CHAPTER 15
PRINCIPLES OF CHEMICAL EQUILIBRIUM
PRACTICE EXAMPLES

1A **(E)** The reaction is as follows:

$$2Cu^{2+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Cu^{+}(aq) + Sn^{4+}(aq)$$

Therefore, the equilibrium expression is as follows:

$$K = \frac{\left[Cu^{+}\right]^2\left[Sn^{4+}\right]}{\left[Cu^{2+}\right]^2\left[Sn^{2+}\right]}$$

Rearranging and solving for Cu^{2+}, the following expression is obtained:

$$\left[Cu^{2+}\right] = \left(\frac{\left[Cu^{+}\right]^2\left[Sn^{4+}\right]}{K\left[Sn^{2+}\right]}\right)^{1/2} = \left(\frac{x^2 \cdot x}{(1.48)x}\right)^{1/2} = \frac{x}{1.22}$$

1B **(E)** The reaction is as follows:

$$2Fe^{3+}(aq) + Hg_2^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + 2Hg^{2+}(aq)$$

Therefore, the equilibrium expression is as follows:

$$K = \frac{\left[Fe^{2+}\right]^2\left[Hg^{2+}\right]^2}{\left[Fe^{3+}\right]^2\left[Hg_2^{2+}\right]} = \frac{(0.0025)^2(0.0018)^2}{(0.015)^2(x)} = 9.14\times10^{-6}$$

Rearranging and solving for Hg_2^{2+}, the following expression is obtained:

$$\left[Hg_2^{2+}\right] = \frac{\left[Fe^{2+}\right]^2\left[Hg^{2+}\right]^2}{\left[Fe^{3+}\right]^2 \cdot K} = \frac{(0.0025)^2(0.0018)^2}{(0.015)^2\left(9.14\times10^{-6}\right)} = 0.009847 \approx 0.0098\text{ M}$$

2A **(E)** The example gives $\underline{K_c} = 5.8\times10^5$ for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$.
The reaction we are considering is one-third of this reaction. If we divide the reaction by 3, we should take the cube root of the equilibrium constant to obtain the value of the equilibrium constant for the "divided" reaction: $K_{c3} = \sqrt[3]{K_c} = \sqrt[3]{5.8\times10^5} = 8.3\times10^2$

2B **(E)** First we reverse the given reaction to put $NO_2(g)$ on the reactant side. The new equilibrium constant is the inverse of the given one.

$$NO_2(g) \rightleftharpoons NO(g) + \tfrac{1}{2}O_2(g) \qquad K_c' = 1/(1.2\times10^2) = 0.0083$$

Then we double the reaction to obtain 2 moles of $NO_2(g)$ as reactant. The equilibrium constant is then raised to the second power.

$$2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g) \qquad K_c = (0.00833)^2 = 6.9\times10^{-5}$$

3A **(E)** We use the expression $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$. In this case, $\Delta n_{gas} = 3+1-2 = 2$ and thus we have

$$K_p = K_c\left(RT\right)^2 = 2.8\times10^{-9}\times\left(0.08314\times298\right)^2 = 1.7\times10^{-6}$$

3B **(M)** We begin by writing the K_p expression. We then substitute $P = \left(n/V\right)RT = [concentration]RT$ for each pressure. We collect terms to obtain an expression relating K_c and K_p, into which we substitute to find the value of K_c.

$$K_p = \frac{\{P(H_2)\}^2\{P(S_2)\}}{\{P(H_2S)\}^2} = \frac{([H_2]RT)^2([S_2]RT)}{([H_2S]RT)^2} = \frac{[H_2]^2[S_2]}{[H_2S]^2}RT = K_cRT$$

The same result can be obtained by using $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$, since $\Delta n_{gas} = 2+1-2 = +1$.

$$K_c = \frac{K_p}{RT} = \frac{1.2\times10^{-2}}{0.08314\ \times\left(1065+273\right)} = 1.1\times10^{-4}$$

But the reaction has been reversed and halved. Thus $K_{\text{final}} = \sqrt{\frac{1}{K_c}} = \sqrt{\frac{1}{1.1\times10^{-4}}} = \sqrt{9091} = 95$

4A **(E)** We remember that neither solids, such as $Ca_5(PO_4)_3OH(s)$, nor liquids, such as $H_2O(l)$, appear in the equilibrium constant expression. Concentrations of products appear in the numerator, those of reactants in the denominator. $K_c = \frac{\left[Ca^{2+}\right]^5\left[HPO_4{}^{2-}\right]^3}{\left[H^+\right]^4}$

4B **(E)** First we write the balanced chemical equation for the reaction. Then we write the equilibrium constant expressions, remembering that gases and solutes in aqueous solution appear in the K_c expression, but pure liquids and pure solids do not.

$$3\ Fe(s) + 4\ H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\ H_2(g)$$

$K_p = \frac{\{P(H_2)\}^4}{\{P(H_2O)\}^4}$ $\qquad$ $K_c = \frac{[H_2]^4}{[H_2O]^4}$ $\qquad$ Because $\Delta n_{gas} = 4-4 = 0$, $K_p = K_c$

5A **(M)** We compute the value of Q_c. Each concentration equals the mass (m) of the substance divided by its molar mass (this quotient is the amount of the substance in moles) and further divided by the volume of the container.

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\dfrac{m \times \dfrac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2}}{V} \times \dfrac{m \times \dfrac{1 \text{ mol } H_2}{2.0 \text{ g } H_2}}{V}}{\dfrac{m \times \dfrac{1 \text{ mol CO}}{28.0 \text{ g CO}}}{V} \times \dfrac{m \times \dfrac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}}{V}} = \frac{\dfrac{1}{44.0 \times 2.0}}{\dfrac{1}{28.0 \times 18.0}} = \frac{28.0 \times 18.0}{44.0 \times 2.0} = 5.7 > 1.00 = K_c$$

(In evaluating the expression above, we cancelled the equal values of V , and we also cancelled the equal values of m.) Because the value of Q_c is larger than the value of K_c, the reaction will proceed to the left to reach a state of equilibrium. Thus, at equilibrium there will be greater quantities of reactants, and smaller quantities of products than there were initially.

5B **(M)** We compare the value of the reaction quotient, Q_p, to that of K_p.

$$Q_p = \frac{\{P(PCl_3)\}\{P(Cl_2)\}}{\{P(PCl_5\}} = \frac{2.19 \times 0.88}{19.7} = 0.098$$

$$K_p = K_c\left(RT\right)^{2-1} = K_c\left(RT\right)^1 = 0.0454 \times \left(0.08206 \times (261+273)\right)^1 = 1.99$$

Because $Q_c < K_c$, the net reaction will proceed to the right, forming products and consuming reactants.

6A **(E)** $O_2(g)$ is a reactant. The equilibrium system will shift right, forming product in an attempt to consume some of the added $O_2(g)$ reactant. Looked at in another way, $[O_2]$ is increased above its equilibrium value by the addition of oxygen. This makes Q_c smaller than K_c. (The $[O_2]$ is in the denominator of the expression.) And the system shifts right to drive Q_c back up to K_c, at which point equilibrium will have been achieved.

6B **(M)**

(a) The position of an equilibrium mixture is affected only by changing the concentration of substances that appear in the equilibrium constant expression, $K_c = [CO_2]$. Since CaO(s) is a pure solid, its concentration does not appear in the equilibrium constant expression and thus adding extra CaO(s) will have no direct effect on the position of equilibrium.

(b) The addition of $CO_2(g)$ will increase $[CO_2]$ above its equilibrium value. The reaction will shift left to alleviate this increase, causing some $CaCO_3(s)$ to form.

(c) Since $CaCO_3$(s) is a pure solid like CaO(s), its concentration does not appear in the equilibrium constant expression and thus the addition of any solid $CaCO_3$ to an equilibrium mixture will not have an effect upon the position of equilibrium.

7A **(E)** We know that a decrease in volume or an increase in pressure of an equilibrium mixture of gases causes a net reaction in the direction producing the smaller number of moles of gas. In the reaction in question, that direction is to the left: one mole of $N_2O_4(g)$ is formed when two moles of $NO_2(g)$ combine. Thus, decreasing the cylinder volume would have the initial effect of doubling both $[N_2O_4]$ and $[NO_2]$. In order to reestablish equilibrium, some NO_2 will then be converted into N_2O_4. Note, however, that the NO_2 concentration will still ultimately end up being higher than it was prior to pressurization.

7B **(E)** In the balanced chemical equation for the chemical reaction, $\Delta n_{\text{gas}} = (1+1)-(1+1)=0$. As a consequence, a change in overall volume or total gas pressure will have no effect on the position of equilibrium. In the equilibrium constant expression, the two partial pressures in the numerator will be affected to exactly the same degree, as will the two partial pressures in the denominator, and, as a result, Q_p will continue to equal K_p.

8A **(E)** The cited reaction is endothermic. Raising the temperature on an equilibrium mixture favors the endothermic reaction. Thus, $N_2O_4(g)$ should decompose more completely at higher temperatures and the amount of $NO_2(g)$ formed from a given amount of $N_2O_4(g)$ will be greater at high temperatures than at low ones.

8B **(E)** The $NH_3(g)$ formation reaction is $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightarrow NH_3(g)$, $\Delta H^\circ = -46.11$ kJ/mol. This reaction is an exothermic reaction. Lowering temperature causes a shift in the direction of this exothermic reaction to the right toward products. Thus, the equilibrium $[NH_3(g)]$ will be greater at $100^\circ C$.

9A **(E)** We write the expression for K_c and then substitute expressions for molar concentrations.

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{0.22}{3.00}\right)^2 \frac{0.11}{3.00}}{\left(\frac{2.78}{3.00}\right)^2} = 2.3\times10^{-4}$$

9B **(M)** We write the equilibrium constant expression and solve for $[N_2O_4]$.

$$K_c = 4.61\times10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} \qquad [N_2O_4] = \frac{[NO_2]^2}{4.61\times10^{-3}} = \frac{(0.0236)^2}{4.61\times10^{-3}} = 0.121\text{ M}$$

Then we determine the mass of N_2O_4 present in 2.26 L.

$$N_2O_4 \text{ mass} = 2.26\text{ L}\times\frac{0.121\text{ mol }N_2O_4}{1\text{ L}}\times\frac{92.01\text{ g }N_2O_4}{1\text{ mol }N_2O_4} = 25.2\text{ g }N_2O_4$$

10A **(M)** We use the initial-change-equilibrium setup to establish the amount of each substance at equilibrium. We then label each entry in the table in the order of its determination (1st, 2nd, 3rd, 4th, 5th), to better illustrate the technique. We know the initial amounts of all substances (1st). There are no products at the start.

Because ''initial''+ ''change''= ''equilibrium'', the equilibrium amount (2nd) of $Br_2(g)$ enables us to determine "change" (3rd) for $Br_2(g)$. We then use stoichiometry to write other entries (4th) on the "change" line. And finally, we determine the remaining equilibrium amounts (5th).

Reaction:	$2\ NOBr(g)$	$\rightleftharpoons$ $2\ NO(g)$	+ $Br_2(g)$
Initial:	1.86 mol (1st)	0.00 mol (1st)	0.00 mol (1st)
Change:	-0.164 mol (4th)	$+0.164$ mol (4th)	$+0.082$ mol (3rd)
Equil.:	1.70 mol (5th)	0.164 mol (5th)	0.082 mol (2nd)

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{\left(\frac{0.164}{5.00}\right)^2\left(\frac{0.082\text{ mol}}{5.00}\right)}{\left(\frac{1.70}{5.00}\right)^2} = 1.5\times10^{-4}$$

Here, $\Delta n_{gas} = 2+1-2 = +1.\quad K_p = K_c(RT)^{+1} = 1.5\times10^{-4}\times(0.08314\times298) = 3.7\times10^{-3}$

10B **(M)** Use the amounts stated in the problem to determine the equilibrium concentration for each substance.

Reaction:	$2\ SO_3(g)$	$\rightleftharpoons$ $2\ SO_2(g)$	+ $O_2(g)$
Initial:	0 mol	0.100 mol	0.100 mol
Changes:	$+0.0916$ mol	-0.0916 mol	$-0.0916/2$ mol
Equil.:	0.0916 mol	0.0084 mol	0.0542 mol
Concentrations:	$\frac{0.0916\text{ mol}}{1.52\text{ L}}$	$\frac{0.0084\text{ mol}}{1.52\text{ L}}$	$\frac{0.0542\text{ mol}}{1.52\text{ L}}$
Concentrations:	0.0603 M	0.0055 M	0.0357 M

We use these values to compute K_c for the reaction and then the relationship $K_p = K_c(RT)^{\Delta n_{gas}}$ (with $\Delta n_{gas} = 2+1-2 = +1$) to determine the value of K_p.

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(0.0055)^2(0.0357)}{(0.0603)^2} = 3.0\times10^{-4}$$

$$K_p = 3.0\times10^{-4}\times(0.08314\times900) \simeq 0.022$$

11A **(M)** The equilibrium constant expression is $K_p = P\{H_2O\}P\{CO_2\} = 0.231$ at $100\,^\circ C$. From the balanced chemical equation, we see that one mole of $H_2O(g)$ is formed for each mole of $CO_2(g)$ produced. Consequently, $P\{H_2O\} = P\{CO_2\}$ and $K_p = \left(P\{CO_2\}\right)^2$. We solve this expression for $P\{CO_2\}$: $P\{CO_2\} = \sqrt{(P\{CO_2\})^2} = \sqrt{K_p} = \sqrt{0.231} = 0.481$ atm.

11B **(M)** The equation for the reaction is $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, $K_p = 0.108$ at $25^\circ C$. The two partial pressures do not have to be equal at equilibrium. The only instance in which they must be equal is when the two gases come solely from the decomposition of $NH_4HS(s)$. In this case, some of the $NH_3(g)$ has come from another source. We can obtain the pressure of $H_2S(g)$ by substitution into the equilibrium constant expression, since we are given the equilibrium pressure of $NH_3(g)$.

$K_p = P\{H_2S\}P\{NH_3\} = 0.108 = P\{H_2S\} \times 0.500 \text{ atm } NH_3 \qquad P\{H_2S\} = \dfrac{0.108}{0.500} = 0.216$ atm

So, $P_{total} = P_{H_2S} + P_{NH_3} = 0.216$ atm + 0.500 atm = 0.716 atm

12A **(M)** We set up this problem in the same manner that we have previously employed, namely designating the equilibrium amount of HI as $2x$. (Note that we have used the same multipliers for x as the stoichiometric coefficients.)

Equation:	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\,HI(g)$
Initial:	0.150 mol		0.200 mol		0 mol
Changes:	$-x$ mol		$-x$ mol		$+2x$ mol
Equil:	$(0.150-x)$ mol		$(0.200-x)$ mol		$2x$ mol

$$K_c = \frac{\left(\dfrac{2x}{15.0}\right)^2}{\dfrac{0.150-x}{15.0}\times\dfrac{0.200-x}{15.0}} = \frac{(2x)^2}{(0.150-x)(0.200-x)} = 50.2$$

We substitute these terms into the equilibrium constant expression and solve for x.

$$4x^2 = (0.150-x)(0.200-x)50.2 = 50.2\left(0.0300 - 0.350x + x^2\right) = 1.51 - 17.6x + 50.2x^2$$

$0 = 46.2x^2 - 17.6x + 1.51$ Now we use the quadratic equation to determine the value of x.

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{17.6 \pm \sqrt{(17.6)^2 - 4\times 46.2 \times 1.51}}{2\times 46.2} = \frac{17.6 \pm 5.54}{92.4} = 0.250 \text{ or } 0.131$$

The first root cannot be used because it would afford a negative amount of H_2 (namely, 0.150-0.250 = -0.100). Thus, we have $2 \times 0.131 = 0.262$ mol HI at equilibrium. We check by substituting the amounts into the K_c expression. (Notice that the volumes cancel.) The slight disagreement in the two values (52 compared to 50.2) is the result of rounding error.

$$K_c = \frac{(0.262)^2}{(0.150 - 0.131)(0.200 - 0.131)} = \frac{0.0686}{0.019 \times 0.069} = 52$$

12B **(D)**

(a) The equation for the reaction is $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ and $K_c = 4.61 \times 10^{-3}$ at $25^\circ C$. In the example, this reaction is conducted in a 0.372 L flask. The effect of moving the mixture to the larger, 10.0 L container is that the reaction will be shifted to produce a greater number of moles of gas. Thus, $NO_2(g)$ will be produced and $N_2O_4(g)$ will dissociate. Consequently, the amount of N_2O_4 will decrease.

(b) The equilibrium constant expression, substituting 10.0 L for 0.372 L, follows.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{10.0}\right)^2}{\frac{0.0240 - x}{10.0}} = \frac{4x^2}{10.0(0.0240 - x)} = 4.61 \times 10^{-3}$$

This can be solved with the quadratic equation, and the sensible result is $x = 0.0118$ moles. We can attempt the method of successive approximations. *First*, assume that $x << 0.0240$. We obtain:

$$x = \frac{\sqrt{4.61 \times 10^{-3} \times 10.0\ (0.0240 - 0)}}{4} = \sqrt{4.61 \times 10^{-3} \times 2.50\ (0.0240 - 0)} = 0.0166$$

Clearly x is not much smaller than 0.0240. So, *second,* assume $x \approx 0.0166$. We obtain:

$$x = \sqrt{4.61 \times 10^{-3} \times 2.50 (0.0240 - 0.0166)} = 0.00925$$

This assumption is not valid either. So, *third*, assume $x \approx 0.00925$. We obtain:

$$x = \sqrt{4.61 \times 10^{-3} \times 2.50 (0.0240 - 0.00925)} = 0.0130$$

Notice that after each cycle the value we obtain for x gets closer to the value obtained from the roots of the equation. The values from the next several cycles follow.

