Chapter 13

13.29 (a) $A_2 + C_2 \rightleftharpoons 2AC$ (most product molecules)

(b) $A_2 + B_2 \rightleftharpoons 2AB$ (fewest product molecules)

13.30 (a) Only rxn. (3), $K_c = \frac{[A][AB]}{[A_2][B]} = \frac{(2)(4)}{(2)(2)} = 2$, is at equil.

(b) $Q_c = \frac{[A][AB]}{[A_2][B]} = \frac{(3)(5)}{(1)(1)} = 15$ for rxn (1)

Since $Q_c > K_c$, the rxn will go in reverse to reach equil.

$Q_c = \frac{[A][AB]}{[A_2][B]} = \frac{(1)(3)}{(3)(3)} = \frac{1}{3}$ for rxn (2)

Since $Q_c < K_c$, the rxn will go in the forward direction.

13.31 (a) $A_2 + 2B \rightleftharpoons 2AB$

(b) The # of AB molecules will increase, because as the volume goes down at a constant temperature, the pressure will increase & the rxn. will shift to the side with fewer molecules to reduce the pressure.

13.37 This equil. mixture has a $K_c \propto \frac{(2)(2)}{(3)^2}$ & is less than 1.

Which means that $k_f < k_r$.

13.40

(a) $K_c = \dfrac{[CO][H_2]^2}{[CH_4][H_2O]}$

(b) $K_c = \dfrac{[ClF_3]^2}{[F_2]^3[Cl_2]}$

(c) $K_c = \dfrac{[HF]^2}{[H_2][F_2]}$

13.41

(a) $K_c = \dfrac{[CH_3CHO]^2}{[C_2H_4]^2[O_2]}$

(b) $K_c = \dfrac{[N_2][O_2]}{[NO]^2}$

(c) $K_c = \dfrac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$

13.44

$$K_c = \frac{[C_2H_5OC_2H_5][H_2O]}{[C_2H_5OH]^2}$$

13.48. The two rxns. are the reverse of each other –

$$K_c(\text{rev}) = \frac{1}{K_c(\text{forward})} = \frac{1}{7.5\times10^{-9}} = 1.3\times10^{8}$$

13.50 $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.5\times10^{-2})(3.2\times10^{-2})}{(8.3\times10^{-3})} = 0.058$

13.60 (a) $K_c = \frac{[CO_2]^3}{[CO]^3}$ [redacted] $K_p = \frac{P_{CO_2}^3}{P_{CO}^3}$

(b) $K_c = \frac{1}{[O_2]^3}$ or $K_p = \frac{1}{P_{O_2}^3}$

(c) $K_c = [SO_3]$ or $K_p = P_{SO_3}$

(d) $K_c = [Ba^{+2}][SO_4^{2-}]$

13.62 (a) Since K_c is very ~~small~~ large, the equil. mixture is mostly product.

(b) Since K_c is very small, the equil. mixture is mostly reactant.

13.63 (a) does not go much in ~~t~~ the forward direction

(b) goes almost to completion –

13.69 $Q_c = \frac{[CO]_t [H_2]_t^3}{[H_2O]_t [CH_4]_t} = \frac{(0.15)(0.20)^3}{(0.035)(0.050)} = 0.69$

The rxn is not at equil. since $Q_c < K_c$ $(0.69 < 4.7)$
The rxn. will proceed from left to right to reach equilibrium

13.70

$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.29$ @ equil $[N_2] = 0.036M$ + $[H_2] = 0.15M$

$[NH_3] = \sqrt{[N_2] \cdot [H_2]^3 \cdot K_c} = \sqrt{0.036 \cdot 0.15^3 \cdot 0.29} =$

$5.9 \times 10^{-3} M$

13.71

$K_c = 2.7 \times 10^2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; Because $[SO_3] = [SO_2]$, then $2.7 \times 10^2 = \frac{1}{[O_2]}$

