1. Solid silver is added to a solution with the initial concentrations: $[Ag^+] = 0.200$ M, $[Fe^{2+}] = 0.100$ M, and $[Fe^{3+}] = 0.300$ M. The following reaction occurs, for which $K_c = 2.98$ at 20 °C.

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

What are the ion concentrations when equilibrium is established?

2. Carbon monoxide and chlorine react to form phosgene, which is used in the manufacture of pesticides, herbicides, and plastics. What will be the amount of each substance when equilibrium is established in a reaction mixture that initially has 0.0100 mol CO, 0.0100 mol Cl_2, and 0.100 mol $COCl_2$ in a 10.0 L flask ($K_c = 1200$ at 668 °C)?

$$\underset{\text{carbon monoxide}}{CO(g)} + \underset{\text{chlorine}}{Cl_2(g)} \rightleftharpoons \underset{\text{phosgene}}{COCl_2(g)}$$

3. The value of K_c for the reaction of acetic acid with ethanol is 3.4 at 25 °C. Calculate the molarity of all species present in an equilibrium mixture prepared by mixing 1.0 L of 1.0 M acetic acid with 1.0 L of 1.0 M ethanol.

$$\underset{\text{acetic acid}}{CH_3COOH(aq)} + \underset{\text{ethanol}}{CH_3CH_2OH(aq)} \rightleftharpoons \underset{\text{ethyl acetate}}{CH_3COOCH_2CH_3(aq)} + \underset{\text{water}}{H_2O(l)}$$

4. The air pollutant NO is produced in automobile engines because of the high-temperature reaction between nitrogen and oxygen gas. If the initial concentrations of nitrogen and oxygen gas are 1.40 M, what are the concentrations of all components when the mixture reaches equilibrium at 2300 K ($K_c = 0.0017$)?

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

5. The equilibrium for the Haber process at 472 °C is $K_c = 0.105$. A 2.00 L flask is filled with 0.500 mol of NH_3 and is allowed to reach equilibrium at 472 °C. What are the equilibrium concentrations of all species?

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

6. For a mixture of N_2, O_2 and NO with the following initial concentrations, what will be the equilibrium concentrations of all the species at 2300 K? $[N_2]_i = 0.60$ M; $[O_2]_i = 1.3$ M; $[NO]_i = 2.2$ M. (See problem 4.)

Eq'm Problems

① initial conditions $[Ag^+] = 0.200\ M$, $[Fe^{2+}] = 0.100\ M$, $[Fe^{3+}] = 0.300\ M$

$$Q = \frac{(0.300)}{(0.200)(0.100)} = 15$$

$Q > K$, rxn shifts **left**

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = 2.98 \text{ @ } 20\,°C$$

$$Ag^+ + Fe^{2+} \rightleftharpoons Fe^{3+} + Ag(s)$$

	Ag^+	Fe^{2+}	Fe^{3+}	$Ag(s)$
I	0.200	0.100	0.300	
R	$+x$	$+x$	$-x$	
E	$0.200+x$	$0.100+x$	$0.300-x$	

$$K = \frac{0.300-x}{(0.200+x)(0.100+x)} = \frac{0.3-x}{x^2+0.3x+0.02} = 2.98$$

$$2.98x^2 + 0.894x + 0.0596 = 0.3 - x$$

$$2.98x^2 + 1.894x - 0.2404 = 0$$

$a = 2.98$
$b = 1.894$
$c = -0.2404$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-1.894 \pm \sqrt{6.4528}}{5.96}$$

$$x = \frac{-1.894 \pm 2.5402}{5.96} \Rightarrow x = 0.1084 \text{ or } x = -0.744$$

$$\boxed{\begin{aligned} [Ag^+]_{eqm} &= 0.200 + 0.1084 = 0.308\ M \\ [Fe^{2+}]_{eqm} &= 0.100 + 0.1084 = 0.208\ M \\ [Fe^{3+}]_{eqm} &= 0.300 - 0.1084 = 0.192\ M \end{aligned}}$$

check: $\dfrac{0.192}{(0.308)(0.208)} = 3.00 \approx 2.98$ ✓

(2)