Cycle	4th	5th	6th	7th	8th	9th	10th	11th
x value	0.0112	0.0121	0.0117	0.0119	0.01181	0.01186	0.01183	0.01184

The amount of N_2O_4 at equilibrium is 0.0118 mol, less than the 0.0210 mol N_2O_4 at equilibrium in the 0.372 L flask, as predicted.

13A **(M)** Again we base our solution on the balanced chemical equation.

Equation:	$Ag^{+}(aq) +$	$Fe^{2+}(aq) \rightleftharpoons$	$Fe^{3+}(aq) + Ag(s)$	$K_c = 2.98$
Initial:	0 M	0 M	1.20 M	
Changes:	$+x$ M	$+x$ M	$-x$ M	
Equil:	x M	x M	$(1.20-x)$ M	

$$K_c = \frac{[Fe^{3+}]}{[Ag^{+}][Fe^{2+}]} = 2.98 = \frac{1.20-x}{x^2} \quad 2.98\ x^2 = 1.20 - x \quad 0 = 2.98x^2 + x - 1.20$$

We use the quadratic formula to obtain a solution.

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-1.00 \pm \sqrt{(1.00)^2 + 4 \times 2.98 \times 1.20}}{2 \times 2.98} = \frac{-1.00 \pm 3.91}{5.96} = 0.488 \text{ M or} -0.824 \text{ M}$$

A negative root makes no physical sense. We obtain the equilibrium concentrations from *x*.

$$[Ag^{+}] = [Fe^{2+}] = 0.488 \text{ M} \qquad [Fe^{3+}] = 1.20 - 0.488 = 0.71 \text{ M}$$

13B **(M)** We first calculate the value of Q_c to determine the direction of the reaction.

$$Q_c = \frac{[V^{2+}][Cr^{3+}]}{[V^{3+}][Cr^{2+}]} = \frac{0.150 \times 0.150}{0.0100 \times 0.0100} = 225 < 7.2 \times 10^2 = K_c$$

Because the reaction quotient has a smaller value than the equilibrium constant, a net reaction to the right will occur. We now set up this solution as we have others, heretofore, based on the balanced chemical equation.

	$V^{3+}(aq)$	$+\ Cr^{2+}(aq)$	$\rightleftharpoons\ V^{2+}(aq)$	$+\ Cr^{3+}(aq)$
initial	0.0100 M	0.0100 M	0.150 M	0.150 M
changes	$-x$ M	$-x$ M	$+x$ M	$+x$ M
equil	$(0.0100 - x)$M	$(0.0100 - x)$M	$(0.150 + x)$M	$(0.150 + x)$M

$$K_c = \frac{[V^{2+}][Cr^{3+}]}{[V^{3+}][Cr^{2+}]} = \frac{(0.150+x)\times(0.150+x)}{(0.0100-x)\times(0.0100-x)} = 7.2 \times 10^2 = \left(\frac{0.150+x}{0.0100-x}\right)^2$$

If we take the square root of both sides of this expression, we obtain

$$\sqrt{7.2 \times 10^2} = \frac{0.150+x}{0.0100-x} = 27$$

$0.150 + x = 0.27 - 27x$ which becomes $28x = 0.12$ and yields 0.0043 M. Then the equilibrium concentrations are: $[V^{3+}] = [Cr^{2+}] = 0.0100 \text{ M} - 0.0043 \text{ M} = 0.0057 \text{ M}$

$$[V^{2+}] = [Cr^{3+}] = 0.150 \text{ M} + 0.0043 \text{ M} = 0.154 \text{ M}$$

INTEGRATIVE EXAMPLE

A. **(E)** We will determine the concentration of F6P and the final enthalpy by adding the two reactions:

$$C_6H_{12}O_6 + ATP \rightleftharpoons G6P + ADP$$
$$G6P \rightleftharpoons F6P$$
$$\overline{C_6H_{12}O_6 + ATP \rightleftharpoons ADP + F6P}$$

$\Delta H_{TOT} = -19.74\ kJ\cdot mol^{-1} + 2.84\ kJ\cdot mol^{-1} = -16.9\ kJ\cdot mol^{-1}$

Since the overall reaction is obtained by adding the two individual reactions, then the overall reaction equilibrium constant is the product of the two individual K values. That is,
$K = K_1 \cdot K_2 = 1278$

The equilibrium concentrations of the reactants and products is determined as follows:

	$C_6H_{12}O_6$	+	ATP	$\rightleftharpoons$	ADP	+	F6P
Initial	1.20×10^{-6}		1×10^{-4}		1×10^{-2}		0
Change	$-x$		$-x$		$+x$		$+x$
Equil	$1.20\times10^{-6}-x$		$1\times10^{-4}-x$		$1\times10^{-2}+x$		x

$$K = \frac{[ADP][F6P]}{[C_6H_{12}O_6][ATP]}$$

$$1278 = \frac{(1\times10^{-2}+x)(x)}{(1.20\times10^{-6}-x)(1\times10^{-4}-x)} = \frac{1.0\times10^{-2}x + x^2}{1.2\times10^{-10} - 1.012\times10^{-4}x + x^2}$$

Expanding and rearranging the above equation yields the following second-order polynomial:
$1277\,x^2 - 0.1393\,x + 1.534\times10^{-7} = 0$
Using the quadratic equation to solve for x, we obtain two roots: $x = 1.113\times10^{-6}$ and 1.080×10^{-4}. Only the first one makes physical sense, because it is less than the initial value of $C_6H_{12}O_6$. Therefore, $[F6P]_{eq} = 1.113\times10^{-6}$.

During a fever, the body generates heat. Since the net reaction above is exothermic, Le Châtelier's principle would force the equilibrium to the left, reducing the amount of F6P generated.

B. **(E)**

(a) The ideal gas law can be used for this reaction, since we are relating vapor pressure and concentration. Since K = 3.3×10^{-29} for decomposition of Br_2 to Br (very small), then it can be ignored.

$$V = \frac{nRT}{P} = \frac{(0.100\text{ mol})(0.08206\text{ L}\cdot\text{atm}\cdot\text{K}^{-1})(298.15\text{ K})}{0.289\text{ atm}} = 8.47\text{ L}$$

(b) At 1000 K, there is much more Br being generated from the decomposition of Br_2. However, K is still rather small, and this decomposition does not notably affect the volume needed.

EXERCISES

Writing Equilibrium Constants Expressions

1. **(E)**

(a) $2\ COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g)$ $\quad K_c = \frac{[CO_2][CF_4]}{[COF_2]^2}$

(b) $Cu(s) + 2\ Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2\ Ag(s)$ $\quad K_c = \frac{[Cu^{2+}]}{[Ag^+]^2}$

(c) $S_2O_8^{2-}(aq) + 2\ Fe^{2+}(aq) \rightleftharpoons 2\ SO_4^{2-}(aq) + 2\ Fe^{3+}(aq)$ $\quad K_c = \frac{[SO_4^{2-}]^2[Fe^{3+}]^2}{[S_2O_8^{2-}][Fe^{2+}]^2}$

2. **(E)**

(a) $4\ NH_3(g) + 3\ O_2(g) \rightleftharpoons 2\ N_2(g) + 6\ H_2O(g)$ $\quad K_P = \frac{P\{N_2\}^2 \cdot P\{H_2O\}^6}{P\{NH_3\}^4 \cdot P\{O_2\}^3}$

(b) $7\ H_2(g) + 2\ NO_2(g) \rightleftharpoons 2\ NH_3(g) + 4\ H_2O(g)$ $\quad K_P = \frac{P\{NH_3\}^2 \cdot P\{H_2O\}^4}{P\{H_2\}^7 \cdot P\{NO_2\}^2}$

(c) $N_2(g) + Na_2CO_3(s) + 4\ C(s) \rightleftharpoons 2\ NaCN(s) + 3\ CO(g)$ $\quad K_c = \frac{[CO]^3}{[N_2]}$

3. **(E)**

(a) $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$ **(b)** $K_c = \frac{[Zn^{2+}]}{[Ag^+]^2}$ **(c)** $K_c = \frac{[OH^-]^2}{[CO_3^{2-}]}$

4. **(E)**

(a) $K_p = \dfrac{P\{CH_4\}P\{H_2S\}^2}{P\{CS_2\}P\{H_2\}^4}$ **(b)** $K_p = P\{O_2\}^{1/2}$ **(c)** $K_p = P\{CO_2\}P\{H_2O\}$

5. **(E)** In each case we write the equation for the formation reaction and then the equilibrium constant expression, K_c, for that reaction.

(a) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightleftharpoons HF(g)$ $K_c = \dfrac{[HF]}{[H_2]^{1/2}[F_2]^{1/2}}$

(b) $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $2\,N_2(g) + O_2(g) \rightleftharpoons 2\,N_2O(g)$ $K_c = \dfrac{[N_2O]^2}{[N_2]^2[O_2]}$

(d) $\frac{1}{2}Cl_2(g) + \frac{3}{2}F_2(g) \rightleftharpoons ClF_3(l)$ $K_c = \dfrac{1}{[Cl_2]^{1/2}[F_2]^{3/2}}$

6. **(E)** In each case we write the equation for the formation reaction and then the equilibrium constant expression, K_p, for that reaction.

(a) $\frac{1}{2}\,N_2(g) + \frac{1}{2}\,O_2(g) + \frac{1}{2}\,Cl_2(g) \rightleftharpoons NOCl(g)$ $K_p = \dfrac{[P_{NOCl}]}{[P_{N_2}]^{1/2}[P_{O_2}]^{1/2}[P_{Cl_2}]^{1/2}}$

(b) $N_2(g) + 2\,O_2(g) + Cl_2(g) \rightleftharpoons 2\,ClNO_2(g)$ $K_p = \dfrac{[P_{ClNO_2}]^2}{[P_{N_2}][P_{O_2}]^2[P_{Cl_2}]}$

(c) $N_2(g) + 2\,H_2(g) \rightleftharpoons N_2H_4(g)$ $K_p = \dfrac{P_{N_2H_4}}{[P_{N_2}][P_{H_2}]^2}$

(d) $\frac{1}{2}\,N_2(g) + 2\,H_2(g) + \frac{1}{2}\,Cl_2(g) \rightleftharpoons NH_4Cl(s)$ $K_p = \dfrac{1}{[P_{N_2}]^{1/2}[P_{H_2}]^2[P_{Cl_2}]^{1/2}}$

7. **(E)** Since $K_p = K_c(RT)^{\Delta n_g}$, it is also true that $K_c = K_p(RT)^{-\Delta n_g}$.

(a) $K_c = \dfrac{[SO_2][Cl_2]}{[SO_2Cl_2]} = K_p(RT)^{-(+1)} = 2.9 \times 10^{-2}(0.08206 \times 303)^{-1} = 0.0012$

(b) $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]} = K_p(RT)^{-(-1)} = 1.48 \times 10^4 \times (0.08206 \times 303) = 5.55 \times 10^5$

(c) $K_c = \dfrac{[H_2S]^3}{[H_2]^3} = K_p(RT)^0 = K_p = 0.429$

8. **(E)** $K_p = K_c (RT)^{\Delta n_g}$, with $R = 0.08206$ L· atm mol^{-1} K^{-1}

(a) $K_p = \dfrac{P\{NO_2\}^2}{P\{N_2O_4\}} = K_c(RT)^{+1} = 4.61 \times 10^{-3}(0.08206 \times 298)^1 = 0.113$

(b) $K_p = \dfrac{P\{C_2H_2\}P\{H_2\}^3}{P\{CH_4\}^2} = K_c(RT)^{(+2)} = (0.154)(0.08206 \times 2000)^2 = 4.15 \times 10^3$

(c) $K_p = \dfrac{P\{H_2\}^4 P\{CS_2\}}{P\{H_2S\}^2 P\{CH_4\}} = K_c(RT)^{(+2)} = (5.27 \times 10^{-8})(0.08206 \times 973)^2 = 3.36 \times 10^{-4}$

9. **(E)** The equilibrium reaction is $H_2O(l) \rightleftharpoons H_2O(g)$ with $\Delta n_{gas} = +1$. $K_p = K_c (RT)^{\Delta n_g}$ gives

$K_c = K_p (RT)^{-\Delta n_g}$. $\quad K_p = P\{H_2O\} = 23.8 \text{ mmHg} \times \dfrac{1 \text{ atm}}{760 \text{ mmHg}} = 0.0313$

$$K_c = K_p (RT)^{-1} = \frac{K_p}{RT} = \frac{0.0313}{0.08206 \times 298} = 1.28 \times 10^{-3}$$

10. **(E)** The equilibrium rxn is $C_6H_6(l) \rightleftharpoons C_6H_6(g)$ with $\Delta n_{gas} = +1$. Using $K_p = K_c (RT)^{\Delta n_g}$,

$K_p = K_c(RT) = 5.12 \times 10^{-3}(0.08206 \times 298) = 0.125 = P\{C_6H_6\}$

$P\{C_6H_6\} = 0.125 \text{ atm} \times \dfrac{760 \text{ mmHg}}{1 \text{ atm}} = 95.0 \text{ mmHg}$

11. **(E)** Add one-half of the reversed 1st reaction with the 2nd reaction to obtain the desired reaction.

$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons NO(g) \qquad K_c = \dfrac{1}{\sqrt{2.1 \times 10^{30}}}$

$NO(g) + \frac{1}{2} Br_2(g) \rightleftharpoons NOBr(g) \qquad K_c = 1.4$

net : $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) + \frac{1}{2} Br_2(g) \rightleftharpoons NOBr(g) \qquad K_c = \dfrac{1.4}{\sqrt{2.1 \times 10^{30}}} = 9.7 \times 10^{-16}$

12. **(M)** We combine the several given reactions to obtain the net reaction.

$2\ N_2O(g) \rightleftharpoons 2\ N_2(g) + O_2(g) \qquad K_c = \dfrac{1}{(2.7 \times 10^{-18})^2}$

$4\ NO_2(g) \rightleftharpoons 2\ N_2O_4(g) \qquad K_c = \dfrac{1}{(4.6 \times 10^{-3})^2}$

$2N_2(g) + 4O_2(g) \rightleftharpoons 4NO_2(g) \qquad K_c = (4.1 \times 10^{-9})^4$

net : $2\ N_2O(g) + 3\ O_2(g) \rightleftharpoons 2\ N_2O_4(g) \quad K_{c(Net)} = \dfrac{(4.1 \times 10^{-9})^4}{(2.7 \times 10^{-18})^2 (4.6 \times 10^{-3})^2} = 1.8 \times 10^6$

13. **(M)** We combine the K_c values to obtain the value of K_c for the overall reaction, and then convert this to a value for K_p.

$$2\ CO_2(g) + 2H_2(g) \rightleftharpoons 2\ CO(g) + 2\ H_2O(g) \qquad K_c = (1.4)^2$$

$$2\ C(\text{graphite}) + O_2(g) \rightleftharpoons 2\ CO(g) \qquad K_c = (1\times10^8)^2$$

$$4\ CO(g) \rightleftharpoons 2\ C(\text{graphite}) + 2\ CO_2(g) \qquad K_c = \frac{1}{(0.64)^2}$$

$$\text{net:}\quad 2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K_{c(\text{Net})} = \frac{(1.4)^2(1\times10^8)^2}{(0.64)^2} = 5\times10^6$$

$$K_p = K_c(RT)^{\Delta n} = \frac{K_c}{RT} = \frac{5\times10^{16}}{0.08206\times1200} = 5\times10^{14}$$

14. **(M)** We combine the K_p values to obtain the value of K_p for the overall reaction, and then convert this to a value for K_c.

$$2\ NO_2Cl(g) \rightleftharpoons 2\ NOCl(g) + O_2(g) \qquad K_p = \left(\frac{1}{1.1\times10^2}\right)^2$$

$$2\ NO_2(g) + Cl_2(g) \rightleftharpoons 2\ NO_2Cl(g) \qquad K_p = (0.3)^2$$

$$N_2(g) + 2\ O_2(g) \rightleftharpoons 2\ NO_2(g) \qquad K_p = (1.0\times10^{-9})^2$$

$$\text{net: } N_2(g) + O_2(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g) \qquad K_{p(\text{Net})} = \frac{(0.3)^2(1.0\times10^{-9})^2}{(1.1\times10^2)^2} = 7.\underline{4}\times10^{-24}$$

$$K_p = K_c(RT)^{\Delta n} \qquad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{7.\underline{4}\times10^{-24}}{(0.08206\times298)^{2-3}} = 2\times10^{-22}$$

15. **(E)** $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

In terms of concentration, K = a(H_2CO_3)/a(CO_2)

In terms of concentration and partial pressure, $K = \dfrac{[H_2CO_3]/c^\circ}{P_{CO_2}/P^\circ}$

16. **(E)** $2\ Fe(s) + 3\ O_2(g) \rightleftharpoons Fe_2O_3(s)$

$K = \dfrac{a_{Fe_2O_3}}{a_{Fe}\cdot a_{O_2}}$. Since activity of solids and liquids is defined as 1, then the expression simplifies to $K = \dfrac{1}{a_{O_2}}$

Similarly, in terms of pressure and concentration, $K = 1/\left(P_{O_2}/P^\circ\right)$

Experimental Determination of Equilibrium Constants

17. **(M)** First, we determine the concentration of PCl_5 and of Cl_2 present initially and at equilibrium, respectively. Then we use the balanced equation to help us determine the concentration of each species present at equilibrium.

