Problems Chapter 15 (Equilibrium)

1. A sample of air with a mole ratio of N_2 to O_2 of 79:21 is heated to 2500 K. When equilibrium is established in a closed container with air initially at 1.00 atm, the mole percent of NO is found to be 1.8%. Calculate K_P for the reaction.
   N_2 (g) + O_2 (g) ⇔ 2 NO (g)

P_{total} initially = 1.00 atm

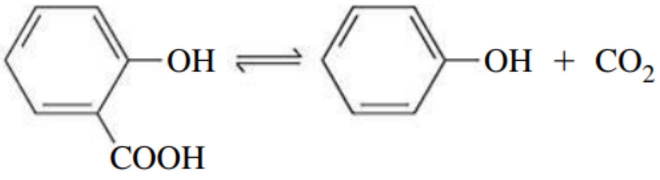
	N_2 (g) +	O_2 (g) ⇔	2 NO (g)
I	0.79 atm	0.21 atm	0
C	- x	- x	+ 2x
E	0.79 - x	0.21 - x	2x

At equilibrium: P_{total} = (0.79 – x) atm + (0.21 – x) atm + (2x) atm = 1.00 atm

P_{NO} at equilibrium = 0.018(1.00 atm) = 0.018 atm = 2x → x = 0.0090
P_{N2} at equilibrium = (0.79 – 0.0090) atm = 0.78 atm
P_{O2} at equilibrium = (0.21 – 0.0090) atm = 0.20 atm

$$\boldsymbol{K_P} = \frac{(0.018\,atm)^2}{(0.78\,atm)(0.20\,atm)} = \mathbf{2.1 \times 10^{-3}}$$

2. The decomposition of salicylic acid to phenol and CO_2 was carried out at 200.0 ˚C, a temperature at which the reactant and products are all gaseous. A 0.300 g sample of salicylic acid was introduced into a 50.0 mL reaction vessel, and equilibrium was established. The equilibrium mixture was rapidly cooled to condense salicylic acid and phenol as solids; the CO_2 (g) was collected and its volume was measured at 20 ˚C and 730 torr. In two independent experiments, the volumes of CO_2 (g) obtained were 48.2 and 48.5 mL, respectively. Calculate K_P for the reaction.



$$0.300\ g\ SA \times \frac{1\ mol\ SA}{138.121\ g\ SA} = 2.17 \times 10^{-3}\ mol\ SA$$

PV = nRT → P(0.0500 L) = (2.17 x 10^{-3} mol)(0.08206 L atm mol^{-1} K^{-1})(473.15 K) → P = 1.69 atm

	SA (g) ⇔	phenol (g) +	CO_2 (g)
I	1.69 atm	0	0
C	- x	+ x	+ x
E	(1.69 – x) atm	x	x

PV = nRT → (730 torr)(0.0484 L) = n(62.36 L torr mol^{-1} K^{-1})(293.15 K) → n = 1.93 x 10^{-3} mol CO_2

$$1.93 \times 10^{-3}\, mol\, CO_2 \times \frac{1.69\, atm}{2.17 \times 10^{-3}\, mol} = 1.50\, atm = x$$

$$\boldsymbol{K_P} = \frac{P_{phenol}P_{CO_2}}{P_{SA}} = \frac{(1.50\, atm)(1.50\, atm)}{(1.69\, atm - 1.50\, atm)} = \mathbf{12.0}$$

3. One of the key reactions in the gasification of coal is the methanation reaction, in which methane is produced from synthesis gas – a mixture of CO and H_2.
   CO (g) + 3 H_2 (g) $\Leftrightarrow$ CH_4 (g) + H_2O (g) BH = –230 kJ; K_c = 190 at 1000 K
   a. Is the equilibrium conversion of synthesis gas to methane favored at higher or lower temperatures? Higher or lower pressures?
   b. Assume you have 4.00 mol of synthesis gas with a 3:1 mol ratio of H_2 (g) to CO (g) in a 15.0 L flask. What will be the mole fraction of CH_4 (g) at equilibrium at 1000 K?

The reaction is exothermic so heat is a product. At **lower temperatures**, with less heat, products will be favored.