$[O_2] = 3.7 \times 10^{-3} M$

13.74 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

	PCl_5	PCl_3	Cl_2
start	0.160	-	-
Δ	-x	+x	+x
equil.	0.160-x	x	x

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 5.8\times10^{-2} = \frac{x^2}{0.160-x}$$

$$x^2 + (5.8\times10^{-2})x - 0.00928 = 0$$

$$x = \frac{-5.8\times10^{-2} \pm \sqrt{(5.8\times10^{-2})^2 - 4(1)(-0.00928)}}{2(1)} = \frac{-5.8\times10^{-2} \pm 0.2}{2}$$

$x = 0.071$ & ~~-0.129~~ $[PCl_3] = [Cl_2] = x = \underline{0.071\,M}$

$[PCl_5] = 0.160 - x = 0.160 - 0.071 = \underline{0.089}\,M$

13.78 $ClF_3(g) \rightleftharpoons ClF(g) + F_2(g)$

	ClF_3	ClF	F_2
start	1.47	-	-
Δ	-x	+x	+x
equil.	1.47-x	x	x

$$K_p = \frac{P_{ClF}\,P_{F_2}}{P_{ClF_3}} = 0.140 = \frac{x^2}{1.47-x}$$

$$x^2 + 0.140x - 0.2058 = 0$$

$$x = \frac{-0.140 \pm \sqrt{0.140^2 - 4\cdot1\cdot-.2058}}{2(1)} = \frac{-0.140 \pm 0.918}{2}$$

$x = 0.389$ & ~~-0.529~~ $P_{ClF} = P_{F_2} = x = 0.389$ atm, $P_{ClF_3} = 1.47 - 0.389 =$ ... atm

13.80 (a) if Cl^- is added, $AgCl(s)$ increases

(b) Ag^+ is added, $AgCl(s)$ increases.

(c) Ag^+ is removed, $AgCl(s)$ decreases

(d) Cl^- removed, $AgCl(s)$ decreases.

if $[Cl^-]\uparrow$ Q_c increases to a value greater than K_c, therefore the rxn must go from right to left. to decrease $AgCl(s)$

13.81

(a) ClNO added, $NO_2 \downarrow$

(b) NO added, $NO_2 \uparrow$

(c) NO removed, $NO_2 \downarrow$

(d) $ClNO_2$ added, $NO_2 \uparrow$

Adding $ClNO_2$ decrease Q_c, the rxn must shift from left to right to ~~[illegible]~~ reach equilibrium, thus increasing the $\underline{\underline{NO_2}}$ conc.

13.83

As the Volume $\uparrow$, the Pressure $\downarrow$ @ constant temp.

(a) the rxn will shift to the side with larger # of molecules - since the stress is the decrease in pressure - or an increase in volume. — Toward Products

(b) The rxn will shift to the reactants, since that is the side with the greater # of moles..

(c) This rxn is not altered by changes in volume or pressure, since there are equal # of molecules on Both sides — No change.

13.86- (a) HCl is a source of Cl^-, the rxn. shifts left, the equil. $[CoCl_4^{2-}]$ increases

(b) $Co(NO_3)_2$ is a source of $Co(H_2O)_6^{+2}$, the rxn. shifts left, the equil. conc. of $[CoCl_4^{2-}]$ increases.

(c) All conc. will initially decrease & the rxn. will shift right, the equil. conc. of $[CoCl_4^{2-}]$ decreases

(d) For an exothermic rxn. the rxn. shifts to the left when the temp increases - the equil $(CoCl_4^{2-})$ increases

13.87

(a) $Fe(NO_3)_3$ is a source of Fe^{+3}. Fe^{+3} added; the $FeCl^{2+}$ conc. increases.

(b) Cl^- removed; the $FeCl^{2+}$ conc. decreases.

(c) An endothermic rxn. shifts to the right as the temperature increases; the $FeCl^{2+}$ conc. increases.

(d) A catalyst does not affect the composition of the equil. mixture; no change in $FeCl^{2+}$ conc.