$[PCl_5]_{initial} = \dfrac{1.00\times10^{-3}\text{ mol }PCl_5}{0.250\text{ L}} = 0.00400\text{ M}$ $\qquad [Cl_2]_{equil} = \dfrac{9.65\times10^{-4}\text{ mol }Cl_2}{0.250\text{ L}} = 0.00386\text{ M}$

Equation:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial:	0.00400M		0 M		0 M
Changes:	$-x$M		$+x$M		$+x$M
Equil:	0.00400M-xM		xM		xM ← 0.00386 M (from above)

At equilibrium, $[Cl_2] = [PCl_3] = 0.00386$ M and $[PCl_5] = 0.00400\text{M} - x\text{M} = 0.00014$ M

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.00386\,\text{M})(0.00386\,\text{M})}{0.00014\,\text{M}} = 0.10\underline{6}$$

18. **(M)** First we determine the partial pressure of each gas.

$$P_{\text{initial}}\{H_2(g)\} = \frac{nRT}{V} = \frac{1.00\,\text{g }H_2 \times \frac{1\,\text{mol }H_2}{2.016\,\text{g }H_2} \times \frac{0.08206\,\text{L atm}}{\text{mol K}} \times 1670\,\text{K}}{0.500\,\text{L}} = 136\,\text{atm}$$

$$P_{\text{initial}}\{H_2S(g)\} = \frac{nRT}{V} = \frac{1.06\,\text{g }H_2S \times \frac{1\,\text{mol }H_2S}{34.08\,\text{g }H_2S} \times \frac{0.08206\,\text{L atm}}{\text{mol K}} \times 1670\,\text{K}}{0.500\,\text{L}} = 8.52\,\text{atm}$$

$$P_{\text{equil}}\{S_2(g)\} = \frac{nRT}{V} = \frac{8.00\times10^{-6}\text{ mol }S_2 \times \frac{0.08206\,\text{L atm}}{\text{mol K}} \times 1670\,\text{K}}{0.500\,\text{L}} = 2.19\times10^{-3}\text{ atm}$$

Equation:	$2\,H_2(g)$	+ $S_2(g)$	$\rightleftharpoons$ $2\,H_2S(g)$
Initial:	136 atm	0 atm	8.52 atm
Changes:	+0.00438 atm	0.00219 atm	−0.00438 atm
Equil:	136 atm	0.00219 atm	8.52 atm

$$K_p = \frac{P\{H_2S(g)\}^2}{P\{H_2(g)\}^2\,P\{S_2(g)\}} = \frac{(8.52)^2}{(136)^2\,0.00219} = 1.79$$

19. **(M)**

(a) $$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{\frac{0.105\ g\ PCl_5}{2.50\ L} \times \frac{1\ mol\ PCl_5}{208.2\ g}}{\left(\frac{0.220\ g\ PCl_3}{2.50\ L} \times \frac{1\ mol\ PCl_3}{137.3\ g}\right) \times \left(\frac{2.12\ g\ Cl_2}{2.50\ L} \times \frac{1\ mol\ Cl_2}{70.9\ g}\right)} = 26.3$$

(b) $$K_p = K_c(RT)^{\Delta n} = 26.3\ (0.08206 \times 523)^{-1} = 0.613$$

20. **(M)**

$$[ICl]_{initial} = \frac{0.682\ g\ ICl \times \frac{1\ mol\ ICl}{162.36\ g\ ICl}}{0.625\ L} = 6.72\times10^{-3}\ M$$

Reaction:	2 ICl(g)	$\rightleftharpoons$	$I_2(g)$	+	$Cl_2(g)$
Initial:	6.72×10^{-3} M		0 M		0 M
Change	$-2x$		$+x$		$+x$
Equilibrium	6.72×10^{-3} M $-2x$		x		x

$$[I_2]_{equil} = \frac{0.0383\ g\ I_2 \times \frac{1\ mol\ I_2}{253.808\ g\ I_2}}{0.625\ L} = 2.41\times10^{-4}\ M \quad = x$$

$$K_c = \frac{x \cdot x}{(6.72\times10^{-3} - 2x)} = \frac{(2.41\times10^{-4})^2}{(6.72\times10^{-3} - 2(2.41\times10^{-4}))} = 9.31\times10^{-6}$$

21. **(E)**

$$K = \frac{[Fe^{3+}]}{[H^+]^3} \Rightarrow 9.1\times10^3 = \frac{[Fe^{3+}]}{(1.0\times10^{-7})^3}$$

$$[Fe^{3+}] = 9.1\times10^{-18}\ M$$

22. **(E)**

$$K = \frac{[NH_3(aq)]}{P_{NH_3(g)}} \Rightarrow 57.5 = \frac{5\times10^{-9}}{P_{NH_3(g)}}$$

$$P_{NH_3(g)} = 5\times10^{-9}/57.5 = 8.7\times10^{-11}$$

Equilibrium Relationships

23. **(M)** $K_c = 281 = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = \dfrac{[SO_3]^2}{[SO_2]^2} \times \dfrac{0.185\text{ L}}{0.00247\text{ mol}} \quad \dfrac{[SO_2]}{[SO_3]} = \sqrt{\dfrac{0.185}{0.00247 \times 281}} = 0.516$

24. **(M)** $K_c = 0.011 = \dfrac{[I]^2}{[I_2]} = \dfrac{\left(\dfrac{0.37\text{ mol I}}{V}\right)^2}{\dfrac{1.00\text{ mol }I_2}{V}} = \dfrac{1}{V} \times 0.14 \quad V = \dfrac{0.14}{0.011} = 13\text{ L}$

25. **(M)**

(a) A possible equation for the oxidation of $NH_3(g)$ to $NO_2(g)$ follows.

$NH_3(g) + \frac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \frac{3}{2}H_2O(g)$

(b) We obtain K_p for the reaction in part (a) by appropriately combining the values of K_p given in the problem.

$NH_3(g) + \frac{5}{4}O_2(g) \rightleftharpoons NO(g) + \frac{3}{2}H_2O(g) \qquad K_p = 2.11 \times 10^{19}$

$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g) \qquad K_p = \dfrac{1}{0.524}$

net: $NH_3(g) + \frac{7}{4}O_2(g) \rightleftharpoons NO_2(g) + \frac{3}{2}H_2O(g) \quad K_p = \dfrac{2.11 \times 10^{19}}{0.524} = 4.03 \times 10^{19}$

26. **(D)**

(a) We first determine $[H_2]$ and $[CH_4]$ and then $[C_2H_2]$. $[CH_4] = [H_2] = \dfrac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\text{ M}$

$K_c = \dfrac{[C_2H_2][H_2]^3}{[CH_4]^2} \quad [C_2H_2] = \dfrac{K_c[CH_4]^2}{[H_2]^3} = \dfrac{0.154 \times 0.10^2}{0.10^3} = 1.54\text{ M}$

In a 1.00 L container, each concentration numerically equals the molar quantities of the substance.

$\chi\{C_2H_2\} = \dfrac{1.54\text{ mol }C_2H_2}{1.54\text{ mol }C_2H_2 + 0.10\text{ mol }CH_4 + 0.10\text{ mol }H_2} = 0.89$

(b) The conversion of $CH_4(g)$ to $C_2H_2(g)$ is favored at low pressures, since the conversion reaction has a larger sum of the stoichiometric coefficients of gaseous products (4) than of reactants (2).

(c) Initially, all concentrations are halved when the mixture is transferred to a flask that is twice as large. To re-establish equilibrium, the system reacts to the right, forming more moles of gas (to compensate for the drop in pressure). We base our solution on the balanced chemical equation, in the manner we have used before.

Equation:	$2\ CH_4(g)$	$\rightleftharpoons C_2H_2(g)$	+	$3\ H_2$
Initial:	$\frac{0.10\,\text{mol}}{2.00\,\text{L}}$	$\frac{1.5\,\text{mol}}{2.00\,\text{L}}$		$\frac{0.10\,\text{mol}}{2.00\,\text{L}}$
	= 0.050 M	= 0.75 M		= 0.050 M
Changes:	$-2x$ M	$+x$ M		$+3x$ M
Equil:	$(0.050-2x)$ M	$(0.0750+x)$ M		$(0.050+3x)$ M

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} = \frac{(0.050+3x)^3(0.750+x)}{(0.050-2x)^2} = 0.154$$

We can solve this 4th-order equation by successive approximations.
First guess: $x = 0.010$ M.

$$x = 0.010 \quad Q_c = \frac{(0.050+3(0.010))^3(0.750+0.010)}{(0.050-2(0.010))^2} = \frac{(0.080)^3(0.760)}{(0.030)^2} = 0.433 > 0.154$$

$$x = 0.020 \quad Q_c = \frac{(0.050+3(0.020))^3(0.750+0.020)}{(0.050-2(0.020))^2} = \frac{(0.110)^3(0.770)}{(0.010)^2} = 10.2 > 0.154$$

$$x = 0.005 \quad Q_c = \frac{(0.050+3(0.005))^3(0.750+0.005)}{(0.050-2(0.005))^2} = \frac{(0.065)^3(0.755)}{(0.040)^2} = 0.129 < 0.154$$

$$x = 0.006 \quad Q_c = \frac{(0.050+3(0.006))^3(0.750+0.006)}{(0.050-2(0.006))^2} = \frac{(0.068)^3(0.756)}{(0.038)^2} = 0.165 > 0.154$$

This is the maximum number of significant figures our system permits. We have $x = 0.006$ M. $[CH_4] = 0.038$ M; $[C_2H_2] = 0.756$ M; $[H_2] = 0.068$ M

Because the container volume is 2.00 L, the molar amounts are double the values of molarities.

$$2.00\ \text{L} \times \frac{0.756\ \text{mol}\ C_2H_2}{1\ \text{L}} = 1.51\ \text{mol}\ C_2H_2 \qquad 2.00\ \text{L} \times \frac{0.038\ \text{mol}\ CH_4}{1\ \text{L}} = 0.076\ \text{mol}\ CH_4$$

$$2.00\ \text{L} \times \frac{0.068\ \text{mol}\ H_2}{1\ \text{L}} = 0.14\ \text{mol}\ H_2$$

Thus, the increase in volume results in the production of some additional C_2H_2.

27. **(M)**

(a) $$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{\frac{n\{CO\}}{V} \times \frac{n\{H_2O\}}{V}}{\frac{n\{CO_2\}}{V} \times \frac{n\{H_2\}}{V}}$$

Since V is present in both the denominator and the numerator, it can be stricken from the expression. This happens here because $\Delta n_g = 0$. Therefore, K_c is independent of V.

(b) Note that $K_p = K_c$ for this reaction, since $\Delta n_{gas} = 0$.

$$K_c = K_p = \frac{0.224 \text{ mol CO} \times 0.224 \text{ mol } H_2O}{0.276 \text{ mol } CO_2 \times 0.276 \text{ mol } H_2} = 0.659$$

28. **(M)** For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ the value of $K_p = 23.2$

The expression for Q_p is $\frac{[CO_2][H_2]}{[CO][H_2O]}$. Consider each of the provided situations

(a) $P_{CO} = P_{H_2O} = P_{H_2} = P_{CO_2}$; $Q_p = 1$ Not an equilibrium position

(b) $\frac{P_{H_2}}{P_{H_2O}} = \frac{P_{CO_2}}{P_{CO}} = x$; $Q_p = x^2$ If $x = \sqrt{23.2}$, this is an equilibrium position.

(c) $\left(P_{CO} \times P_{H_2O}\right) = \left(P_{CO_2} \times P_{H_2}\right)$; $Q_p = 1$ Not an equilibrium position

(d) $\frac{P_{H_2}}{P_{CO}} = \frac{P_{CO_2}}{P_{H_2O}} = x$; $Q_p = x^2$ If $x = \sqrt{23.2}$, this is an equilibrium position.

Direction and Extent of Chemical Change

29. **(M)** We compute the value of Q_c for the given amounts of product and reactants.

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{1.8 \text{ mol } SO_3}{7.2 \text{ L}}\right)^2}{\left(\frac{3.6 \text{ mol } SO_2}{7.2 \text{ L}}\right)^2 \frac{2.2 \text{ mol } O_2}{7.2 \text{ L}}} = 0.82 < K_c = 100$$

The mixture described cannot be maintained indefinitely. In fact, because $Q_c < K_c$, the reaction will proceed to the right, that is, toward products, until equilibrium is established. We do not know how long it will take to reach equilibrium.

30. **(M)** We compute the value of Q_c for the given amounts of product and reactants.

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{0.0205\,mol\,NO_2}{5.25\,L}\right)^2}{\frac{0.750\,mol\,N_2O_4}{5.25\,L}} = 1.07 \times 10^{-4} < K_c = 4.61 \times 10^{-3}$$

The mixture described cannot be maintained indefinitely. In fact, because $Q_c < K_c$, the reaction will proceed to the right, that is, toward products, until equilibrium is established. If E_a is large, however, it may take some time to reach equilibrium.

31. **(M)**

(a) We determine the concentration of each species in the gaseous mixture, use these concentrations to determine the value of the reaction quotient, and compare this value of Q_c with the value of K_c.

$$[SO_2] = \frac{0.455 \text{ mol } SO_2}{1.90 \text{ L}} = 0.239 \text{ M} \qquad [O_2] = \frac{0.183 \text{ mol } O_2}{1.90 \text{ L}} = 0.0963 \text{ M}$$

$$[SO_3] = \frac{0.568 \text{ mol } SO_3}{1.90 \text{ L}} = 0.299 \text{ M} \qquad Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.299)^2}{(0.239)^2\, 0.0963} = 16.3$$

Since $Q_c = 16.3 \neq 2.8 \times 10^2 = K_c$, this mixture is not at equilibrium.

(b) Since the value of Q_c is smaller than that of K_c, the reaction will proceed to the right, forming product and consuming reactants to reach equilibrium.

32. **(M)** We compute the value of Q_c. Each concentration equals the mass (m) of the substance divided by its molar mass and further divided by the volume of the container.

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{\dfrac{m \times \frac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2}}{V} \times \dfrac{m \times \frac{1 \text{ mol } H_2}{2.0 \text{ g } H_2}}{V}}{\dfrac{m \times \frac{1 \text{ mol CO}}{28.0 \text{ g CO}}}{V} \times \dfrac{m \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}}{V}} = \frac{\frac{1}{44.0 \times 2.0}}{\frac{1}{28.0 \times 18.0}} = \frac{28.0 \times 18.0}{44.0 \times 2.0} = 5.7 < 31.4 (\text{value of } K_c)$$

(In evaluating the expression above, we cancelled the equal values of V, along with, the equal values of m.) Because the value of Q_c is smaller than the value of K_c, (a) the reaction is not at equilibrium and (b) the reaction will proceed to the right (formation of products) to reach a state of equilibrium.

33. **(M)** The information for the calculation is organized around the chemical equation. Let $x =$ mol H_2 (or I_2) that reacts. Then use stoichiometry to determine the amount of HI formed, in terms of x, and finally solve for x.

Equation:	$H_2(g)$	+	$I_2(g) \rightleftharpoons$	$2\ HI(g)$
Initial:	0.150 mol		0.150 mol	0.000 mol
Changes:	$-x$ mol		$-x$ mol	$+2x$ mol
Equil:	$0.150-x$		$0.150-x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{3.25\ L}\right)^2}{\frac{0.150-x}{3.25\,L} \times \frac{0.150-x}{3.25\ L}}$$

Then take the square root of both sides: $\sqrt{K_c} = \sqrt{50.2} = \dfrac{2x}{0.150-x} = 7.09$

$2x = 1.06 - 7.09x \qquad x = \dfrac{1.06}{9.09} = 0.117$ mol, amount HI $= 2x = 2 \times 0.117$ mol $= 0.234$ mol HI

amount H_2 = amount $I_2 = (0.150 - x)$ mol $= (0.150 - 0.117)$ mol $= 0.033$ mol H_2 (or I_2)

34. **(M)** We use the balanced chemical equation as a basis to organize the information

Equation:	$SbCl_5(g) \rightleftharpoons$	$SbCl_3(g)$	+	$Cl_2(g)$
Initial:	$\frac{0.00\ mol}{2.50\ L}$	$\frac{0.280\ mol}{2.50\ L}$		$\frac{0.160\ mol}{2.50\ L}$
Initial:	0.000 M	0.112 M		0.0640 M
Changes:	$+x$ M	$-x$ M		$-x$ M
Equil:	x M	$(0.112-x)$ M		$(0.0640-x)$ M

$$K_c = 0.025 = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{(0.112-x)(0.0640-x)}{x} = \frac{0.00717 - 0.176x + x^2}{x}$$

$$0.025x = 0.00717 - 0.176x + x^2 \qquad x^2 - 0.201x + 0.00717 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{0.201 \pm \sqrt{0.0404 - 0.0287}}{2} = 0.0464 \text{ or } 0.155$$

The second of the two values for x gives a negative value of $[Cl_2]\,(= -0.091\ M)$, and thus is physically meaningless in our universe. Thus, concentrations and amounts follow.

$[SbCl_5] = x = 0.0464$ M $\qquad$ amount $SbCl_5 = 2.50\ L \times 0.0464\ M = 0.116$ mol $SbCl_5$

$[SbCl_3] = 0.112 - x = 0.066$ M $\qquad$ amount $SbCl_3 = 2.50\ L \times 0.066\ M = 0.17$ mol $SbCl_3$

$[Cl_2] = 0.0640 - x = 0.0176$ M $\qquad$ amount $Cl_2 = 2.50\ L \times 0.0176\ M = 0.0440$ mol Cl_2

35. **(M)** We use the chemical equation as a basis to organize the information provided about the reaction, and then determine the final number of moles of $Cl_2(g)$ present.

