Worksheet 4

1. At 298 K, F_3SSF (*g*) decomposes partially to SF_2 (*g*). At equilibrium, the partial pressure of SF_2 (*g*) is 1.1×10^{-4} atm and the partial pressure of F_3SSF is 0.0484 atm.
(a) Write a balanced equilibrium equation to represent this reaction.

F_3SSF (*g*) ⇋ 2 SF_2 (*g*)

(b) Compute the equilibrium constant corresponding to the equation you wrote.

$K = (P_{SF2}) / (P_{F3SSF}) = (1.1 \times 10^{-4}\ atm)^2 / (0.0484\ atm) = 2.5 \times 10^{-7}$

2. Isopropyl alcohol can dissociate into acetone and hydrogen via the following reaction

$$(CH_3)_2CHOH\ (g) \leftrightharpoons (CH_3)_2CO\ (g) + H_2\ (g)$$

At 179°C, the equilibrium constant for this dehydrogenation reaction is 0.444.
(a) If 10.00 g of isopropyl alcohol is placed in a 10.00-L vessel and heated to 179°C, what is the partial pressure of acetone when equilibrium is attained?

T = 179°C = 452 K
K = 0.444
m = 10 g × 1 mol / 60 g = 0.167 mol $(CH_3)_2CHOH$
V = 10.0 L
$P = nRT / V = (0.167\ mol)(0.08206\ atm\ L\ mol^{-1}\ K^{-1})(452\ K) / 10\ L$
$P_{(CH3)2CHOH} = 0.619$ atm

	$(CH_3)_2CHOH$ (*g*) ⇋	**$(CH_3)_2CO$ (*g*) +**	**H_2 (*g*)**
initial P	**0.619 atm**	**0**	**0**
Δ P	**-x**	**+x**	**+x**
eq. P	**0.619 - x**	**x**	**x**

$(0.444) = x^2 / (0.619 - x)$
$0.275 - 0.444x = x^2$
$x^2 - 0.444x - 0.275 = 0$
$x = (-0.44 \pm \sqrt{(0.444)^2 - 4(1)(-0.275)}) / 2 = 0.347\ atm = P_{(CH3)2COH}$

(b) What fraction of isopropyl alcohol is dissociated at equilibrium?

The actual $P_{(CH3)2CHOH} = 0.619 - 0.347 = 0.272$ atm
The fraction of dissociated isopropyl alcohol = (0.619 -0.272) / 0.619 = 0.562

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3. The equilibrium constant the reaction

$$H_2S\ (g) + I_2\ (g) \leftrightharpoons 2\ HI\ (g) + S\ (s)$$

at 110°C is equal to 0.0023. Calculate the reaction quotient *Q* for each of the following conditions and determine whether solid sulfur is consumed or produced as the reaction comes to equilibrium.
(a) $P_{I2} = 0.461$ atm; $P_{H2S} = 0.050$ atm; $P_{HI} = 0.0$ atm

$Q = (P_{HI})^2 / (P_{H2S})(P_{I2})$
Q = 0 because only reactants are present. Some sulfur must be produced to reach equilibrium.

(b) $P_{I2} = 0.461$ atm; $P_{H2S} = 0.050$ atm; $P_{HI} = 9.0$ atm

$Q = (9.0)^2 / (0.461)(0.050) = 3514.1$
This is bigger than K (0.0023). Solid sulfur is consumed by the reaction coming to equilibrium.

4. Methanol is made via the exothermic reaction

$$CO\ (g) + 2\ H_2\ (g) \rightharpoonup CH_3OH\ (g)$$

Describe how you would control the temperature and pressure to maximize the yield of methanol.

The reaction is exothermic and a high yield of product is favored by using a low temperature. In addition, the chemical amount of gas decreases in the course of the reaction, so high total pressure favors production of methanol.

5. Barium nitride vaporizes slightly at high temperature as it undergoes the dissociation

$$Ba_3N_2\ (s) \leftrightharpoons 3\ Ba\ (g) + N_2\ (g)$$

At 1000 K the equilibrium constant is 4.5×10^{-19}. At 1200 K the equilibrium constant is 6.2×10^{-12}.
(a) Estimate $\Delta H°$ for the reaction.