The reaction has more moles of gas on the reactant side (4 vs. 2). At **high pressures**, to relieve pressure, the equilibrium will shift to the side with fewer gas moles (here, product side) so the reaction will be favored at high pressures.

Initial [CO] = (1.00 mol)/(15.0 L) = 0.0667 M
Initial [H_2] = (3.00 mol)/(15.0 L) = 0.200 M

	CO (g) +	3 H_2 (g) $\Leftrightarrow$	CH_4 (g) +	H_2O (g)
I	0.0667 M	0.200 M	0	0
C	- x	- 3x	+ x	+ x
E	0.0667 - x	0.200 – 3x	x	x

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = 190 = \frac{x^2}{(0.0667 - x)(0.200 - 3x)^3}$$

x = 0.0424 M
V = 15.0 L

[CO] = 0.0243 M → 0.365 mol CO
[H_2] = 0.0729 M → 1.09 mol H_2
[CH_4] = 0.0424 M → 0.635 mol CH_4
[H_2O] = 0.0424 M → 0.635 mol H_2O

The mole fraction of CH_4 at equilibrium is 0.233

4. A mixture of H_2S (g) and CH_4 (g) in the mole ratio 2:1 was brought to equilibrium at 700 ˚C and a total pressure of 1 atm. On analysis, the equilibrium mixture was found to contain 9.54 x 10^{-3} mol H_2S. The CS_2 present at equilibrium was converted successively to H_2SO_4 and then to $BaSO_4$; 1.42 x 10^{-3} mol $BaSO_4$ was obtained. Use these data to determine K_P at 700 ˚C for the reaction

$$2\ H_2S\ (g) + CH_4\ (g) \Leftrightarrow CS_2\ (g) + 4\ H_2\ (g)$$

$$1.42 \times 10^{-3}\ mol\ BaSO_4 \times \frac{1\ mol\ H_2SO_4}{1\ mol\ BaSO_4} \times \frac{1\ mol\ S}{1\ mol\ H_2SO_4} \times \frac{1\ mol\ CS_2}{2\ mol\ S} = 7.10 \times 10^{-4}\ mol\ CS_2$$

	$2\ H_2S$ (g) +	CH_4 (g) ⇔	CS_2 (g) +	$4\ H_2$ (g)
I	0.667P	0.333P	0	0
C	- 2x	- x	+ x	+ 4x
E	0.667P - 2x	0.333P - x	x	4x

7.10 x 10^{-4} mol CS_2 have a partial pressure of x

$$9.54 \times 10^{-3}\ mol\ H_2S \times \frac{x\ atm}{7.10 \times 10^{-4}\ mol} = 13.4\,x\ atm$$

0.667P – 2x = 13.4x → 0.667P = 15.4x → P = 23.1x
Equilibrium pressure = 1.00 atm = 1.00P – 3x + 5x → 1.00 atm = 23.1x + 2x → 1.00 atm = 25.1x → x = 0.0398 atm

P_{H2S} = 13.4x atm = 0.534 atm
P_{CH4} = 0.333(23.1x) – x = 0.267 atm
P_{CS2} = x = 0.0398 atm
P_{H2} = 4x = 0.159 atm

$$\boldsymbol{K_P} = \frac{P_{CS_2}(P_{H_2})^4}{P_{CH_4}(P_{H_2S})^2} = \frac{(0.0398\ atm)(0.159\ atm)^4}{(0.267\ atm)(0.534\ atm)^2} = \mathbf{3.33 \times 10^{-4}}$$

5. The formation of nitrosyl chloride is given by the following equation:

   $2\ NO\ (g) + Cl_2\ (g) \Leftrightarrow 2\ NOCl\ (g)$ $\quad K_c = 4.6 \times 10^4$ at 298 K

   In a 1.50 L flask, there are 4.125 mol of NOCl and 0.01125 mol of Cl_2 present at equilibrium (298 K).

   a. Determine the partial pressure of NO at equilibrium.
   b. What is the total pressure of the system at equilibrium?