Equation:	$CO(g)$ +	$Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$
Initial:	0.3500 mol	0.0000 mol		0.05500 mol
Changes:	$+x$ mol	$+x$ mol		$-x$ mol
Equil.:	$(0.3500+x)$ mol	x mol		$(0.05500-x)$ mol

$$K_c = 1.2\times10^3 = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{\dfrac{(0.0550-x)\,\text{mol}}{3.050\,\text{L}}}{\dfrac{(0.3500+x)\text{mol}}{3.050\,\text{L}}\times\dfrac{x\text{ mol}}{3.050\text{ L}}}$$

$$\frac{1.2\times10^3}{3.050} = \frac{0.05500-x}{(0.3500+x)\,x}$$ Assume $x << 0.0550$ This produces the following expression.

$$\frac{1.2\times10^3}{3.050} = \frac{0.05500}{0.3500\,x} \qquad x = \frac{3.050\times0.05500}{0.3500\times1.2\times10^3} = 4.0\times10^{-4}\text{ mol }Cl_2$$

We use the first value we obtained, 4.0×10^{-4} (= 0.00040), to arrive at a second value.

$$x = \frac{3.050\times(0.0550-0.00040)}{(0.3500+0.00040)\times1.2\times10^3} = 4.0\times10^{-4}\text{ mol }Cl_2$$

Because the value did not change on the second iteration, we have arrived at a solution.

36. **(M)** Compute the initial concentration of each species present. Then determine the equilibrium concentrations of all species. Finally, compute the mass of CO_2 present at equilibrium.

$$[CO]_{int} = \frac{1.00\text{ g}}{1.41\text{ L}}\times\frac{1\text{ mol CO}}{28.01\text{ g CO}} = 0.0253\text{ M} \qquad [H_2O]_{int} = \frac{1.00\text{ g}}{1.41\text{ L}}\times\frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O} = 0.0394\text{ M}$$

$$[H_2]_{int} = \frac{1.00\text{ g}}{1.41\text{ L}}\times\frac{1\text{ mol }H_2}{2.016\text{ g }H_2} = 0.352\text{ M}$$

Equation :	$CO(g)$ +	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$ +	$H_2(g)$
Initial :	0.0253 M	0.0394 M		0.0000 M	0.352 M
Changes :	$-x$ M	$-x$ M		$+x$ M	$+x$ M
Equil :	$(0.0253-x)$ M	$(0.0394-x)$ M		x M	$(0.352+x)$ M

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 23.2 = \frac{x(0.352+x)}{(0.0253-x)(0.0394-x)} = \frac{0.352x+x^2}{0.000997-0.0647x+x^2}$$

$$0.0231-1.50x+23.2x^2 = 0.352x+x^2 \qquad 22.2x^2-1.852x+0.0231=0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{1.852 \pm \sqrt{3.430 - 2.051}}{44.4} = 0.0682 \text{ M}, \quad 0.0153 \text{ M}$$

The first value of x gives negative concentrations for reactants ([CO] = -0.0429 M and [H_2O] = -0.0288 M). Thus, $x = 0.0153 \text{ M} = [CO_2]$. Now we can find the mass of CO_2.

$$1.41 \text{ L} \times \frac{0.0153 \text{ mol } CO_2}{1 \text{ L mixture}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 0.949 \text{ g } CO_2$$

37. **(D)** We base each of our solutions on the balanced chemical equation.

(a)

Equation:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial:	$\frac{0.550 \text{ mol}}{2.50 \text{ L}}$		$\frac{0.550 \text{ mol}}{2.50 \text{ L}}$		$\frac{0 \text{ mol}}{2.50 \text{ L}}$
Changes:	$\frac{-x \text{ mol}}{2.50 \text{ L}}$		$\frac{+x \text{ mol}}{2.50 \text{ L}}$		$\frac{+x \text{ mol}}{2.50 \text{ L}}$
Equil:	$\frac{(0.550 - x) \text{ mol}}{2.50 \text{ L}}$		$\frac{(0.550 + x) \text{ mol}}{2.50 \text{ L}}$		$\frac{x \text{ mol}}{2.50 \text{ L}}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 3.8 \times 10^{-2} = \frac{\frac{(0.550 + x)\text{mol}}{2.50\text{L}} \times \frac{x\text{mol}}{2.50\text{L}}}{\frac{(0.550 - x)\text{mol}}{2.50\text{L}}} \qquad \frac{x(0.550 + x)}{2.50(0.550 - x)} = 3.8 \times 10^{-2}$$

$$x^2 + 0.550x = 0.052 - 0.095x \qquad x^2 + 0.645x - 0.052 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.645 \pm \sqrt{0.416 + 0.208}}{2} = 0.0725 \text{ mol}, \quad -0.717 \text{ mol}$$

The second answer gives a negative quantity. of Cl_2, which makes no physical sense.

$n_{PCl_5} = (0.550 - 0.0725) = 0.478$ mol PCl_5 $\quad n_{PCl_3} = (0.550 + 0.0725) = 0.623$ mol PCl_3

$n_{Cl_2} = x = 0.0725$ mol Cl_2

(b)

Equation:	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial:	$\frac{0.610 \text{ mol}}{2.50 \text{ L}}$		0 M		0 M
Changes:	$\frac{-x \text{ mol}}{2.50 \text{ L}}$		$\frac{+x \text{ mol}}{2.50 \text{ L}}$		$\frac{+x \text{ mol}}{2.50 \text{ L}}$
Equil:	$\frac{0.610 - x \text{ mol}}{2.50 \text{ L}}$		$\frac{(x \text{ mol})}{2.50 \text{ L}}$		$\frac{(x \text{ mol})}{2.50 \text{ L}}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 3.8\times10^{-2} = \frac{\dfrac{(x\,\text{mol})}{2.50\,\text{L}}\times\dfrac{(x\ \text{mol})}{2.50\ \text{L}}}{\dfrac{0.610 - x\,\text{mol}}{2.50\ \text{L}}}$$

$$2.50\times3.8\times10^{-2} = \frac{x^2}{0.610 - x} = 0.095 \qquad 0.058 - 0.095x = x^2 \quad x^2 + 0.095x - 0.058 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-0.095\pm\sqrt{0.0090+0.23}}{2} = 0.20\ \text{mol},\ -0.29\ \text{mol}$$

amount $PCl_3 = 0.20$ mol = amount Cl_2; amount $PCl_5 = 0.610 - 0.20 = 0.41$ mol

38. (D)

(a) We use the balanced chemical equation as a basis to organize the information we have about the reactants and products.

Equation:	$2\ COF_2(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$CF_4(g)$
Initial:	$\dfrac{0.145\ \text{mol}}{5.00\ \text{L}}$		$\dfrac{0.262\ \text{mol}}{5.00\ \text{L}}$		$\dfrac{0.074\ \text{mol}}{5.00\ \text{L}}$
Initial:	0.0290 M		0.0524 M		0.0148 M

And we now compute a value of Q_c and compare it to the given value of K_c.

$$Q_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{(0.0524)(0.0148)}{(0.0290)^2} = 0.922 < 2.00 = K_c$$

Because Q_c is not equal to K_c, the mixture is not at equilibrium.

(b) Because Q_c is smaller than K_c, the reaction will shift right, that is, products will be formed at the expense of COF_2, to reach a state of equilibrium.

(c) We continue the organization of information about reactants and products.

Equation:	$2\ COF_2(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$CF_4(g)$
Initial:	0.0290 M		0.0524 M		0.0148 M
Changes:	$-2x$ M		$+x$ M		$+x$ M
Equil:	$(0.0290-2x)$M		$(0.0524+x)$M		$(0.0148+x)$M

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{(0.0524+x)(0.0148+x)}{(0.0290-2x)^2} = 2.00 = \frac{0.000776+0.0672x+x^2}{0.000841-0.1160x+4x^2}$$

$$0.00168-0.232x+8x^2 = 0.000776+0.0672x+x^2 \quad 7x^2-0.299x+0.000904=0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{0.299 \pm \sqrt{0.0894-0.0253}}{14} = 0.0033\text{ M}, 0.0394\text{ M}$$

The second of these values for x (0.0394) gives a negative $[COF_2](=-0.0498\text{ M})$, clearly a nonsensical result. We now compute the concentration of each species at equilibrium, and check to ensure that the equilibrium constant is satisfied.

$$[COF_2] = 0.0290-2x = 0.0290-2(0.0033) = 0.0224\text{ M}$$

$$[CO_2] = 0.0524+x = 0.0524+0.0033 = 0.0557\text{ M}$$

$$[CF_4] = 0.0148+x = 0.0148+0.0033 = 0.0181\text{ M}$$

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{0.0557\text{ M}\times 0.0181\text{ M}}{(0.0224\text{ M})^2} = 2.01$$

The agreement of this value of K_c with the cited value (2.00) indicates that this solution is correct. Now we determine the number of moles of each species at equilibrium.

$$\text{mol } COF_2 = 5.00\text{ L}\times 0.0224\text{ M} = 0.112\text{ mol } COF_2$$

$$\text{mol } CO_2 = 5.00\text{ L}\times 0.0557\text{ M} = 0.279\text{ mol } CO_2$$

$$\text{mol } CF_4 = 5.00\text{ L}\times 0.0181\text{ M} = 0.0905\text{ mol } CF_4$$

But suppose we had incorrectly concluded, in part (b), that reactants would be formed in reaching equilibrium. What result would we obtain? The set-up follows.

Equation :	$2\ COF_2(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$CF_4(g)$
Initial :	0.0290 M		0.0524 M		0.0148 M
Changes :	$+2y$ M		$-y$ M		$-y$ M
Equil :	$(0.0290+2y)$ M		$(0.0524-y)$ M		$(0.0148-y)$ M

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2} = \frac{(0.0524-y)(0.0148-y)}{(0.0290+2y)^2} = 2.00 = \frac{0.000776-0.0672y+y^2}{0.000841+0.1160y+4y^2}$$

$$0.00168+0.232y+8y^2 = 0.000776-0.0672y+y^2 \quad 7y^2+0.299y+0.000904=0$$

$$y = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.299 \pm \sqrt{0.0894-0.0253}}{14} = -0.0033\text{ M}, -0.0394\text{ M}$$

The second of these values for $x(-0.0394)$ gives a negative $[COF_2](=-0.0498\text{ M})$, clearly a nonsensical result. We now compute the concentration of each species at equilibrium, and check to ensure that the equilibrium constant is satisfied.

$$[COF_2] = 0.0290 + 2y = 0.0290 + 2(-0.0033) = 0.0224\text{ M}$$

$$[CO_2] = 0.0524 - y = 0.0524 + 0.0033 = 0.0557\text{ M}$$

$$[CF_4] = 0.0148 - y = 0.0148 + 0.0033 = 0.0181\text{ M}$$

These are the same equilibrium concentrations that we obtained by making the correct decision regarding the direction that the reaction would take. Thus, you can be assured that, if you perform the algebra correctly, it will guide you even if you make the incorrect decision about the direction of the reaction.

39. **(D)**

(a) We calculate the initial amount of each substance.

$$n\{C_2H_5OH\} = 17.2\text{ g }C_2H_5OH \times \frac{1\text{ mol }C_2H_5OH}{46.07\text{ g }C_2H_5OH} = 0.373\text{ mol }C_2H_5OH$$

$$n\{CH_3CO_2H\} = 23.8\text{ g }CH_3CO_2H \times \frac{1\text{ mol }CH_3CO_2H}{60.05\text{ g }CH_3CO_2H} = 0.396\text{ mol }CH_3CO_2H$$

$$n\{CH_3CO_2C_2H_5\} = 48.6\text{ g }CH_3CO_2C_2H_5 \times \frac{1\text{ mol }CH_3CO_2C_2H_5}{88.11\text{ g }CH_3CO_2C_2H_5}$$

$$n\{CH_3CO_2C_2H_5\} = 0.552\text{ mol }CH_3CO_2C_2H_5$$

$$n\{H_2O\} = 71.2\text{ g }H_2O \times \frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O} = 3.95\text{ mol }H_2O$$

Since we would divide each amount by the total volume, and since there are the same numbers of product and reactant stoichiometric coefficients, we can use moles rather than concentrations in the Q_c expression.

$$Q_c = \frac{n\{CH_3CO_2C_2H_5\}n\{H_2O\}}{n\{C_2H_5OH\}n\{CH_3CO_2H\}} = \frac{0.552\text{ mol} \times 3.95\text{ mol}}{0.373\text{ mol} \times 0.396\text{ mol}} = 14.8 > K_c = 4.0$$

Since $Q_c > K_c$ the reaction will shift to the left, forming reactants, as it attains equilibrium.

(b)

Equation:	C_2H_5OH	+ CH_3CO_2H	$\rightleftharpoons$	$CH_3CO_2C_2H_5$	+ H_2O
Initial	0.373 mol	0.396 mol		0.552 mol	3.95 mol
Changes	$+x$ mol	$+x$ mol		$-x$ mol	$-x$ mol
Equil	$(0.373+x)$ mol	$(0.396+x)$ mol		$(0.552-x)$ mol	$(3.95-x)$ mol

$$K_c = \frac{(0.552-x)(3.95-x)}{(0.373+x)(0.396+x)} = \frac{2.18-4.50x+x^2}{0.148+0.769\,x+x^2} = 4.0$$

$$x^2 - 4.50x + 2.18 = 4x^2 + 3.08x + 0.59 \qquad 3x^2 + 7.58x - 1.59 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-7.58 \pm \sqrt{57+19}}{6} = 0.19 \text{ moles}, -2.72 \text{ moles}$$

Negative amounts do not make physical sense. We compute the equilibrium amount of each substance with $x = 0.19$ moles.

$$n\{C_2H_5OH\} = 0.373 \text{ mol} + 0.19 \text{ mol} = 0.56 \text{ mol } C_2H_5OH$$

$$\text{mass } C_2H_5OH = 0.56 \text{mol } C_2H_5OH \times \frac{46.07 \text{ g } C_2H_5OH}{1 \text{ mol } C_2H_5OH} = 26 \text{ g } C_2H_5OH$$

$$n\{CH_3CO_2H\} = 0.396 \text{ mol} + 0.19 \text{ mol} = 0.59 \text{ mol } CH_3CO_2H$$

$$\text{mass } CH_3CO_2H = 0.59 \text{mol } CH_3CO_2H \times \frac{60.05 \text{ g } CH_3CO_2H}{1 \text{ mol } CH_3CO_2H} = 35 \text{ g } CH_3CO_2H$$

$$n\{CH_3CO_2C_2H_5\} = 0.552 \text{ mol} - 0.19 \text{ mol} = 0.36 \ CH_3CO_2C_2H_5$$

$$\text{mass } CH_3CO_2C_2H_5 = 0.36 \text{mol } CH_3CO_2C_2H_5 \times \frac{88.10 \text{ g } CH_3CO_2C_2H_5}{1 \text{ mol } CH_3CO_2C_2H_5} = 32 \text{ g } CH_3CO_2C_2H_5$$

$$n\{H_2O\} = 3.95 \text{ mol} - 0.19 \text{ mol} = 3.76 \text{ mol } H_2O$$

$$\text{mass } H_2O = 3.76 \text{mol } H_2O \times \frac{18.02 \text{ g } H_2O}{1 \text{ mol } H_2O} = 68 \text{ g } H_2O$$

$$\text{To check } K_c = \frac{n\{CH_3CO_2C_2H_5\}\,n\{H_2O\}}{n\{C_2H_5OH\}\,n\{CH_3CO_2H\}} = \frac{0.36 \text{ mol} \times 3.76 \text{ mol}}{0.56 \text{ mol} \times 0.59 \text{ mol}} = 4.1$$

40. **(M)** The final volume of the mixture is $0.750 \text{ L} + 2.25 \text{ L} = 3.00 \text{ L}$. Then use the balanced chemical equation to organize the data we have concerning the reaction. The reaction should shift to the right, that is, form products in reaching a new equilibrium, since the volume is greater.