$T_1 = 1000$ K, $T_2 = 1200$ K
$K_1 = 4.5 \times 10^{-19}$, $K_2 = 6.2 \times 10^{-12}$
$\ln K_2 / K_1 = - \Delta H / R\ (1 / T_2 - 1 / T_1)$
$\ln 6.2 \times 10^{-12} / 4.5 \times 10^{-19} = - \Delta H / 8.314$ J mol^{-1} (1 / 1200 K - 1 / 1000 K)
$\Delta H = +820021.5$ J mol^{-1} = + 820 kJ mol^{-1}

(b) The equation is rewritten as

$$2\ Ba_3N_2\ (s) \leftrightharpoons 6\ Ba\ (g) + 2\ N_2\ (g)$$

Now the equilibrium constant is 2.0×10^{-37} at 1000 K and 3.8×10^{-23} at 1200 K. Estimate $\Delta H°$ of *this* reaction.

$\ln 3.8 \times 10^{-23} / 2.0 \times 10^{-37} = - \Delta H / 8.314\ J\ mol^{-1} (1 / 1200\ K - 1 / 1000\ K)$
$\Delta H = + 1640\ kJ\ mol^{-1}$

6. At 300°C the equilibrium constant for the reaction

$$PCl_5\ (g) \leftrightharpoons PCl_3\ (g) + Cl_2\ (g)$$

is K = 11.5.
(a) Calculate the reaction quotient *Q* if initially P_{PCl3} = 2.0 atm, P_{Cl2} = 6.0 atm, and P_{PCl5} = 1.0 atm. State whether the reaction proceeds to the right or to the left as equilibrium is approached.

$Q = (P_{PCl3})(P_{Cl2}) / P_{PCl5} = (2.0)(6.0) / 0.10 = 120 > K$
Thus the reaction proceeds toward the left (reactants).

(b) Calculate P_{PCl3}, P_{Cl2}, and P_{PCl5} at equilibrium.

	$PCl_5\ (g) \leftrightharpoons$	**$PCl_3\ (g) +$**	**$Cl_2\ (g)$**
initial P	**0.10 atm**	**2.0 atm**	**6.0 atm**
ΔP	**+y**	**-y**	**-y**
eq. P	**0.10 + y**	**2.0 - y**	**6.0 - y**

$K = (P_{PCl3})(P_{Cl2}) / P_{PCl5} = (2.0 - y)(6.0 - y) / (0.10 + y) = 11.5$
$1.15 + 11.5y = 12.0 - 8.0y + y^2$
$y^2 - 19.5y + 10.85 = 0$
$y = (19.5 \pm \sqrt{(-19.5)^2 - 4(1)(10.85)}) / 2 = 0.573$ atm
$P_{PCl5} = 0.10 + 0.573 = 0.673$ atm
$P_{PCl3} = 2.0 - 0.573 = 1.427$ atm
$P_{Cl2} = 6.0 - 0.573 = 5.427$ atm

(c) If the volume of the system is then increased, will the amount of PCl_5 present increase or decrease?

The increase in volume causes the reaction to shift to the side having more moles of gas.
The amount of PCl_5 (*g*) will decrease.

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7. A treatment recommended in case of accidental swallowing of ammonia-containing cleanser is to drink large amounts of diluted vinegar. Write an equation for the chemical reaction on which this procedure depends.

NH_3 (*aq*) + CH_3COOH (*aq*) ⇀ NH_4^+ (*aq*) + CH_3COO^- (*aq*)

8. Zinc oxide is amphoteric. Write balanced chemical equations for its reactions with an aqueous solution of hydrochloric acid and with an aqueous solution of sodium hydroxide. (Note: The hydroxide complex ion of zinc is $[Zn(OH)_4]^{2-}$)

ZnO (*s*) + 2 HCl (*aq*) ⇀ Zn^{2+} (*aq*) + 2 Cl^- (*aq*) + H_2O (*l*)
ZnO (*s*) + 2 NaOH (*aq*) + H_2O (*l*) ⇀ $[Zn(OH)_4]^{2-}$ (*aq*) + 2 Na^+ (*aq*)

9. The concentration of OH^- in a solution of household bleach is 3.6×10^{-2} M. Calculate the pH of the bleach.

pOH = -log 3.6×10^{-2} M
pOH = 1.44
pH = 14 - 1.44 = 12.56

10. At body temperature (98.6°F = 37.0°C), K_w has the value 2.4×10^{-14}. If the pH of blood is 7.4 under these conditions, what are the concentrations of H_3O^+ and OH^-?

pH = -log $[H^+]$
7.4 = -log $[H^+]$
$[H^+] = 4 \times 10^{-8}$
$[OH^-] = K_w / [H^+] = 2.4 \times 10^{-14} / 4 \times 10^{-8}$ M = 6×10^{-7} M

11. Niacin (C_5H_4NCOOH), one of the B vitamins, is an acid.
(a) Write an equation for its equilibrium reaction with water.