13.52 $K_c = k_f / k_r = 0.13 / 6.2 \times 10^{-4} = 210$

13.99 V = 5.0 L

$[H_2] = [I_2] = 1\,mol/5L = 0.2M$

$[HI] = 2.5\,mol/5L = 0.5M$

	$H_2(g)$	+ $I_2(g)$	$\rightleftharpoons$ 2 HI(g)
start	0.2	0.2	0.5
Δ	−x	−x	+2x
equil.	0.2−x	0.2−x	0.5+2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 129 = \frac{(0.50+2x)^2}{(0.20-x)^2}$$

$$\sqrt{129} = \sqrt{\frac{(0.50+2x)^2}{(0.2-x)^2}} = 11.4 = \frac{0.50+2x}{0.2-x}\ ;\ x = 0.133$$

$[H_2] = [I_2] = 0.2 - 0.133 = 0.067M$; $[HI] = 0.5 + 2(0.133) = 0.76$

13.104

$[PCl_5] = 1\,mol/5L = 0.2M$

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	+ $Cl_2(g)$
start	0.2	−	−
Δ	−(0.2)(0.7850)	+(0.2)(0.7850)	+(0.2)(0.7850)
equil.	0.0430	+0.1570	+0.1570

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.1570)^2}{(0.0430)} = 0.573$$

$\Delta n = 1$ + $K_p = K_c(RT)^{\Delta n} = 0.573(0.0821)(500) = 23.5$

13.104 cont

(b) $Q_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.150)(0.60)}{(0.500)} = 0.18$

Since $Q_c < K_c$ the rxn will proceed to the right to reach equilibrium

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

	$PCl_5(g)$	$PCl_3(g)$	$Cl_2(g)$
start	0.50	0.150	0.600
Δ	−x	+x	+x
equil.	0.5 − x	0.150 + x	0.150 + x

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.573 = \frac{(0.150+x)(0.600+x)}{(0.50-x)}$;

$x^2 = 1.323x - 0.1965 = 0$

$x = \frac{-1.323 \pm \sqrt{1.323^2 - 4 \cdot 1 \cdot (-0.1965)}}{2(1)} = \frac{-1.323 \pm 1.593}{2}$

$x = ~~-1.458~~ + 0.135$

$[PCl_5] = 0.5 - x = 0.5 - 0.135 = 0.365M$

$[PCl_3] = 0.150 + x = 0.150 - .135 = 0.285M$

$[Cl_2] = 0.60 + x = 0.60 + 0.135 = 0.735M.$

$Q_p = \frac{(2.0)(1.50)}{(3.0)} = 1$, $Q_p < K_p$ ∴ rxn. goes toward products.

13.105

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

	PCl_5	PCl_3	Cl_2
start	3.0	2.0	1.5
Δ	−x	+x	+x
equil.	3.0−x	2.0+x	1.5+x

$$K_p = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}} = \frac{(1.5+x)(2.0+x)}{(3.0-x)} = 1.42 \Rightarrow x^2 + 4.92x - 1.26 = 0$$

using the quadratic −

$$x = \frac{-4.92 \pm \sqrt{(4.92^2) - 4(1)(-1.26)}}{2(1)} = \frac{-4.92 \pm 5.41}{2}$$

$x = 0.245$ ~~+ −5.165~~

$P_{PCl_5} = 3.0 - x = 2.76$ atm

$P_{PCl_3} = 2.0 + x = 2.24$ atm

$P_{Cl_2} = 1.5 + x = 1.74$ atm.

$P_{total} = P_{Cl_5} + P_{Cl_2} + P_{PCl_3} = 2.76 + 2.24 + 1.74 = 6.74$ atm.

15.112 (a) $PV = nRT \rightarrow n_{total} = \frac{PV}{RT} = \frac{(0.588\,atm)(1.0\,L)}{(0.0821\,\frac{L\cdot atm}{mol\,K})(300\,K)} = 0.0239$ mol

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

	$2\,NOBr(g)$	$2\,NO(g)$	$Br_2(g)$
start	0.2	—	—
Δ	$-2x$	$+2x$	$+x$
equil.	$0.2-2x$	$2x$	x

$n_{total} = 0.0239\,mol = (0.02-2x) + 2x + x = 0.2 + x$

$x = 0.0239 - 0.02 = 0.0039$ mol.

Because the volume is 1.0 L, the molarity equals the # of moles.