Equation:	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
Initial:	$\frac{0.971 \text{ mol}}{3.00 \text{ L}}$		$\frac{0.0580 \text{ mol}}{3.00 \text{ L}}$
Initial:	$0.324\,M$		$0.0193\,M$
Changes:	$-x\,M$		$+2x\,M$
Equil :	$(0.324-x)M$		$(0.0193+2x)M$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0193 + 2x)^2}{0.324 - x} = \frac{0.000372 + 0.0772x + 4x^2}{0.324 - x} = 4.61 \times 10^{-3}$$

$$0.000372 + 0.0772x + 4x^2 = 0.00149 - 0.00461x \qquad 4x^2 + 0.0818x - 0.00112 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0818 \pm \sqrt{0.00669 + 0.0179}}{8} = 0.00938 \text{ M}, \ -0.0298 \text{ M}$$

$[NO_2] = 0.0193 + (2 \times 0.00938) = 0.0381$ M
amount NO_2 = 0.0381 M × 3.00 L = 0.114 mol NO_2

$[N_2O_4] = 0.324 - 0.00938 = 0.3146$ M
amount N_2O_4 = 0.3146 M × 3.00 L = 0.944 mol N_2O_4

41. **(M)** $[HCONH_2]_{init} = \frac{0.186 \text{ mol}}{2.16 \text{ L}} = 0.0861$ M

Equation:	$HCONH_2(g) \rightleftharpoons$	$NH_3(g)$	+	$CO(g)$
Initial:	0.0861 M	0 M		0 M
Changes:	$-x$ M	$+x$ M		$+x$ M
Equil :	(0.0861-x) M	x M		x M

$$K_c = \frac{[NH_3][CO]}{[HCONH_2]} = \frac{x \cdot x}{0.0861 - x} = 4.84 \qquad x^2 = 0.417 - 4.84x \qquad 0 = x^2 + 4.84x - 0.417$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.84 \pm \sqrt{23.4 + 1.67}}{2} = 0.084 \text{ M}, \ -4.92 \text{ M}$$

The negative concentration obviously is physically meaningless. We determine the total concentration of all species, and then the total pressure with $x = 0.084$.

$$[\text{total}] = [NH_3] + [CO] + [HCONH_2] = x + x + 0.0861 - x = 0.0861 + 0.084 = 0.170 \text{ M}$$

$$P_{tot} = 0.170 \text{ mol L}^{-1} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 400. \text{ K} = 5.58 \text{ atm}$$

42. **(E) C**ompare Q_p to K_p. We assume that the added solids are of negligible volume so that the initial partial pressures of CO_2(g) and H_2O(g) do not significantly change.

$$P\{H_2O\} = \left(715 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}\right) = 0.941 \text{ atm } H_2O$$

$$Q_p = P\{CO_2\}P\{H_2O\} = 2.10 \text{ atm } CO_2 \times 0.941 \text{ atm } H_2O = 1.98 > 0.23 = K_p$$

Because Q_p is larger than K_p, the reaction will proceed left toward reactants to reach equilibrium. Thus, the partial pressures of the two gases will decrease.

43. (M)
We organize the solution around the balanced chemical equation.

Equation:	$2\ Cr^{3+}(aq)\ +\ Cd(s)$	$\rightleftharpoons$	$2\ Cr^{2+}(aq)$	$+\ Cd^{2+}(aq)$
Initial:	1.00 M		0 M	0 M
Changes:	$-2x$ M		$+2x$	$+x$
Equil:	$(1.00-2x)$ M		$2x$	x

$$K_c = \frac{[Cr^{2+}]^2[Cd^{2+}]}{[Cr^{3+}]^2} = \frac{(2x)^2(x)}{(1.00-2x)^2} = 0.288$$

Via successive approximations, one obtains $x = 0.257$ M

Therefore, at equilibrium, $[Cd^{2+}]$ = 0.257 M, $[Cr^{2+}]$ = 0.514 M and $[Cr^{3+}]$ = 0.486 M

Minimum mass of Cd(s) = 0.350L × 0.257 M × 112.41 g/mol = 10.1 g of Cd metal

44. (M) Again we base the set-up of the problem around the balanced chemical equation.

Equation:	$Pb(s) + 2\ Cr^{3+}(aq)$		$\xrightleftharpoons{K_c=3.2\times10^{-10}}$	$Pb^{2+}(aq)$	$+\ 2\ Cr^{2+}(aq)$
Initial:	–	0.100 M		0 M	0 M
Changes:	–	$-2x$ M		$+x$M	$+2x$ M
Equil :	–	$(0.100-2x)$M		xM	$2x$ M

$$K_c = \frac{x(2x)^2}{(0.100)^2} = 3.2\times10^{-10} \qquad 4x^3 = (0.100)^2\times3.2\times10^{-10} = 3.2\times10^{-12}$$

$$x = \sqrt[3]{\frac{3.2\times10^{-12}}{4}} = 9.3\times10^{-5}\ \text{M}$$ Assumption that $2x << 0.100$, is valid and thus

$[Pb^{2+}] = x = 9.3\times10^{-5}$ M, $[Cr^{2+}]$ = 1.9 × 10^{-4} M and $[Cr^{3+}]$ = 0.100 M

45. (M) We are told in this question that the reaction $SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$ has K_c = 4.0 at a certain temperature *T*. This means that at the temperature *T*, $[SO_2Cl_2]$ = 4.0 × $[Cl_2]$ × $[SO_2]$. Careful scrutiny of the three diagrams reveals that sketch (b) is the best representation because it contains numbers of SO_2Cl_2, SO_2, and Cl_2 molecules that are consistent with the K_c for the reaction. In other words, sketch (b) is the best choice because it contains 12 SO_2Cl_2 molecules (per unit volume), 1 Cl_2 molecule (per unit volume) and 3 SO_2 molecules (per unit volume), which is the requisite number of each type of molecule needed to generate the expected K_c value for the reaction at temperature *T*.

46. (M) In this question we are told that the reaction 2 NO(g) + Br_2(g) $\rightleftharpoons$ 2 NOBr(g) has K_c = 3.0 at a certain temperature *T*. This means that at the temperature *T*, $[NOBr]^2$ = 3.0 × $[Br_2][NO]^2$. Sketch (c) is the most accurate representation because it contains 18 NOBr molecules (per unit volume), 6 NO molecules (per unit volume), and 3 Br_2 molecules (per unit volume), which is the requisite number of each type of molecule needed to generate the expected K_c value for the reaction at temperature *T*.

47. **(E)**

$$K = \frac{[\text{aconitate}]}{[\text{citrate}]}$$

$$Q = \frac{4.0 \times 10^{-5}}{(0.00128)} = 0.031$$

Since Q = K, the reaction is at equilibrium,

48. **(E)**

$$K = \frac{[CO_2][NAD_{red}][\text{oxoglut.}]}{[\text{citrate}][NAD_{ox}]}$$

$$Q = \frac{(0.00868)(0.00132)(0.00868)}{(0.00128)(0.00868)} = 0.00895$$

Since Q < K, the reaction needs to proceed to the right (products).

Partial Pressure Equilibrium Constant, K_p

49. **(M)** The $I_2(s)$ maintains the presence of I_2 in the flask until it has all vaporized. Thus, if enough HI(g) is produced to completely consume the $I_2(s)$, equilibrium will not be achieved.

$$P\{H_2S\} = 747.6 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.9837 \text{ atm}$$

Equation:	$H_2S(g) +$	$I_2(s)$	$\rightleftharpoons$	$2\ HI(g) +$	$S(s)$
Initial:	0.9837 atm			0 atm	
Changes:	$-x$ atm			$+2x$ atm	
Equil:	$(0.9837 - x)$ atm			$2x$ atm	

$$K_p = \frac{P\{HI\}^2}{P\{H_2S\}} = \frac{(2x)^2}{(0.9837 - x)} = 1.34 \times 10^{-5} = \frac{4x^2}{0.9837}$$

$$x = \sqrt{\frac{1.34 \times 10^{-5} \times 0.9837}{4}} = 1.82 \times 10^{-3} \text{ atm}$$

The assumption that $0.9837 >> x$ is valid. Now we verify that sufficient $I_2(s)$ is present by computing the mass of I_2 needed to produce the predicted pressure of HI(g). Initially, 1.85 g I_2 is present (given).

$$\text{mass } I_2 = \frac{1.82 \times 10^{-3} \text{ atm} \times 0.725 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 333 \text{ K}} \times \frac{1 \text{ mol } I_2}{2 \text{ mol HI}} \times \frac{253.8 \text{ g } I_2}{1 \text{ mol } I_2} = 0.00613 \text{ g } I_2$$

$$P_{tot} = P\{H_2S\} + P\{HI\} = (0.9837 - x) + 2x = 0.9837 + x = 0.9837 + 0.00182 = 0.9855 \text{ atm}$$

$$P_{tot} = 749.0 \text{ mmHg}$$

50. **(M)** We first determine the initial pressure of NH_3.

$$P\{NH_3(g)\}=\frac{nRT}{V}=\frac{0.100\text{ mol }NH_3\times 0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}\times 298\text{ K}}{2.58\text{ L}}=0.948\text{ atm}$$

Equation:	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$
Initial:			0.948 atm		0 atm
Changes:			$+x$ atm		$+x$ atm
Equil:			$(0.948+x)$atm		x atm

$$K_p = P\{NH_3\}P\{H_2S\} = 0.108 = (0.948+x)x = 0.948x + x^2 \quad 0 = x^2 + 0.948x - 0.108$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.948 \pm \sqrt{0.899+0.432}}{2} = \ 0.103\text{ atm},\ -1.05\text{ atm}$$

The negative root makes no physical sense. The total gas pressure is obtained as follows.
$P_{tot} = P\{NH_3\} + P\{H_2\ S\} = (0.948+x)+x = 0.948+2x = 0.948+2\times 0.103 = 1.154$ atm

51. **(M)** We substitute the given equilibrium pressure into the equilibrium constant expression and solve for the other equilibrium pressure. $K_p = \frac{P\{O_2\}^3}{P\{CO_2\}^2} = 28.5 = \frac{P\{O_2\}^3}{(0.0721\text{ atm }CO_2)^2}$

$$P\{O_2\}=\sqrt[3]{P\{O_2\}^3}=\sqrt[3]{28.5(0.0712\text{ atm})^2}=0.529\text{ atm }O_2$$

$$P_{total} = P\{CO_2\} + P\{O_2\} = 0.0721\text{ atm }CO_2 + 0.529\text{ atm }O_2 = 0.601\text{ atm total}$$

52. **(M)** The composition of dry air is given in volume percent. Division of these percentages by 100 gives the volume fraction, which equals the mole fraction and also the partial pressure in atmospheres, if the total pressure is 1.00 atm. Thus, we have $P\{O_2\} = 0.20946$ atm and $P\{CO_2\} = 0.00036$ atm. We substitute these two values into the expression for Q_p.

$$Q_p = \frac{P\{O_2\}^3}{P\{CO_2\}^2} = \frac{(0.20946\text{ atm }O_2)^3}{(0.00036\text{ atm }CO_2)^2} = 6.4\times 10^4 > 28.5 = K_p$$

The value of Q_p is much larger than the value of K_p. Thus this reaction should be spontaneous in the reverse direction until equilibrium is achieved. It will only be spontaneous in the forward direction when the pressure of O_2 drops or that of CO_2 rises (as would be the case in self-contained breathing devices).

53. **(M)**
(a) We first determine the initial pressure of each gas.

$$P\{CO\} = P\{Cl_2\} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 668 \text{ K}}{1.75 \text{ L}} = 31.3 \text{ atm}$$

Then we calculate equilibrium partial pressures, organizing our calculation around the balanced chemical equation. We see that the equilibrium constant is not very large, meaning that we must solve the polynomial exactly (or by successive approximations).

Equation	$CO(g)$	$+\ Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$	$K_p = 22.5$
Initial:	31.3 atm	31.3 atm		0 atm	
Changes:	$-x$ atm	$-x$ atm		$+x$ atm	
Equil:	$31.3-x$ atm	$31.3-x$ atm		x atm	

$$K_p = \frac{P\{COCl_2\}}{P\{CO\}\,P\{Cl_2\}} = 22.5 = \frac{x}{(31.3-x)^2} = \frac{x}{(979.\underline{7} - 62.6x + x^2)}$$

$$22.5(979.\underline{7} - 62.6x + x^2) = x = 220\underline{43} - 140\underline{8.5}x + 22.5x^2 = x$$

$$220\underline{43} - 140\underline{9.5}x + 22.5x^2 = 0 \quad \text{(Solve by using the quadratic equation)}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-1409.5) \pm \sqrt{(-140\underline{9.5})^2 - 4(22.5)(220\underline{43})}}{2(22.5)}$$

$$x = \frac{1409.5 \pm \sqrt{2818}}{45} = 30.1\underline{4},\ 32.5 \text{(too large)}$$

$$P\{CO\} = P\{Cl_2\} = 31.3 \text{ atm} - 30.1\underline{4} \text{ atm} = 1.16 \text{ atm} \qquad P\{COCl_2\} = 30.1\underline{4} \text{ atm}$$

(b) $P_{total} = P\{CO\} + P\{Cl_2\} + P\{COCl_2\} = 1.1\underline{6} \text{ atm} + 1.1\underline{6} \text{ atm} + 30.1\underline{4} \text{ atm} = 32.46 \text{ atm}$

54. **(M)** We first find the value of K_p for the reaction.

$$2\ NO_2(g) \rightleftharpoons 2\ NO(g) + O_2(g), \quad K_c = 1.8 \times 10^{-6} \text{ at } 184\ ^\circ C = 457 \text{ K}.$$

For this reaction $\Delta n_{gas} = 2 + 1 - 2 = +1$.

$$K_p = K_c(RT)^{\Delta n_g} = 1.8 \times 10^{-6}\,(0.08206 \times 457)^{+1} = 6.8 \times 10^{-5}$$

To obtain the required reaction $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ from the initial reaction, that initial reaction must be reversed and then divided by two. Thus, in order to determine the value of the equilibrium constant for the final reaction, the value of K_p for the initial reaction must be inverted, and the square root taken of the result.

$$K_{p,\,final} = \sqrt{\frac{1}{6.8 \times 10^{-5}}} = 1.2 \times 10^2$$

Le Châtelier's Principle

55. **(E)** Continuous removal of the product, of course, has the effect of decreasing the concentration of the products below their equilibrium values. Thus, the equilibrium system is disturbed by removing the products and the system will attempt (in vain, as it turns out) to re-establish the equilibrium by shifting toward the right, that is, to generate more products.

56. **(E)** We notice that the density of the solid ice is smaller than is that of liquid water. This means that the same mass of liquid water is present in a smaller volume than an equal mass of ice. Thus, if pressure is placed on ice, attempting to force it into a smaller volume, the ice will be transformed into the less-space-occupying water at $0^\circ C$. Thus, at $0^\circ C$ under pressure, $H_2O(s)$ will melt to form $H_2O(l)$. This behavior is *not* expected in most cases because generally a solid is *more* dense than its liquid phase.

57. **(M)**

(a) This reaction is exothermic with $\Delta H^\circ = -150.$ kJ. Thus, high temperatures favor the reverse reaction (endothermic reaction). The amount of $H_2(g)$ present at high temperatures will be less than that present at low temperatures.

(b) $H_2O(g)$ is one of the reactants involved. Introducing more will cause the equilibrium position to shift to the right, favoring products. The amount of $H_2(g)$ will increase.

(c) Doubling the volume of the container will favor the side of the reaction with the largest sum of gaseous stoichiometric coefficients. The sum of the stoichiometric coefficients of gaseous species is the same (4) on both sides of this reaction. Therefore, increasing the volume of the container will have no effect on the amount of $H_2(g)$ present at equilibrium.

(d) A catalyst merely speeds up the rate at which a reaction reaches the equilibrium position. The addition of a catalyst has no effect on the amount of $H_2(g)$ present at equilibrium.

58. **(M)**

(a) This reaction is endothermic, with $\Delta H^o = +92.5$ kJ. Thus, a higher temperature will favor the forward reaction and increase the amount of HI(g) present at equilibrium.

(b) The introduction of more product will favor the reverse reaction and decrease the amount of HI(g) present at equilibrium.

(c) The sum of the stoichiometric coefficients of gaseous products is larger than that for gaseous reactants. Increasing the volume of the container will favor the forward reaction and increase the amount of HI(g) present at equilibrium.

(d) A catalyst merely speeds up the rate at which a reaction reaches the equilibrium position. The addition of a catalyst has no effect on the amount of HI(g) present at equilibrium.

(e) The addition of an inert gas to the constant-volume reaction mixture will not change any partial pressures. It will have no effect on the amount of HI(g) present at equilibrium.

59. **(M)**

(a) The formation of NO(g) from its elements is an endothermic reaction ($\Delta H^{\circ} = +181$ kJ/mol). Since the equilibrium position of endothermic reactions is shifted toward products at higher temperatures, we expect more NO(g) to be formed from the elements at higher temperatures.

(b) Reaction rates always are enhanced by higher temperatures, since a larger fraction of the collisions will have an energy that surmounts the activation energy. This enhancement of rates affects both the forward and the reverse reactions. Thus, the position of equilibrium is reached more rapidly at higher temperatures than at lower temperatures.

60. **(M)** If the reaction is endothermic ($\Delta H^{\circ} > 0$), the forward reaction is favored at high temperatures. If the reaction is exothermic ($\Delta H^{\circ} < 0$), the forward reaction is favored at low temperatures.

(a) $\Delta H^{\circ} = \Delta H_f^{\circ}\left[PCl_5(g)\right] - \Delta H_f^{\circ}\left[PCl_3(g)\right] - \Delta H_f^{\circ}\left[Cl_2(g)\right]$

$\Delta H^{\circ} = -374.9\text{ kJ} - (-287.0\text{ kJ}) - 0.00\text{ kJ} = -87.9\text{ kJ/mol}$ (favored at low temperatures)

(b) $\Delta H^{\circ} = 2\Delta H_f^{\circ}[H_2O(g)] + 3\Delta H_f^{\circ}[S(\text{rhombic})] - \Delta H_f^{\circ}[SO_2(g)] - 2\,\Delta H_f^{\circ}[H_2S(g)]$

$\Delta H^{\circ} = 2(-241.8\text{ kJ}) + 3(0.00\text{ kJ}) - (-296.8\text{ kJ}) - 2(-20.63\text{ kJ})$

$\Delta H^{\circ} = -145.5\text{ kJ/mol}$ (favored at low temperatures)

(c) $\Delta H^{\circ} = 4\Delta H_f^{\circ}\left[NOCl(g)\right] + 2\Delta H_f^{\circ}\left[H_2O(g)\right]$

$-2\Delta H_f^{\circ}\left[N_2(g)\right] - 3\Delta H_f^{\circ}\left[O_2(g)\right] - 4\Delta H_f^{\circ}\left[HCl(g)\right]$

$\Delta H^{\circ} = 4(51.71\text{ kJ}) + 2(-241.8\text{ kJ}) - 2(0.00\text{ kJ}) - 3(0.00\text{ kJ}) - 4(-92.31\text{ kJ})$

$\Delta H^{\circ} = +92.5\text{ kJ/mol}$ (favored at higher temperatures)

61. **(E)** If the total pressure of a mixture of gases at equilibrium is doubled by compression, the equilibrium will shift to the side with fewer moles of gas to counteract the increase in pressure. Thus, if the pressure of an equilibrium mixture of $N_2(g)$, $H_2(g)$, and $NH_3(g)$ is doubled, the reaction involving these three gases, i.e., $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, will proceed in the forward direction to produce a new equilibrium mixture that contains additional ammonia and less molecular nitrogen and molecular hydrogen. In other words, $P\{N_2(g)\}$ will have decreased when equilibrium is re-established. It is important to note, however, that the final equilibrium partial pressure for the N_2 will, nevertheless, be higher than its original partial pressure prior to the doubling of the total pressure.