	$CO_{(g)}$ +	$Cl_{2(g)}$ ⇌	$COCl_{2(g)}$
I	0.001	0.001	0.01 ← remember molarity not moles
R	+ x	+ x	− x
E	0.001 + x	0.001 + x	0.01 − x

use this info to choose + so +x is pos

$K_c = 1200$; $Q = \dfrac{0.01}{(0.001)(0.001)} = 10{,}000$

Reaction shifts left!

$$K_c = 1200 = \frac{0.01 - x}{(0.001 + x)(0.001 + x)} = \frac{0.01 - x}{1\times10^{-6} + 0.002x + x^2}$$

$$1.2\times10^{-3} + 2.4x + 1200x^2 = 0.01 - x$$

$$1200x^2 + 3.4x - 8.8\times10^{-3} = 0$$

$a = 1200$

$b = 3.4$

$c = -8.8\times10^{-3}$

$$x = \frac{-3.4 \pm \sqrt{11.56 + 42.24}}{2400}$$

$$x = \frac{-3.4 \pm 7.335}{2400} \; ; \quad x = 1.639\times10^{-3}$$

$$x = -4.47\times10^{-3}$$

$[CO]_{eqm} = 0.00100 + 0.00164 = 0.00264$ M

$[Cl_2]_{eqm} = 0.00100 + 0.00164 = 0.00264$ M

$[COCl_2]_{eqm} = 0.0100 - 0.00164 = 0.00836$ M

check: $\dfrac{0.00836}{(0.00264)(0.00264)} = 1199.5$ ✓

③ $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$

mix $\begin{pmatrix} 1\text{ L} \\ 1.0\,M\ CH_3COOH \end{pmatrix} + \begin{pmatrix} 1\text{ L} \\ 1.0\,M\ C_2H_5OH \end{pmatrix}$ = makes 2 L sol'n
w/ 0.50 M CH_3COOH
0.50 M C_2H_5OH

	CH_3COOH +	C_2H_5OH $\rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
I	0.50	0.50	—	
R	$-x$	$-x$	$+x$	
E	$(0.50-x)$	$(0.50-x)$	x	

$$K_{eq} = 3.4 = \frac{x}{(0.50-x)(0.50-x)} \Longrightarrow 3.4(x^2 - x + 0.25) = x$$

$$3.4x^2 - 3.4x + 0.85 = x$$

$$3.4x^2 - 4.4x + 0.85 = 0$$

$$\left.\begin{array}{l} a = 3.4 \\ b = -4.4 \\ c = 0.85 \end{array}\right\} x = \frac{4.4 \pm \sqrt{19.36 - 11.56}}{2(3.4)}$$

$$x = \frac{4.4 \pm 2.79}{6.8} \Longrightarrow x = 1.06;\ \underline{\underline{0.237}}$$

$$[CH_3COOH]_{eq} = 0.50 - 0.237 = 0.263\ \underline{M}$$

$$[C_2H_5OH]_{eq} = 0.50 - 0.237 = 0.263\ \underline{M}$$

$$[CH_3COOC_2H_5]_{eq} = 0.237\ \underline{M}$$

check: $K = \frac{0.237}{(0.263)(0.263)} = 3.43$

(4) $[N_2]_{initial} = 1.40\ \underline{M}$
$[O_2]_{initial} = 1.4\ \underline{M}$
$K_c = 0.0017$

	N_2	$+ O_2$	$\rightleftharpoons 2\ NO$
I	1.40	1.40	—
R	$-x$	$-x$	$+2x$
E	$1.40-x$	$1.40-x$	$2x$

$$K = \frac{(2x)^2}{(1.40-x)(1.40-x)} = 0.0017$$

could do quadratic, but take square root of both sides.