$$[NOCl] = \frac{4.125\ mol}{1.50\ L} = 2.75\ M$$

$$[Cl_2] = \frac{0.1125\ mol}{1.50\ L} = 0.0750\ M$$

$$K_c = 4.6 \times 10^4 = \frac{[NOCl]^2}{[NO]^2[Cl_2]} = \frac{(2.75)^2}{[NO]^2(0.0750)} \rightarrow [NO] = 0.047\ M$$

$$1.50\ L \times \frac{0.047\ mol\ NO}{1\ L} = 0.070\ mol\ NO$$

$$n_{total} = 0.070\ mol\ NO + 4.125\ mol\ NOCl + 0.1125\ mol\ Cl_2 = 4.308\ mol\ gas$$

PV = nRT → P(1.50 L) = (4.308 mol)(0.08206 L atm mol^{-1} K^{-1})(298 K) → **P = 70.2 atm**

$$\boldsymbol{P_{NO}} = Px_{NO} = (70.2\ atm) \times \frac{0.0702\ mol\ NO}{4.308\ mol\ gas} = \mathbf{1.14\ atm}$$

6. Consider the reaction

   IO_4^- (aq) + 2 H_2O (l) ⇔ $H_4IO_6^-$ (aq) $K_c = 3.5 \times 10^{-2}$

   If you start with 25.0 mL of a 0.905 M solution of $NaIO_4$, and then dilute it with water to 500.0 mL, what is the concentration of $H_4IO_6^-$ at equilibrium?

	IO_4^- (aq)	+ H_2O (l)	⇔	$H_4IO_6^-$ (aq)
I	0.905			0
C	− x			+ x
E	0.905 – x			x

$$K_c = 0.035 = \frac{[H_4IO_6^-]}{[IO_4^-]} = \frac{x}{0.905 - x} \rightarrow x = 0.031$$

$[H_4IO_6]$ = 0.031 M

$[IO_4^-]$ = 0.905 M – 0.031 M = 0.874 M

Dilute to 500.0 mL

$M_1V_1 = M_2V_2$ → (0.031 M)(25.0 mL) = $[H_4IO_6]$(500.0 mL) → **$[H_4IO_6^-]$ = 1.5 x 10^{-3} M**

$M_1V_1 = M_2V_2$ → (0.874 M)(25.0 mL) = $[IO_4^-]$ (500.0 mL) → $[IO_4^-]$ = 0.0437 M

$$Q = \frac{[H_4IO_6^-]}{[IO_4^-]} = \frac{0.00153\ M}{0.0437\ M} = 0.035 = K$$

7. The reaction

   PCl_3 (g) + Cl_2 (g) ⇔ PCl_5 (g)

   has K_P = 0.0870 at 300 ˚C. A flask is charged with 0.50 atm PCl_3, 0.50 atm Cl_2, and 0.20 atm PCl_5 at this temperature.
   a. Use the reaction quotient to determine the direction the reaction must proceed to reach equilibrium.
   b. Calculate the equilibrium partial pressures of the gases.
   c. What effect will increasing the volume of the system have on the mole fraction of Cl_2 in the equilibrium mixture?

d. The reaction is exothermic. What effect will increasing the temperature of the system have on the mole fraction of Cl_2 in the equilibrium mixture?

$$Q = \frac{P_{PCl_5}}{P_{PCl_3}P_{Cl_2}} = \frac{0.20}{(0.50)(0.50)} = 0.80 > K_P \rightarrow \boldsymbol{reaction\ will\ shift\ to\ the\ left}$$

	PCl_3 (g)	+ Cl_2 (g)	⇔	PCl_5 (g)
I	0.50 atm	0.50 atm		0.20 atm
C	+ x	+ x		– x
E	0.50 + x	0.50 + x		0.20 – x

$$K = \frac{P_{PCl_5}}{P_{PCl_3}P_{Cl_2}} = 0.0870 = \frac{(0.20 - x)}{(0.50 + x)^2} \rightarrow x = 0.16$$

PCl_5: P = 0.20 atm – 0.16 atm = **0.04 atm**
Cl_2 and PCl_3: P = 0.50 atm + 0.16 atm = **0.66 atm**

Increasing the volume of the system will cause overall pressure to decrease. The reaction will shift to the side with more moles of gas – that is, to the left. So the **mole fraction of Cl_2 will increase**.

For exothermic reactions, K decreases as T increases. So the reaction will shift to the left and the **mole fraction of Cl_2 will increase**.