62. **(M)**

(a) Because $\Delta H^{o} = 0$, the position of the equilibrium for this reaction will not be affected by temperature. Since the equilibrium position is expressed by the value of the equilibrium constant, we expect K_p to be unaffected by, or to remain constant with, temperature.

(b) From part (a), we know that the value of K_p will not change when the temperature is changed. The pressures of the gases, however, will change with temperature. (Recall the ideal gas law: $P = nRT/V$.) In fact, all pressures will increase. The stoichiometric coefficients in the reaction are such that at higher pressures the formation of more reactant will be favored (the reactant side has fewer moles of gas). Thus, the amount of D(g) will be smaller when equilibrium is reestablished at the higher temperature for the cited reaction.

$$A(s) \rightleftharpoons B(s) + 2\ C(g) + \frac{1}{2}\ D(g)$$

63. **(M)** Increasing the volume of an equilibrium mixture causes that mixture to shift toward the side (reactants or products) where the sum of the stoichiometric coefficients of the gaseous species is the larger. That is: shifts to the right if $\Delta n_{gas} > 0$, shifts to the left if $\Delta n_{gas} < 0$, and does not shift if $\Delta n_{gas} = 0$.

(a) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g), \Delta n_{gas} > 0,$ shift right, toward products

(b) $Ca(OH)_2(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + H_2O(g),\ \ \Delta n_{gas} = 0,$ no shift, no change in equilibrium position.

(c) $4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g),\ \ \Delta n_{gas} > 0,$ shifts right, towards products

64. **(M)** The equilibrium position for a reaction that is exothermic shifts to the left (reactants are favored) when the temperature is raised. For one that is endothermic, it shifts right (products are favored) when the temperature is raised.

(a) $NO(g) \rightleftharpoons \frac{1}{2}\ N_2(g) + \frac{1}{2}\ O_2(g)$ $\quad \Delta H^{o} = -90.2$ kJ shifts left, % dissociation ↓

(b) $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}\ O_2(g)$ $\quad \Delta H^{o} = +98.9$ kJ shifts right, % dissociation ↑

(c) $N_2H_4(g) \rightleftharpoons N_2(g) + 2\ H_2(g)$ $\quad \Delta H^{o} = -95.4$ kJ shifts left, % dissociation ↓

(d) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ $\quad \Delta H^{o} = +108.3$ kJ shifts right, % dissociation ↑

65. **(E)**

(a) Hb:O_2 is reduced, because the reaction is exothermic and heat is like a product.

(b) No effect, because the equilibrium involves O_2 (aq). Eventually it will reduce the Hb:O_2 level because removing O_2(g) from the atmosphere also reduces O_2 (aq) in the blood.

(c) Hb:O_2 level increases to use up the extra Hb.

66. (E)
(a) CO_2 (g) increases as the equilibrium is pushed toward the reactant side
(b) Increase CO_2 (aq) levels, which then pushes the equilibrium to the product side
(c) It has no effect, but it helps establish the final equilibrium more quickly
(d) CO_2 increases, as the equilibrium shifts to the reactants

67. (E) The pressure on N_2O_4 will initially increase as the crystal melts and then vaporizes, but over time the new concentration decreases as the equilibrium is shifted toward NO_2.

68. (E) If the equilibrium is shifted to the product side by increasing temperature, that means that heat is a "reactant" (or being consumed). Therefore, HI decomposition is endothermic.

69. (E) Since ΔH is >0, the reaction is endothermic. If we increase the temperature of the reaction, we are adding heat to the reaction, which shifts the reaction toward the decomposition of calcium carbonate. While the amount of calcium carbonate will decrease, its concentration will remain the same because it is a solid.

70. (E) The amount of N_2 increases in the body. As the pressure on the body increases, the equilibrium shifts from N_2 gas to N_2 (aq).

Integrative and Advanced Exercises

71. (E) In a reaction of the type $I_2(g) \rightarrow 2\ I(g)$ the bond between two iodine atoms, the I—I bond, must be broken. Since $I_2(g)$ is a stable molecule, this bond breaking process must be endothermic. Hence, the reaction cited is an endothermic reaction. The equilibrium position of endothermic reactions will be shifted toward products when the temperature is raised.

72. (M)
(a) In order to determine a value of K_c, we first must find the CO_2 concentration in the gas phase. Note, the total volume for the gas is 1.00 L (moles and molarity are numerically equal)

$$[CO_2] = \frac{n}{V} = \frac{P}{RT} = \frac{1.00\text{ atm}}{0.08206\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\times 298\text{ K}} = 0.0409\text{ M} \qquad K_c = \frac{[CO_2(aq)]}{[CO_2(g)]} = \frac{3.29\times10^{-2}\text{ M}}{0.0409\text{ M}} = 0.804$$

(b) It does not matter to which phase the radioactive $^{14}CO_2$ is added. This is an example of a Le Châtelier's principle problem in which the stress is a change in concentration of the reactant $CO_2(g)$. To find the new equilibrium concentrations, we must solve and I.C.E. table. Since $Q_c < K_c$, the reaction shifts to the product, CO_2 (aq) side.

Reaction:	$CO_2(g)$ $\rightleftharpoons$	$CO_2(aq)$
Initial:	0.0409 mol	3.29×10^{-3} mol
Stress	+0.01000 mol	–
Changes:	$-x$ mol	$+x$ mol
Equilibrium:	$(0.05090-x)$ mol	$3.29\times10^{-3}+x$ mol

$$K_C = \frac{[CO_2(aq)]}{[CO_2(g)]} = \frac{\dfrac{3.29\times10^{-3} + x \text{ mol}}{0.1000 \text{ L}}}{\dfrac{(0.05090 - x)\text{ mol}}{1.000 \text{ L}}} = 0.804 = \frac{3.29\times10^{-2} + 10x}{0.05090 - x} \qquad x = 7.43\times10^{-4}\text{ mol } CO_2$$

Total moles of CO_2 in the aqueous phase $(0.1000 \text{ L})(3.29\times10^{-2} + 7.43\times10^{-3}) = 4.03\times10^{-3}$ moles

Total moles of CO_2 in the gaseous phase $(1.000 \text{ L})(5.090\times10^{-2} - 7.43\times10^{-4}) = 5.02\times10^{-2}$ moles
Total moles of $CO_2 = 5.02\times10^{-2}$ moles $+ 4.03\times10^{-3}$ moles $= 5.42\times10^{-2}$ moles
There is continuous mixing of the ^{12}C and ^{14}C such that the isotopic ratios in the two phases is the same. This ratio is given by the mole fraction of the two isotopes.
For $^{14}CO_2$ in either phase its mole fraction is $\dfrac{0.01000 \text{ mol}}{5.41\underline{9}\times10^{-2}\text{ mol}}\times100 = 18.4\underline{5}\ \%$

Moles of $^{14}CO_2$ in the gaseous phase $= 5.02\times10^{-2}$ moles$\times0.1845 = 0.00926$ moles
Moles of $^{14}CO_2$ in the aqueous phase $= 4.03\times10^{-3}$ moles$\times0.1845 = 0.000744$ moles

73. **(M)** Dilution makes Q_c larger than K_c. Thus, the reaction mixture will shift left in order to regain equilibrium. We organize our calculation around the balanced chemical equation.

Equation:	$Ag^+(aq)$	+	$Fe^{2+}(aq)$	$\rightleftharpoons$	$Fe^{3+}(aq)$ + $Ag(s)$	$K_c = 2.98$
Equil:	0.31 M		0.21 M		0.19 M −	
Dilution:	0.12 M		0.084 M		0.076 M −	
Changes:	$+x$ M		$+x$ M		$-x$ M −	
New equil:	$(0.12 + x)$ M		$(0.084 + x)$ M		$(0.076 - x)$ M −	

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = 2.98 = \frac{0.076 - x}{(0.12 + x)\,(0.084 + x)} \qquad 2.98\,(0.12 + x)\,(0.084 + x) = 0.076 - x$$

$$0.076 - x = 0.030 + 0.61x + 2.98\,x^2 \qquad 2.98\,x^2 + 1.61\,x - 0.046 = 0$$

$x = \dfrac{-1.61 \pm \sqrt{2.59 + 0.55}}{5.96} = 0.027, -0.57$ Note that the negative root makes no physical sense; it gives $[Fe^{2+}] = 0.084 - 0.57 = -0.49$ M.
Thus, the new equilibrium concentrations are

$[Fe^{2+}] = 0.084 + 0.027 = 0.111$ M $\qquad [Ag^+] = 0.12 + 0.027 = 0.15$ M
$[Fe^{3+}] = 0.076 - 0.027 = 0.049$ M We can check our answer by substitution.

$$Kc = \frac{0.049 \text{ M}}{0.111 \text{ M} \times 0.15 \text{ M}} = 2.94 \approx 2.98 \text{ (within precision limits)}$$

74. **(M)** The percent dissociation should increase as the pressure is lowered, according to Le Châtelier's principle. Thus the total pressure in this instance should be more than in Example 15-12, where the percent dissociation is 12.5%. The total pressure in Example 15-12 was computed starting from the total number of moles at equilibrium.
The total amount = (0.0240 – 0.00300) moles N_2O_4 + 2 × 0.00300 mol NO_2 = 0.027 mol gas.

$$P_{total} = \frac{nRT}{V} = \frac{0.0270 mol \times 0.08206\, L\, atm\, K^{-1}\, mol^{-1} \times 298\, K}{0.372\, L} = 1.77\, atm \text{ (Example 15-12)}$$

We base our solution on the balanced chemical equation. We designate the initial pressure of N_2O_4 as P. The change in $P\{N_2O_4\}$ is given as –0.10 P atm. to represent the 10.0 % dissociation.

Equation:	$N_2O_4(g)$	$\rightleftharpoons$	$2\,NO_2(g)$
Initial:	P atm		0 atm
Changes:	$-0.10\,P$ atm		$+2(0.10\,P$ atm)
Equil:	0.90 P atm		0.20 P atm

$$K_p = \frac{P\{NO_2\}^2}{P\{N_2O_4\}} = \frac{(0.20\,P)^2}{0.90\,P} = \frac{0.040\,P}{0.90} = 0.113 \qquad P = \frac{0.113 \times 0.90}{0.040} = 2.54\, atm.$$

Thus, the total pressure at equilibrium is 0.90 P + 0.20 P and 1.10 P (where P = 2.54 atm) Therefore, total pressure at equilibrium = 2.79 atm.

75. **(M)**

Equation:	$2\,SO_3(g)$	$\rightleftharpoons$	$2\,SO_2(g)$	+	$O_2(g)$
Initial:	1.00 atm		0 atm		0 atm
Changes:	$-2x$ atm		$+2x$ atm		$+x$ atm
Equil:	$(1.00-2x)$atm		$2x$ atm		x atm

Because of the small value of the equilibrium constant, the reaction does not proceed very far toward products in reaching equilibrium. Hence, we assume that $x \ll 1.00$ atm and calculate an approximate value of x (small K problem).

$$K_P = \frac{P\{SO_2\}^2\; P\{O_2\}}{P\{SO_3\}^2} = \frac{(2x)^2\, x}{(1.00-2x)^2} = 1.6\times10^{-5} \approx \frac{4x^3}{(1.00)^2} \qquad x = 0.016 \text{ atm}$$

A second cycle may get closer to the true value of x.

$$1.6\times10^{-5} \approx \frac{4x^3}{(1.00-0.032)^2} = \quad x = 0.016\, atm$$

Our initial value was sufficiently close. We now compute the total pressure at equilibrium.

$$P_{total} = P\{SO_3\} + P\{SO_2\} + P\{O_2\} = (1.00-2x) + 2x + x = 1.00 + x = 1.00 + 0.016 = 1.02\, atm$$

76. **(M)** Let us start with one mole of air, and let $2x$ be the amount in moles of NO formed.

Equation:	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\,NO(g)$
Initial:	0.79 mol		0.21 mol		0 mol
Changes:	$-x$ mol		$-x$ mol		$+2x$ mol
Equil:	$(0.79-x)$mol		$(0.21-x)$mol		$2x$ mol

$$\chi_{NO} = \frac{n\{NO\}}{n\{N_2\} + n\{O_2\} + n\{NO\}} = \frac{2x}{(0.79 - x) + (0.21 - x) + 2x} = 0.018 = \frac{2x}{1.00}$$

$x = 0.0090$ mol $\qquad 0.79 - x = 0.78$ mol N_2 $\qquad 0.21 - x = 0.20$ mol O_2

$2x = 0.018$ mol NO

$$K_p = \frac{P\{NO\}^2}{P(N_2\}\, P\{O_2\}} = \frac{\left(\dfrac{n\{NO\}\, RT}{V_{total}}\right)^2}{\dfrac{n\{N_2)\, RT}{V_{total}}\,\dfrac{n\{O_2\}\, RT}{V_{total}}} = \frac{n\{NO\}^2}{n\{N_2\}\, n\{O_2\}} = \frac{(0.018)^2}{0.78 \times 0.20} = 2.1 \times 10^{-3}$$

77. (D) We organize the data around the balanced chemical equation. Note that the reaction is stoichimoetrically balanced.

(a) Equation: $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

	$2\ SO_2(g)$	$O_2(g)$	$2\ SO_3(g)$
Equil:	0.32 mol	0.16 mol	0.68 mol
Add SO_3	0.32 mol	0.16 mol	1.68 mol
Initial:	$\frac{0.32\text{ mol}}{10.0\text{ L}}$	$\frac{0.16\text{ mol}}{10.0\text{ L}}$	$\frac{1.68\text{ mol}}{10.0\text{ L}}$
Initial:	0.032 M	0.016 M	0.168 M
To right:	0.000 M	0.000 M	0.200 M
Changes:	$+2x$ M	$+x$ M	$-2x$ M
Equil:	$2x$ M	x M	$(0.200 - 2x)$M

In setting up this problem, we note that solving this question exactly involves finding the roots for a cubic equation. Thus, we assumed that all of the reactants have been converted to products. This gives the results in the line labeled "To right." We then reach equilibrium from this position by converting some of the product back into reactants. Now, we substitute these expressions into the equilibrium constant expression, and we solve this expression approximately by assuming that $2x << 0.200$.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.200 - 2x)^2}{(2x)^2 x} = 2.8 \times 10^2 \approx \frac{(0.200)^2}{4x^3} \text{ or } x = 0.033$$

We then substitute this approximate value into the expression for K_c.

$$K_c = \frac{(0.200 - 0.066)^2}{4x^3} = 2.8 \times 10^2 \textit{ or } x = 0.025$$

Let us try one more cycle. $K_c = \dfrac{(0.200 - 0.050)^2}{4x^3} = 2.8 \times 10^2$ or $x = 0.027$

This gives the following concentrations and amounts of each species.

$[SO_3] = 0.200 - (2 \times 0.027) = 0.146\ M$ amount $SO_3 = 10.0\ L \times 0.146\ M = 1.46\ mol\ SO_3$

$[SO_2] = 2 \times 0.027 = 0.054\ M$ amount $SO_2 = 10.0\ L \times 0.054\ M = 0.54\ mol\ SO_2$

$[O_2] = 0.027\ M$ amount $O_2 = 10.0\ L \times 0.027\ M = 0.27\ mol\ O_2$

(b)

Equation:	$2\ SO_2(g)$	+ $O_2(g)$	$\rightleftharpoons 2\ SO_3(g)$
Equil:	0.32 mol	0.16 mol	0.68 mol
Equil:	$\frac{0.32\ mol}{10.0\ L}$	$\frac{0.16\ mol}{10.0\ L}$	$\frac{0.68\ mol}{10.0\ L}$
Equil:	0.032 M	0.016 M	0.068 M
0.10 V:	0.32 M	0.16 M	0.68 M
To right:	0.00 M	0.00 M	1.00 M
Changes:	$+2x$ M	$+x$ M	$-2x$ M
Equil:	$2x$ M	x M	$(1.00-2x)$M

Again, notice that an exact solution involves finding the roots of a cubic. So we have taken the reaction 100% in the forward direction and then sent it back in the reverse direction to a small extent to reach equilibrium. We now solve the K_c expression for x, obtaining first an approximate value by assuming $2x << 1.00$.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.00-2x)^2}{(2x)^2 x} = 2.8\times10^2 \approx \frac{(1.00)^2}{4x^3}\ or\ x = 0.096$$

We then use this approximate value of x to find a second approximation for x.

$$K_c = \frac{(1.00-0.19)^2}{4x^3} = 2.8\times10^2 \qquad \text{or} \qquad x = 0.084$$

Another cycle gives $K_c = \frac{(1.00-0.17)^2}{4x^3} = 2.8\times10^2$ or $x = 0.085$

Then we compute the equilibrium concentrations and amounts.