$$\frac{2x}{1.40-x} = \sqrt{0.0017}$$

$$2x = (1.40-x)(0.0412)$$

$$2x = 0.0577 - 0.0412x$$

$$2.0412x = 0.0577$$

$$x = 0.02828$$

$[N_2]_{eq} = (1.40 - 0.02828)M = 1.37\ \underline{M}$
$[O_2]_{eq} = (1.40 - 0.02828)M = 1.37\ \underline{M}$
$[NO]_{eq} = 2(0.02828)M = 0.0566\ \underline{M}$

Check: $\dfrac{(0.0566)^2}{(1.37)(1.37)} = 1.71\times10^{-3}$ ✓

(5) $K_c = 0.105$

$0.500 \text{ mol } NH_3 / 2L = 0.25 \, \underline{M} \, NH_3$ initially

	N_2 +	$3H_2$ ⇌	$2NH_3$
I	—	—	0.25
R	$+x$	$+3x$	$-2x$
E	x	$3x$	$0.25-2x$

chose "2x" to avoid fractions

$$K = \frac{(0.25-2x)^2}{x(3x)^3} = \frac{(0.25-2x)^2}{27x^4} = 0.105$$

take square root of both sides:

$$\frac{0.25-2x}{x^2(\sqrt{27})} = \sqrt{0.105}$$

$$x^2(\sqrt{27})(\sqrt{0.105}) = 0.25-2x$$

$$1.684x^2 + 2x - 0.25 = 0$$

$a = 1.684$
$b = 2$
$c = -0.25$

$$x = \frac{-2 \pm \sqrt{4+1.684}}{3.368} = \frac{-2 \pm 2.38}{3.368}$$

$x = 0.114$ or $x = 1.30$

$[N_2]_{eq} = 0.114 \, \underline{M}$
$[H_2]_{eq} = 0.342 \, \underline{M}$
$[NH_3]_{eq} = 0.022 \, \underline{M}$

check: $K = \frac{(0.022)^2}{(0.114)(0.342)^3} = 0.106$ ✓

(6) $[N_2]_i = 0.60\ M$ $K_{eq} = 0.0017$

$[O_2]_i = 1.3\ M$

$[NO]_i = 2.2\ M$

First, calculate Q

$$Q = \frac{[NO]_i^2}{[N_2]_i[O_2]_i} = \frac{(2.2)^2}{(0.6)(1.3)}$$

$Q = 6.2$ $(Q > K)$

shift back toward reactants

	N_2	+	O_2	$\rightleftharpoons$	$2\ NO$
I	0.6		1.3		2.2
R	$+x$		$+x$		$-2x$
E	$(0.6+x)$		$(1.3+x)$		$(2.2-2x)$

$$K = \frac{(2.2-2x)^2}{(0.6+x)(1.3+x)} = \frac{4.84 - 8.8x + 4x^2}{0.78 + 1.9x + x^2} = 0.0017$$

$$4x^2 - 8.8x + 4.84 = (0.0017)[x^2 + 1.9x + 0.78]$$

$$4x^2 - 8.8x + 4.84 = 0.0017x^2 + 0.00323x + 0.001326$$

$$3.9983x^2 - 8.80323x + 4.8387 = 0 \quad \begin{cases} a = 3.9983 \\ b = -8.80323 \\ c = 4.8387 \end{cases}$$

$$x = 1.143,\ \underline{1.059}$$

$[N_2]_{eq} = 0.6 + 1.06 = 1.66M = [N_2]_{eq}$

$[O_2]_{eq} = 1.3 + 1.06 = 2.36M = [O_2]_{eq}$

$[NO]_{eq} = 2.2 - 2(1.06) = 0.08M = [NO]_{eq}$

check:

$$K_{eq} \stackrel{?}{=} \frac{[0.08]^2}{[1.66][2.36]} = 0.0016\ \checkmark$$