare: $Qsp = 1.0 \times 10^{-9} < Ksp = 7.4 \times 10^{-8}$

Since Qsp < Ksp, the solution is unsaturated; NO precipitation of copper iodate occurs.

Answer: $Qsp = 1.0 \times 10^{-9} < Ksp = 7.4 \times 10^{-8}$; no precipitation of $Cu(IO_3)_2$ occurs.

Q70 The ionization constant of benzoic acid is 6.46×10^{-5} and Ksp for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

SOLUTION

Given: $Ka(C_6H_5COOH) = 6.46 \times 10^{-5}$; $Ksp(AgC_6H_5COO) = 2.5 \times 10^{-13}$; buffer pH = 3.19

Solubility in pure water:
$AgBenz \rightleftharpoons Ag^+ + C_6H_5COO^-$; $Ksp = S_w^2$
$S_w = \sqrt{Ksp} = \sqrt{2.5 \times 10^{-13}} = 5.00 \times 10^{-7}$ M

Solubility in buffer (pH 3.19):
$[H^+]$ at pH 3.19 = 10^(-3.19) = 6.46×10^{-4} M
pKa(benzoic acid) = $-\log(6.46 \times 10^{-5}) = 4.19$
$[H^+]/Ka = 6.46 \times 10^{-4} / 6.46 \times 10^{-5} = 10.0$

In acidic buffer, benzoate ion is partly protonated; effective solubility increases.
$S_{buf} = \sqrt{Ksp \times (1 + [H^+]/Ka)} = \sqrt{Ksp \times 11}$
$S_{buf} = \sqrt{2.5 \times 10^{-13} \times 11} = \sqrt{2.75 \times 10^{-12}} = 1.658 \times 10^{-6}$ M

Ratio = $S_{buf} / S_w = 1.658 \times 10^{-6} / 5.00 \times 10^{-7} = \sqrt{11} = 3.32$

Answer: Silver benzoate is 3.32 times more soluble in the buffer of pH 3.19 than in pure water.

Q71 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $Ksp = 6.3 \times 10^{-18}$).

SOLUTION

Given: $Ksp(FeS) = 6.3 \times 10^{-18}$
Equimolar solutions of $FeSO_4$ and Na_2S; mixed in equal volumes.

After mixing, concentrations are halved:
$[Fe^{2+}] = c/2$; $[S^{2-}] = c/2$

For no precipitation: $[Fe^{2+}][S^{2-}] \leq Ksp$
$(c/2)(c/2) \leq Ksp$
$c^2/4 \leq 6.3 \times 10^{-18}$
$c^2 \leq 25.2 \times 10^{-18}$
$c \leq 5.02 \times 10^{-9}$ M

Answer: Maximum concentration c = 5.02×10^{-9} M

Q72 What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K? (For calcium sulphate, Ksp is 9.1×10^{-6}).

SOLUTION

Given: Ksp($CaSO_4$) = 9.1×10^{-6}; to dissolve 1 g of $CaSO_4$
M($CaSO_4$) = 40 + 32 + 64 = 136 g/mol

Molar solubility:
$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$; Ksp = S^2
S = sqrt(9.1×10^{-6}) = 3.017×10^{-3} mol/L

Mass dissolved per litre = S × M = $3.017 \times 10^{-3} \times 136 = 0.4103$ g/L

Volume needed to dissolve 1 g:
V = 1 / 0.4103 = 2.44 L

Answer: Minimum volume of water required = 2.44 L

Q73 The concentration of sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$. In which of these solutions will precipitation take place?

SOLUTION

Given: $[S^{2-}]$ in HCl = 1.0×10^{-19} M; V_1 = 10 mL added to V_2 = 5 mL of 0.04 M metal salt.
Total volume = 15 mL

After mixing:
$[S^{2-}] = (10/15) \times 1.0 \times 10^{-19} = 6.67 \times 10^{-20}$ M
$[M^{2+}] = (5/15) \times 0.04 = 1.33 \times 10^{-2}$ M

Ionic product Q = $[M^{2+}][S^{2-}] = 1.33 \times 10^{-2} \times 6.67 \times 10^{-20} = 8.87 \times 10^{-22}$

Ksp values (from Table 6.9):
FeS: Ksp = 6.3×10^{-18}; Q = 8.87×10^{-22} < Ksp → NO precipitation
MnS: Ksp = 2.5×10^{-10}; Q = 8.87×10^{-22} < Ksp → NO precipitation
ZnS: Ksp = 1.6×10^{-24}; Q = 8.87×10^{-22} > Ksp → PRECIPITATION occurs
CdS: Ksp = 8.0×10^{-28}; Q = 8.87×10^{-22} > Ksp → PRECIPITATION occurs

Answer: Precipitation occurs in $ZnCl_2$ and $CdCl_2$ solutions. No precipitation in $FeSO_4$ and $MnCl_2$ solutions.