$[SO_3] = 1.00 - (2 \times 0.085) = 0.83\ M$ amount $SO_3 = 1.00\ L \times 0.83\ M = 0.83\ mol\ SO_3$

$[SO_2] = 2 \times 0.085 = 0.17\ M$ amount $SO_2 = 1.00\ L \times 0.17\ M = 0.17\ mol\ SO_2$

$[O_2] = 0.085\ M$ amount $O_2 = 1.00\ L \times 0.085\ M = 0.085\ mol\ O_2$

78. (M)

Equation: $HOC_6H_4COOH(g) \rightleftharpoons C_6H_5OH(g) + CO_2(g)$

$$n_{CO_2} = \frac{PV}{RT} = \left(\frac{\frac{730mmHg}{760mmHg/atm}}{0.0821L-atm/mol-K}\right)\left(\frac{\left(\frac{48.2+48.5}{2}\right)\times\frac{1\ L}{1000\ mL}}{(293K)}\right) = 1.93\times10^{-3}\ mol\ CO_2$$

Note that moles of CO_2 = moles phenol

$$n_{\text{salicylic acid}} = \frac{0.300g}{138g/mol} = 2.17\times10^{-3} \text{ mol salicylic acid}$$

$$K_c = \frac{[C_6H_5OH][CO_2(g)]}{[HOC_6H_4COOH]} = \frac{\left(\frac{1.93 \text{ mmol}}{50.0 \text{ mL}}\right)^2}{\frac{(2.17-1.93)\text{ mmol}}{50.0 \text{ mL}}} = 0.310$$

$$K_p = K_c(RT)^{(2-1)} = (0.310)\times\left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right)\times(473 \text{ K}) = 12.0$$

79. (D)

(a) This reaction is exothermic and thus, conversion of synthesis gas to methane is favored at lower temperatures. Since $\Delta n_{\text{gas}} = (1+1)-(1+3) = -2$, high pressure favors the products.

(b) The value of K_c is a large number, meaning that almost all of the reactants are converted to products (note that the reaction is stoichiometrically balanced). Thus, after we set up the initial conditions we force the reaction to products and then allow the system to reach equilibrium.

Equation:	$3\ H_2(g)$	+ $CO(g)$	$\rightleftharpoons CH_4(g)$	+ $H_2O(g)$
Initial:	$\frac{3.00 \text{ mol}}{15.0 \text{ L}}$	$\frac{1.00 \text{ mol}}{15.0 \text{ L}}$	0 M	0 M
Initial:	0.200 M	0.0667 M	0 M	0 M
To right:	0.000 M	0.000 M	0.0667 M	0.0667 M
Changes:	$+3x$ M	$+x$ M	$-x$ M	$-x$ M
Equil:	$3x$ M	x M	$(0.0667-x)$M	$(0.0667-x)$M

$$K_c = \frac{[CH_4][H_2O]}{[H_2]^3[CO]} = \frac{(0.0667-x)^2}{(3x)^3x} = 190. \qquad \sqrt{190.} = \frac{0.0667-x}{\sqrt{27}\ x^2}$$

$$\sqrt{190\times27}\ x^2 = 0.0667-x = 71.6\ x^2 \qquad 71.6\ x^2 + x - 0.0667 = 0$$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a} = \frac{-1.00\pm\sqrt{1.00+19.1}}{143} = 0.0244 \text{ M}$$

$$[CH_4] = [H_2O] = 0.0667 - 0.0244 = 0.0423 \text{ M}$$

$$[H_2] = 3\times0.0244 = 0.0732 \text{ M}$$

$$[CO] = 0.0244 \text{ M}$$

We check our calculation by computing the value of the equilibrium constant.

$$K_c = \frac{[CH_4][H_2O]}{[H_2]^3[CO]} = \frac{(0.0423)^2}{(0.0732)^3\ 0.0244} = 187$$

Now we compute the amount in moles of each component present at equilibrium, and finally the mole fraction of CH_4.

$$\text{amount } CH_4 = \text{amount } H_2O = 0.0423 \text{ M} \times 15.0 \text{ L} = 0.635 \text{ mol}$$
$$\text{amount } H_2 = 0.0732 \text{ M} \times 15.0 \text{ L} = 1.10 \text{ mol}$$
$$\text{amount CO} = 0.0244 \text{ M} \times 15.0 \text{ L} = 0.366 \text{ mol}$$

$$\chi_{CH_4} = \frac{0.635 \text{ mol}}{0.635 \text{ mol} + 0.635 \text{ mol} + 1.10 \text{ mol} + 0.366 \text{ mol}} = 0.232$$

80. **(M)** We base our calculation on 1.00 mole of PCl_5 being present initially.

Equation:	$PCl_5(g)$ $\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial:	1.00 mol	0 M		0 M
Changes:	$-\alpha$ mol	$+\alpha$ mol		$+\alpha$ mol
Equil:	$(1.00-\alpha)$ mol	α mol		α mol

$n_{\text{total}} = 1.00 - \alpha + \alpha + \alpha = 1.00 + \alpha$

Equation:	$PCl_5(g)$ $\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Mol fract.	$\dfrac{1.00-\alpha}{1.00+\alpha}$	$\dfrac{\alpha}{1.00+\alpha}$		$\dfrac{\alpha}{1.00+\alpha}$

$$K_p = \frac{P\{Cl_2\}\,P\{PCl_3\}}{P\{PCl_5\}} = \frac{[\chi\{Cl_2\}P_{\text{total}}]\,[\chi\{PCl_3\}P_{\text{total}}]}{[\chi\{PCl_5\}P_{\text{total}}]} = \frac{\left(\dfrac{\alpha}{1.00+\alpha}P_{\text{total}}\right)^2}{\dfrac{1.00-\alpha}{1.00+\alpha}P_{\text{total}}} = \frac{\alpha^2\,P_{\text{total}}}{(1.00+\alpha)(1.00-\alpha)} = \frac{\alpha^2\,P_{\text{total}}}{1-\alpha^2}$$

<u>81</u>. **(M)** We assume that the entire 5.00 g is N_2O_4 and reach equilibrium from this starting point.

$$[N_2O_4]_i = \frac{5.00 \text{ g}}{0.500 \text{ L}} \times \frac{1 \text{ mol } N_2O_4}{92.01 \text{ g } N_2O_4} = 0.109 \text{ M}$$

Equation:	N_2O_4 (g)	$\rightleftharpoons$	2 NO_2 (g)
Initial:	0.109		0 M
Changes:	$-x$ M		$+2x$ M
Equil:	$(0.0109-x)$ M		$2x$ M

$$K_C = \frac{[NO_2]^2}{[N_2O_4]} = 4.61\times10^{-3} = \frac{(2x)^2}{0.109-x} \qquad 4x^2 = 5.02\times10^{-4} - 4.61\times10^{-3}\,x$$

$$4x^2 + 0.00461\,x - 0.000502 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.00461 \pm \sqrt{2.13\times10^{-5} + 8.03\times10^{-3}}}{8} = 0.0106 \text{ M},\ -0.0118 \text{ M}$$

(The method of successive approximations yields 0.0106 after two iterations)

amount $N_2O_4 = 0.500\ \text{L}\ (0.109 - 0.0106)\ \text{M} = 0.0492\ \text{mol}\ N_2O_4$

amount $NO_2 = 0.500\ \text{L} \times 2 \times 0.0106\ \text{M} = 0.0106\ \text{mol}\ NO_2$

$$\text{mol fraction } NO_2 = \frac{0.0106\ \text{mol}\ NO_2}{0.0106\ \text{mol}\ NO_2 + 0.0492\ \text{mol}\ N_2O_4} = 0.177$$

82. **(M)** We let P be the initial pressure in atmospheres of $COCl_2(g)$.

Equation:	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
Initial:	P		0 M		0 M
Changes:	$-x$		$+x$		$+x$
Equil:	$P - x$		x		x

Total pressure $= 3.00\ \text{atm} = P - x + x + x = P + x \qquad P = 3.00 - x$

$P\{COCl_2\} = P - x = 3.00 - x - x = 3.00 - 2x$

$$K_p = \frac{P\{CO\}P\{Cl_2\}}{P(COCl_2\}} = 0.0444 = \frac{x \cdot x}{3.00 - 2x}$$

$x^2 = 0.133 - 0.0888\,x \quad x^2 + 0.0888\,x - 0.133 = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0888 \pm \sqrt{0.00789 + 0.532}}{2} = 0.323, \ -0.421$$

Since a negative pressure is physically meaningless, $x = 0.323$ atm.
(The method of successive approximations yields $x = 0.323$ after four iterations.)

$P\{CO\} = P\{Cl_2\} = 0.323\ \text{atm}$

$P\{COCl_2\} = 3.00 - 2 \times 0.323 = 2.35\ \text{atm}$

The mole fraction of each gas is its partial pressure divided by the total pressure. And the contribution of each gas to the apparent molar mass of the mixture is the mole fraction of that gas multiplied by the molar mass of that gas.

$$M_{avg} = \frac{P\{CO\}}{P_{tot}} M\{CO\} + \frac{P\{Cl_2\}}{P_{tot}} M\{Cl_2\} + \frac{P\{COCl_2\}}{P_{tot}} M\{COCl_2\}$$

$$= \left(\frac{0.323\ \text{atm}}{3.00\ \text{atm}} \times 28.01\ \text{g/mol}\right) + \left(\frac{0.323\ \text{atm}}{3.00\ \text{atm}} \times 70.91\ \text{g/mol}\right) + \left(\frac{2.32\ \text{atm}}{3.00\ \text{atm}} \times 98.92\ \text{g/mol}\right)$$

$$= 87.1\ \text{g/mol}$$

83. (M) Each mole fraction equals the partial pressure of the substance divided by the total pressure. Thus $\chi\{NH_3\} = P\{NH_3\}/P_{tot}$ or $P\{NH_3\} = \chi\{NH_3\}\,P_{tot}$

$$K_p = \frac{P\{NH_3\}^2}{P\{N_2\}\,P\{H_2\}^3} = \frac{(\chi\{NH_3\}P_{tot})^2}{(\chi\{N_2\}P_{tot})(\chi\{H_2\}P_{tot})^3} = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,\chi\{H_2\}^3}\frac{(P_{tot})^2}{(P_{tot})^4}$$
$$= \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,\chi\{H_2\}^3}\frac{1}{(P_{tot})^2}$$

This is the expression we were asked to derive.

84. (D) Since the mole ratio of N_2 to H_2 is 1:3, $\chi\{H_2\} = 3\chi\{N_2\}$. Since P_{tot} = 1.00 atm, it follows.

$$K_p = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}(3\chi\{N_2\})^3}\frac{1}{(1.00)^2} = 9.06\times10^{-2} = 0.0906$$

$$3^3\times0.0906 = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}\,\chi\{N_2\}^3} = \frac{\chi\{NH_3\}^2}{\chi\{N_2\}^4} \qquad \frac{\chi\{NH_3\}}{\chi\{N_2\}^2} = \sqrt{3^3\times0.0906} = 1.56$$

We realize that $\chi\{NH_3\} + \chi\{N_2\} + \chi\{H_2\} = 1.00 = \chi\{NH_3\} + \chi\{N_2\} + 3\chi\{N_2\}$
This gives $\chi\{NH_3\} = 1.00 - 4\chi\{N_2\}$ And we have

$$1.56 = \frac{1.00 - 4\chi\{N_2\}}{\chi\{N_2\}^2}$$ For ease of solving, we let $x = \chi\{N_2\}$

$$1.56 = \frac{1.00 - 4x}{x^2} \qquad 1.56\,x^2 = 1.00 - 4x \qquad 1.56\,x^2 + 4x - 1.00 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-4.00 \pm \sqrt{16.00 + 6.24}}{3.12} = 0.229,\ -2.794$$

Thus $\chi\{N_2\} = 0.229$ Mole % NH_3 = (1.000 mol –(4 × 0.229 mol)) × 100% = 8.4%

85. (M) Since the initial mole ratio is 2 $H_2S(g)$ to 1 $CH_4(g)$, the reactants remain in their stoichiometric ratio when equilibrium is reached. Also, the products are formed in their stoichiometric ratio.

$$\text{amount } CH_4 = 9.54\times10^{-3}\text{ mol } H_2S\times\frac{1\text{ mol } CH_4}{2\text{ mol } H_2S} = 4.77\times10^{-3}\text{ mol } CH_4$$

$$\text{amount } CS_2 = 1.42\times10^{-3}\text{ mol } BaSO_4\times\frac{1\text{ mol S}}{1\text{ mol } BaSO_4}\times\frac{1\text{ mol } CS_2}{2\text{ mol S}} = 7.10\times10^{-4}\text{ mol } CS_2$$

$$\text{amount } H_2 = 7.10\times10^{-4}\text{ mol } CS_2\times\frac{4\text{ mol } H_2}{1\text{ mol } CS_2} = 2.84\times10^{-3}\text{ mol } H_2$$

$$\text{total amount } = 9.54\times10^{-3}\text{mol } H_2S + 4.77\times10^{-3}\text{ mol } CH_4 + 7.10\times10^{-4}\text{mol } CS_2 + 2.84\times10^{-3}\text{ mol } H_2$$
$$= 17.86\times10^{-3}\text{ mol}$$

The partial pressure of each gas equals its mole fraction times the total pressure.

$$P\{H_2S\} = 1.00 \text{ atm } \times \frac{9.54\times10^{-3} \text{ mol } H_2S}{17.86\times10^{-3} \text{ mol total}} = 0.534 \text{ atm}$$

$$P\{CH_4\} = 1.00 \text{ atm} \times \frac{4.77\times10^{-3} \text{ mol } CH_4}{17.86\times10^{-3} \text{ mol total}} = 0.267 \text{ atm}$$

$$P\{CS_2\} = 1.00 \text{ atm} \times \frac{7.10\times10^{-4} \text{ mol } CS_2}{17.86\times10^{-3} \text{ mol total}} = 0.0398 \text{ atm}$$

$$P\{H_2\} = 1.00 \text{ atm } \times \frac{2.84\times10^{-3} \text{ mol } H_2}{17.86\times10^{-3} \text{ mol total}} = 0.159 \text{ atm}$$

$$K_p = \frac{P\{H_2\}^4 \; P\{CS_2\}}{P\{H_2S\}^2 \; P\{CH_4\}} = \frac{0.159^4 \times 0.0398}{0.534^2 \times 0.267} = 3.34\times10^{-4}$$

86. **(D)** We base our calculation on an I.C.E. table, after we first determine the direction of the reaction by computing :

$$Q_c = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]} = \frac{(0.03000)^2(0.03000)^2}{(0.5000)^2(0.5000)} = 6.48\times10^{-6}$$

Because this value is smaller than K_c, the reaction will shift to the right to reach equilibrium. Since the value of the equilibrium constant for the forward reaction is quite small, let us assume that the reaction initially shifts all the way to the left (line labeled "to left:"), and then reacts back in the forward direction to reach a position of equilibrium.

Equation:	$2\ Fe^{3+}(aq)$	+	$Hg_2{}^{2+}(aq)$	$\rightleftharpoons$	$2\ Fe^{2+}(aq)$	+	$2\ Hg^{2+}(aq)$
Initial:	0.5000 M		0.5000 M		0.03000 M		0.03000 M
$\longleftarrow$	$+0.03000$ M		$+0.0150$ M		-0.03000 M		-0.03000 M
To left:	0.5300 M		0.5150 M		0 M		0 M
Changes:	$-2x$ M		$-x$ M		$+2x$ M		$+2x$ M
Equil:	$(0.5300-2x)$M		$(0.5150-x)$M		$2x$ M		$2x$ M

$$K_c = \frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]} = 9.14\times10^{-6} = \frac{(2x)^2(2x)^2}{(0.5300-2x)^2(0.5150-x)} \approx \frac{4x^2 \; 4x^2}{(0.5300)^2 \; 0.5150}$$

Note that we have assumed that $2x << 0.5300$ and $x < 0.5150$

$$x^4 = \frac{9.14\times10^{-6} \; (0.5300)^2 \; (0.5150)}{4\times4} = 8.26\times10^{-8} \qquad x = 0.0170$$

Our assumption, that $2x\,(=0.0340) << 0.5300$, is reasonably good.

$[Fe^{3+}] = 0.5300 - 2\times0.0170 = 0.4960$ M $\qquad [Hg_2{}^{2+}] = 0.5150 - 0.0170 = 0.4980$

$[Fe^{2+}] = [Hg^{2+}] = 2\times0.0170 = 0.0340$ M

We check by substituting into the K_c expression.

$$9.14\times10^{-6}=K_c=\frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]}=\frac{(0.0340)^2(0.0340)^2}{(0.4960)^2\ 0.4980}=11\times10^{-6}\quad \text{Not a substantial difference.}$$

M*athematica* (version 4.0, Wolfram Research, Champaign, IL) gives a root of 0.0163.