C_5H_4NCOOH (*aq*) + H_2O (*l*) ⇋ $C_5H_4NCOO^-$ (*aq*) + H_3O^+ (*aq*)

(b) The K_a for niacin is 1.5×10^{-5}. Calculate the K_b for its conjugate base.

$K_w = K_aK_b$
$K_b = K_w / K_a = 1.0 \times 10^{-14} / 1.5 \times 10^{-5} = 6.7 \times 10^{-10}$

(c) Is the conjugate base of niacin a stronger or a weaker base than pyridine, C_5H_5N?

Niacin is a stronger acid than the pyridinium ion, which means that its conjugate base is a weaker base than pyridine.

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12. Vitamin C is ascorbic acid ($HC_6H_7O_6$), for which K_a is 8.0×10^{-5}. Calculate the pH of a solution made by dissolving a 500-mg tablet of pure vitamin C in water and diluting to 100 mL.

m = 0.500 g $HC_6H_7O_6$ × 1 mol / 176 g = 2.84×10^{-3} mols
V = 100 mL = 0.100 L
$K_a = 8.0 \times 10^{-5}$
[ascorbic acid] = 2.84×10^{-3} mols / 0.100 L = 2.84×10^{-2} M

$HC_6H_7O_6$ (*aq*) + H_2O (*l*) ⇋ H_3O^+ (*aq*) + $C_6H_7O_6^-$ (*aq*)

$K_a = [H_3O^+][C_6H_7O_6^-] / [HC_6H_7O_6] = x^2 / 2.84 \times 10^{-2} - x = 8.0 \times 10^{-5}$
$x^2 = 2.272 \times 10^{-6} - 8.0 \times 10^{-5}x$
$x^2 + 8.0 \times 10^{-5}x - 2.272 \times 10^{-6} = 0$
$x = (-8.0 \times 10^{-5} \pm \sqrt{(8.0 \times 10^{-5})^2 - 4(1)(-2.272 \times 10^{-6})}) / 2 = 1.47 \times 10^{-3}$

$[H_3O^+] = 1.47 \times 10^{-3}$
pH = -log $[H_3O^+]$ = 2.83

13. Methylamine is a weak base for which K_b is 4.4×10^{-4}. Calculate the pH of a solution made by dissolving 0.070 mol of methylamine in water and diluting to 800.0 mL.

[methylamine] = 0.070 mol / 0.800 L = 0.085 M

CH_3NH_2 (*aq*) + H_2O (*l*) ⇋ $CH_3NH_3^+$ (*aq*) + OH^- (*aq*)
MA **HMA^+**

$K_b = [HMA^+][OH^-] / [MA] = x^2 / 0.0875 - x = 4.4 \times 10^{-4}$
$x^2 + 4.4 \times 10^{-4}x - 3.85 \times 10^{-5} = 0$
$x = (-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 - 4(1)(-3.85 \times 10^{-5})}) / 2 = 6.0 \times 10^{-3}$

$[OH^-] = 6.0 \times 10^{-3}$
pOH = 2.22
pH = 14 - 2.22 = 11.78

14. A 75.00 mL portion of a solution that is 0.0460 M in $HClO_4$ is treated with 150.00 mL of 0.0230 M KOH (*aq*). Is the pH of the resulting mixture greater than, less than, or equal to 7.0? Explain.

$HClO_4$ (*aq*) + KOH (*aq*) ⇋ ClO_4^- (*aq*) + K^+ (*aq*) + H_2O (*l*)

$HClO_4$ ⇀ 0.075 L × 0.0460 M = 0.00345 mols
KOH ⇀ 0.150 L × 0.0230 M = 0.00345 mols
The numbers of mols of each are equal. Therefore they neutralize each other so the pH = 7.0.