8. Carbon monoxide replaces oxygen in oxygenated hemoglobin according to the reaction
HbO_2 (aq) + CO (aq) ⇔ HbCO (aq) + O_2 (aq)
   a. Use the reactions and associated equilibrium constants at body temperature to find the equilibrium constant for the reaction just shown.
   Hb (aq) + O_2 (aq) ⇔ HbO_2 (aq) $K_c = 1.8$
   Hb (aq) + CO (aq) ⇔ HbCO (aq) $K_c = 306$
   b. Suppose that an air mixture becomes polluted with CO at a level of 0.10%. Assuming the air contains 20.0% O_2, and that the O_2 and CO ratios that dissolve in the blood are identical to the ratios in the air, what is the ratio of HbCO to HbO_2 in the blood stream? Comment on the toxicity of CO.

HbO_2 (aq) ⇔ ~~Hb (aq)~~ + O_2 (aq) $K_c = 1.8^{-1} = 0.55$
~~Hb (aq)~~ + CO (aq) ⇔ HbCO (aq) $K_c = 306$
K = (0.55)(306) = **170**

$$\boldsymbol{K} = 170 = \frac{[HbCO][O_2]}{[HbO_2][CO]} = \frac{[HbCO](0.20)}{[HbO_2](0.001)} \rightarrow \frac{[HbCO]}{[HbO_2]} = \boldsymbol{0.85}$$

Almost half the Hb units (46% of them) are now bound to CO and cannot transport O_2. Even in such low quantity, CO is very toxic.

9. Consider the exothermic reaction

   $$C_2H_4\ (g) + Cl_2\ (g) \Leftrightarrow C_2H_4Cl_2\ (g)$$

   If you were trying to maximize the amount of $C_2H_4Cl_2$ produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.
   a. Increasing the reaction volume
   b. Removing $C_2H_4Cl_2$ from the reaction mixture as it forms
   c. Lowering the reaction temperature
   d. Adding Cl_2

Increasing the volume of the system will cause overall pressure to decrease. The reaction will shift to the side with more moles of gas – that is, to the **left**. This will cause the amount of product **$C_2H_4Cl_2$ to decrease**, so it's **not a good tactic**.

Removing $C_2H_4Cl_2$ as it forms will decrease Q and cause the reaction to shift to the **right**, producing **more $C_2H_4Cl_2$**. This is a **good tactic**.

For exothermic reactions, K increases as T decreases. So the reaction will shift to the **right**. This will cause the amount of product **$C_2H_4Cl_2$ to increase**, so it is **a good tactic**.

Adding Cl_2 will decrease Q and cause the reaction to shift to the **right**, producing **more $C_2H_4Cl_2$**. This is a **good tactic**.

10. Consider the reaction
    $H_2\ (g) + I_2\ (g) \Leftrightarrow 2\ HI\ (g)$
    A reaction mixture at equilibrium at 175 K contains $P_{H2} = 0.958$ atm, $P_{I2} = 0.877$ atm, and $P_{HI} = 0.020$ atm. A second reaction mixture, also at 175 K, contains $P_{H2} = P_{I2} = 0.621$ atm and $P_{HI} = 0.101$. Is the second reaction at equilibrium? If not, what will be the partial pressure of HI when the reaction reaches equilibrium at 175 K?

$$K_P = \frac{[P_{HI}]^2}{P_{H_2}P_{I_2}} = \frac{(0.020)^2}{(0.958)(0.877)} = 4.8 \times 10^{-4}$$

$$\frac{(0.101)^2}{(0.621)^2} = 0.0264 > K_P \rightarrow reaction\ will\ shift\ to\ the\ left$$

	H_2 (g)	+ I_2 (g)	⇔	2 HI (g)
I	0.621 atm	0.621 atm		0.101 atm
C	+ x	+ x		– 2x
E	0.621 + x	0.621 + x		0.101 – 2x

$$K_P = \frac{(P_{HI})^2}{P_{H_2}P_{I_2}} = 4.8 \times 10^{-4} = \frac{(0.101 - 2x)^2}{(0.621 + x)^2} \rightarrow 0.020 = \frac{0.101 - 2x}{0.621 + x} \rightarrow x = 0.044$$

$\mathbf{P_{HI}}$ = 0.101 atm – 2(0.044 atm) = **0.014 atm**