$[NOBr] = 0.02 - 2x = 0.02 - 2(0.0039) = 0.0122\,M$

$[NO] = 2x = 2(0.0039) = 0.0078\,M$

$[Br_2] = x = 0.0039\,M$

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{(0.0078)^2(0.0039)}{(0.0122)^2} = 1.6\times10^{-3}$$

(b) $\Delta n = 3 - 2 = 1$, $K_p = K_c(RT) = (1.6\times10^{-3})(0.0821)(300)$

$= \underline{0.039}$

13.116 $2NO_2(g) \rightleftharpoons N_2O_4(g)$

$\Delta n = 1-2=-1 \quad K_p = K_c(RT)^{-1} = [(216)(0.0821)(298)]^{-1}$

$= 8.83$

$K_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = 8.83$

Let $X = P_{N_2O_4}$ & $Y = P_{NO_2}$

$P_{total} = 1.50$ atm $= X + Y$ & $\frac{X}{Y^2} = 8.83$

Now using these 2 equations we can solve for X & Y

$X = 1.50 - Y$

$\frac{1.50-Y}{Y^2} = 8.83 \longrightarrow 8.83Y^2 + Y - 1.50 = 0$

$Y = \frac{-1 \pm \sqrt{1^2 - 4(8.83)(-1.50)}}{2(8.83)} = \frac{-1 \pm 7.35}{17.7}$

$Y =$ ~~$-.472$~~ & 0.359

$Y = P_{NO_2} = 0.359$ atm

$X = P_{N_2O_4} = 1.50 - Y = 1.5 - 0.359 = 1.14$ atm

13.125 - $H_2O = 18.015\ g\ mol^{-1} \rightarrow 125.4\ g\ H_2O = 6.96\ mol\ H_2O$

since mol CO = mol H_2O = 6.96 mol.

$$P_{CO} = P_{H_2O} = \frac{nRT}{V} = \frac{(6.96\ mol)(0.0821\ \frac{L\cdot atm}{mol\ K})(700)}{10.0\ L} = 40.0\ atm$$

	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
start	40.0	40.0	–	–
equil.	9.80	9.80	40.0−9.80 = 30.2	40.0−9.80 = 30.2

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{30.2^2}{9.80^2} = 9.50$$

(b) 31.4 g $H_2O \Rightarrow 1.743$ mol H_2O, $P_{H_2O} = \frac{nRT}{V} = \frac{(1.743)(0.0821)(700)}{10.0\ L}$
$= 10.0\ atm$

P_{H_2O} has increased by 10.0 atm, + a new equilibrium will be established.

	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
start	9.80	9.80+10.0	30.2	30.2
Δ	−x	−x	+x	+x
equil.	9.8−x	19.8−x	30.2+x	30.2+x

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = 9.50 = \frac{(30.2+x)(30.2+x)}{(9.80-x)(19.80-x)}$$

cont - Nxt. Pg →

13.125 cont.

$$8.50x^2 - 341.6x + 931.34 = 0$$

$$x = \frac{-(-341.6) \pm \sqrt{(-341.6)^2 - 4(8.50)(931.34)}}{2(8.50)} =$$

$$\frac{341.6 \pm 291.6}{17.0} \Rightarrow x = 37.25 \text{ (too large)},\ 2.94$$

$$P_{CO} = 9.80 - x = 9.80 - 2.94 = 6.86 \text{ atm}$$

$$P_{H_2O} = 19.8 - x = 19.8 - 2.94 = 16.9 \text{ atm}$$

$$P_{CO_2} = P_{H_2} = 30.2 + x = 30.2 + 2.94 = 33.1 \text{ atm}$$

$$n_{H_2} = \frac{PV}{RT} = \frac{(33.1 \text{ atm})(10.0 \text{ L})}{\left(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol K}}\right)(700)} = 5.76 \text{ mol } H_2$$

$$\frac{5.76 \text{ mol } H_2}{10.0 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times \frac{6.02 \times 10^{23} \text{ } H_2 \text{ molecules}}{1 \text{ mol } H_2} =$$

$$3.47 \times 10^{20} \text{ } H_2 \text{ molecules/cm}^3$$