87. **(D)** Again we base our calculation on an I.C.E. table. In the course of solving the Integrative Example, we found that we could obtain the desired equation by reversing equation (2) and adding the result to equation (1)

$$-(2)\quad H_2O(g)+CH_4(g)\rightleftharpoons CO(g)+3\,H_2(g)\quad K=1/190$$

$$+(1)\quad CO(g)+H_2O(g)\rightleftharpoons CO_2(g)+H_2(g)\quad K=1.4$$

$$\text{Equation:}CH_4(g)+2\,H_2O(g)\rightleftharpoons CO_2(g)+4\,H_2(g)\quad K=1.4/190=0.0074$$

$$-(2)\quad H_2O(g)+CH_4(g)\rightleftharpoons CO(g)+3\,H_2(g)\quad K=1/190$$

$$+(1)\quad CO(g)+H_2O(g)\rightleftharpoons CO_2(g)+H_2(g)\quad K=1.4$$

Equation:	$CH_4(g)$ +	$2\,H_2O(g)$ $\rightleftharpoons$	$CO_2(g)$ +	$4\,H_2(g)$	$K=1.4/190=0.0074$
Initial:	0.100 mol	0.100 mol	0.100 mol	0.100 mol	
$\longleftarrow$	$+0.025$ mol	$+0.050$ mol	-0.025 mol	-0.100 mol	
To left:	0.125 mol	0.150 mol	0.075 mol	0.000 mol	
Concns:	0.0250 M	0.0300 M	0.015 M	0.000 M	
Changes:	$-x$ M	$-2x$ mol	$+x$ mol	$+4x$ mol	
Equil:	$(0.0250-x)$ M	$(0.0300-2x)$	$(0.015\ +x)$ M	$4x$ mol	

Notice that we have a fifth order polynomial to solve. Hence, we need to try to approximate its final solution as closely as possible. The reaction favors the reactants because of the small size of the equilibrium constant. Thus, we approach equilibrium from as far to the left as possible.

$$K_c=0.0074=\frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}=\frac{(0.0150+x)(4x)^4}{(0.0250-x)\ (0.0300-2x)^2}\approx\frac{0.0150\ (4x)^4}{0.0250\ (0.0300)^2}$$

$$x\approx\sqrt[4]{\frac{0.0250\,(0.0300)^2\ 0.0074}{0.0150\times256}}=0.014\text{ M}$$

Our assumption is terrible. We substitute to continue successive approximations.

$$0.0074=\frac{(0.0150\ +\ 0.014)\ (4x)^4}{(0.0250-0.014)\ \ (0.0300-2\times0.014)^2}=\frac{(0.029)(4x)^4}{(0.011)(0.002)^2}$$

Next, try $x_2 = 0.0026$

$$0.074=\frac{(0.0150+0.0026)(4x)^4}{(0.0250-\ 0.0026)\ (0.0300-2\times0.0026)^2}$$

then, try $x_3 = 0.0123$.

After 18 iterations, the x value converges to 0.0080.

Considering that the equilibrium constant is known to only two significant figures, this is a pretty good result. Recall that the total volume is 5.00 L. We calculate amounts in moles.

$CH_4(g)$	$(0.0250-0.0080)\times 5.00\text{ L} = 0.017\text{ M}\times 5.00\text{ L} = 0.085\text{ moles }CH_4(g)$
$H_2O(g)$	$(0.0300-2\times 0.0080)\text{ M}\times 5.00\text{ L} = 0.014\text{ M}\times 5.00\text{ L} = 0.070\text{ moles }H_2O(g)$
$CO_2(g)$	$(0.015 + 0.0080)\text{ M}\times 5.00\text{ L} = 0.023\text{ M}\times 5.00\text{ L} = 0.12\text{ mol }CO_2$
$H_2(g)$	$(4\times 0.0080)\text{ M}\times 5.00\text{ L} = 0.032\text{ M}\times 5.00\text{ L} = 0.16\text{ mol }H_2$

88. **(M)** The initial mole fraction of C_2H_2 is $\chi_i = 0.88$. We use molar amounts at equilibrium to compute the equilibrium mole fraction of C_2H_2, χ_{eq}. Because we have a 2.00-L container, molar amounts are double the molar concentrations.

$$\chi_{eq} = \frac{(2\times 0.756)\text{ mol }C_2H_2}{(2\times 0.756)\text{ mol }C_2H_2 + (2\times 0.038)\text{ mol }CH_4 + (2\times 0.068)\text{ mol }H_2} = 0.87\underline{7}$$

Thus, there has been only a slight decrease in mole fraction.

89. **(M)**

(a) $K_{eq} = 4.6\times 10^4 \quad \dfrac{P\{NOCl\}^2}{P\{NO\}^2\,P\{Cl_2\}} = \dfrac{(4.125)^2}{P\{NO\}^2(0.1125)}$

$$P\{NO\} = \sqrt{\frac{(4.125)^2}{4.6\times 10^4(0.1125)}} = 0.057\underline{3}\text{ atm}$$

(b) $P_{total} = P_{NO} + P_{Cl_2} + P_{NOCl} = 0.057\underline{3}\text{ atm} + 0.1125\text{ atm} + 4.125\text{ atm} = 4.295\text{ atm}$

90. **(M)** We base our calculation on an I.C.E. table.

Reaction:	$N_2(g)$	+	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial:	$\dfrac{0.424\text{ mol}}{10.0\text{ L}}$		$\dfrac{1.272\text{ mol}}{10.0\text{ L}}$		$\dfrac{0\text{ mol}}{10.0\text{ L}}$
Change	$\dfrac{-x\text{ mol}}{10.0\text{ L}}$		$\dfrac{-3x\text{ mol}}{10.0\text{ L}}$		$\dfrac{+2x\text{ mol}}{10.0\text{ L}}$
Equilibrium	$\dfrac{(0.424-x)\text{ mol}}{10.0\text{ L}}$		$\dfrac{(1.272-3x)\text{ mol}}{10.0\text{ L}}$		$\dfrac{2x\text{ mol}}{10.0\text{ L}}$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 152 = \frac{\left(\frac{2x\,\text{mol}}{10.0\,\text{L}}\right)^2}{\left(\frac{(0.424\text{-}x)\text{ mol}}{10.0\,\text{L}}\right)\left(\frac{(1.272\text{-}3x)\,\text{mol}}{10.0\,\text{L}}\right)^3}$$

$$K_c = \frac{100\left(2x\,\text{mol}\right)^2}{\left((0.424\text{-}x)\text{ mol}\right)\left(3\left(0.424\text{-}x\right)\text{ mol}\right)\right)^3}$$

$$K_c = \frac{100\left(2x\,\text{mol}\right)^2}{3^3\left(0.424\text{-}x\right)\text{ mol}\right)^4} = 152 \qquad \frac{\left(2x\,\text{mol}\right)^2}{\left(0.424\text{-}x\right)\text{ mol}\right)^4} = 41.0\underline{4} \qquad \text{Take root of both sides}$$

$$\frac{\left(2x\,\text{mol}\right)}{\left(0.424\text{-}x\right)\text{ mol}\right)^2} = 6.41 \qquad 6.41(0.424\text{-}x)^2 = 2x$$

$$3.20(0.180 - 0.848x + x^2) = x = 3.20x^2 - 2.71x + 0.576 \qquad 3.20x^2 - 3.71x + 0.576 = 0$$

Now solve using the quadratic equation: $x = 0.184\underline{6}$ mol or $0.975\underline{6}$ mol (too large)

amount of $NH_3 = 2x = 2(0.1846\,\text{mol}) = 0.369\,\text{mol}$ in 10.0 L or 0.0369 M

$([H_2] = 0.0718\,M \textit{ and } [N_2] = 0.0239\,M)$

<u>91.</u> **(D)**

Equation: $2\ H_2(g) \quad + \quad CO(g) \quad \rightleftharpoons \quad CH_3OH(g) \quad K_c = 14.5$ at 483 K

$$K_p = K_c(RT)^{\Delta n} = 14.5\left(0.08206\ \frac{\text{L-atm}}{\text{mol-K}} \times 483\text{K}\right)^{-2} = 9.23 \times 10^{-3}$$

We know that mole percents equal pressure percents for ideal gases.

$P_{CO} = 0.350 \times 100$ atm $= 35.0$ atm

$P_{H_2} = 0.650 \times 100$ atm $= 65.0$ atm

Equation:	$2\ H_2(g)$	+	$CO(g)$	$\rightleftharpoons$	$CH_3OH(g)$
Initial:	65 atm		35 atm		
Changes:	-2P atm		$-$P atm		$+$P atm
Equil:	65-2P		35-P		P

$$K_p = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}{}^2} = \frac{P}{(35.0 - P)(65.0 - 2P)^2} = 9.23 \times 10^{-3}$$

By successive approximations, P = 24.6 atm = P_{CH_3OH} at equilibrium.

Mathematica (version 4.0, Wolfram Research, Champaign, IL) gives a root of 24.5.

FEATURE PROBLEMS

92. **(M)** We first determine the amount in moles of acetic acid in the equilibrium mixture.

$$\text{amount } CH_3CO_2H = 28.85 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.1000 \text{ mol Ba}(OH)_2}{1 \text{ L}} \times \frac{2 \text{ mol } CH_3CO_2H}{1 \text{ mol Ba}(OH)_2}$$

$$\times \frac{\text{complete equilibrium mixture}}{0.01 \text{ of equilibrium mixture}} = 0.5770 \text{ mol } CH_3CO_2H$$

$$K_c = \frac{[CH_3CO_2C_2H_5][H_2O]}{[C_2H_5OH][CH_3CO_2H]} = \frac{\frac{0.423\,\text{mol}}{V} \times \frac{0.423\,\text{mol}}{V}}{\frac{0.077\,\text{mol}}{V} \times \frac{0.577\,\text{mol}}{V}} = \frac{0.423 \times 0.423}{0.077 \times 0.577} = 4.0$$

93. **(D)** In order to determine whether or not equilibrium has been established in each bulb, we need to calculate the concentrations for all three species at the time of opening. The results from these calculations are tabulated below and a typical calculation is given beneath this table.

Bulb No.	Time Bulb Opened (hours)	Initial Amount HI(g) (in mmol)	Amount of I_2(g) and H_2(g) at Time of Opening (in mmol)	Amount HI(g) at Time of Opening (in mmol)	[HI] (mM)	$[I_2]$ & $[H_2]$ (mM)	$\frac{[H_2][I_2]}{[HI]^2}$
1	2	2.34$\underline{5}$	0.1572	2.03	5.08	0.393	0.00599
2	4	2.51$\underline{8}$	0.2093	2.10	5.25	0.523	0.00992
3	12	2.46$\underline{3}$	0.2423	1.98	4.95	0.606	0.0150
4	20	3.17$\underline{4}$	0.3113	2.55	6.38	0.778	0.0149
5	40	2.18$\underline{9}$	0.2151	1.76	4.40	0.538	0.0150

Consider, for instance, bulb #4 (opened after 20 hours).

Initial moles of HI(g) = $0.406 \text{ g HI(g)} \times \frac{1 \text{ mole HI}}{127.9 \text{ g HI}} = 0.00317\underline{4}$ mol HI(g) or $3.17\underline{4}$ mmol

moles of I_2(g) present in bulb when opened.

$$= 0.04150 \text{ L } Na_2S_2O_3 \times \frac{0.0150 \text{ mol } Na_2S_2O_3}{1 \text{ L } Na_2S_2O_3} \times \frac{1 \text{ mol } I_2}{2 \text{ mol } Na_2S_2O_3} = 3.113 \times 10^{-4} \text{ mol } I_2$$

millimoles of I_2(g) present in bulb when opened = 3.113×10^{-4} mol I_2

moles of H_2 present in bulb when opened = moles of I_2(g) present in bulb when opened.

HI reacted = $3.113 \times 10^{-4} \text{ mol } I_2 \times \frac{2 \text{ mole HI}}{1 \text{ mol } I_2} = 6.226 \times 10^{-4}$ mol HI (0.6226 mmol HI)

moles of HI(g) in bulb when opened= $3.17\underline{4}$ mmol HI − 0.6226 mmol HI = 2.55 mmol HI

Concentrations of HI, I_2, and H_2

$[HI] = 2.55 \text{ mmol HI} \div 0.400 \text{ L} = 6.38 \text{ mM}$

$[I_2] = [H_2] = 0.3113 \text{ mmol} \div 0.400 \text{ L} = 0.778 \text{ mM}$

Ratio: $\frac{[H_2][I_2]}{[HI]^2} = \frac{(0.778 \text{ mM})(0.778 \text{ mM})}{(6.38 \text{ mM})^2} = 0.0149$

As the time increases, the ratio $\frac{[H_2][I_2]}{[HI]^2}$ initially climbs sharply, but then plateaus at

0.0150 somewhere between 4 and 12 hours. Consequently, it seems quite reasonable to conclude that the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ has a $K_c \sim 0.015$ at 623 K.

94. **(D)** We first need to determine the number of moles of ammonia that were present in the sample of gas that left the reactor. This will be accomplished by using the data from the titrations involving HCl(aq).

Original number of moles of HCl(aq) in the 20.00 mL sample

$= 0.01872 \text{ L of KOH} \times \frac{0.0523 \text{ mol KOH}}{1 \text{ L KOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol KOH}}$

$= 9.79\underline{06} \times 10^{-4}$ moles of $HCl_{(initially)}$

Moles of unreacted HCl(aq)

$= 0.01542 \text{ L of KOH} \times \frac{0.0523 \text{ mol KOH}}{1 \text{ L KOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol KOH}} =$
$8.06\underline{47} \times 10^{-4}$ moles of $HCl_{(unreacted)}$

Moles of HCl that reacted and /or moles of NH_3 present in the sample of reactor gas
$= 9.79\underline{06} \times 10^{-4} \text{ moles} - 8.06\underline{47} \times 10^{-4} \text{ moles} = 1.73 \times 10^{-4}$ mole of NH_3 (or HCl).

The remaining gas, which is a mixture of $N_2(g)$ and $H_2(g)$ gases, was found to occupy 1.82 L at 273.2 K and 1.00 atm. Thus, the total number of moles of N_2 and H_2 can be found via the

ideal gas law: $n_{H_2+N_2} = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(1.82 \text{ L})}{(0.08206 \frac{\text{L atm}}{\text{K mol}})(273.2 \text{ K})} = 0.0811\underline{8}$ moles of $(N_2 + H_2)$

According to the stoichiometry for the reaction, 2 parts NH_3 decompose to give 3 parts H_2 and 1 part N_2. Thus the non-reacting mixture must be 75% H_2 and 25% N_2.

So, the number of moles of $N_2 = 0.25 \times 0.0811\underline{8}$ moles $= 0.0203$ moles N_2 and the number of moles of $H_2 = 0.75 \times 0.0811\underline{8}$ moles $= 0.0609$ moles H_2.

Before we can calculate K_c, we need to determine the volume that the NH_3, N_2, and H_2 molecules occupied in the reactor. Once again, the ideal gas law ($PV = nRT$) will be employed. $n_{gas} = 0.0811\underline{8}$ moles ($N_2 + H_2$) + 1.73×10^{-4} moles $NH_3 = 0.0813\underline{5}$ moles

$$V_{gases} = \frac{nRT}{P} = \frac{(0.08135\text{ mol})(0.08206\ \frac{\text{L atm}}{\text{K mol}})(1174.2\text{ K})}{30.0\text{ atm}} = 0.261\underline{3}\text{ L}$$

$$\text{So, } K_c = \frac{\left[\frac{1.73\times10^{-4}\text{ moles}}{0.2613\text{ L}}\right]^2}{\left[\frac{0.0609\text{ moles}}{0.2613\text{ L}}\right]^3\left[\frac{0.0203\text{ moles}}{0.2613\text{ L}}\right]^1} = 4.46\times10^{-4}$$

To calculate K_p at 901 °C, we need to employ the equation $K_p = K_c\left(RT\right)^{\Delta n_{gas}}$; $\Delta n_{gas} = -2$

$K_p = 4.46 \times 10^{-4}$ [(0.08206 L atm $K^{-1}mol^{-1}$)] × (1174.2 K)]$^{-2}$ = 4.80×10^{-8} at 901°C for the reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$

95. **(M)** For step 1, rate of the forward reaction = rate of the reverse reaction, so,

$$k_1[I_2] = k_{-1}[I]^2 \text{ or } \frac{k_1}{k_{-1}} = \frac{[I]^2}{[I_2]} = K_c \text{ (step 1)}$$

Like the first step, the rates for the forward and reverse reactions are equal in the second step and thus,

$$k_2[I]^2[H_2] = k_{-2}[HI]^2 \text{ or } \frac{k_2}{k_{-2}} = \frac{[HI]^2}{[I]^2[H_2]} = K_c \text{ (step 2)}$$

Now we combine the two elementary steps to obtain the overall equation and its associated equilibrium constant.

$I_2(g) \rightleftharpoons 2\ I(g)$ $\qquad K_c = \frac{k_1}{k_{-1}} = \frac{[I]^2}{[I_2]}$ (STEP 1)

and

$H_2(g) + 2\ I(g) \rightleftharpoons$ □2 HI(g) $\qquad K_c = \frac{k_2}{k_{-2}} = \frac{[HI]^2}{[I]^2[H_2]}$ (STEP 2)

$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$ $\qquad K_{c(overall)} = K_{c(step\ 1)} \times K_{c(step\ 2)}$

$$K_{c(overall)} = \frac{k_1}{k_{-1}} \times \frac{k_2}{k_{-2}} = \frac{[I]^2}{[I_2]} \times \frac{[HI]^2}{[I]^2[H_2]}$$

$$K_{c(overall)} = \frac{k_1k_2}{k_{-1}k_{-2}} = \frac{[I]^2[HI]^2}{[I]^2[I_2][H_2]} = \frac{[HI]^2}{[I_2][H_2]}$$

96. **(M)** The equilibrium expressions for the two reactions are:

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]};\ K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

First, start with $[H^+] = 0.1$ and $[HCO_3^-] = 1$. This means that $[H^+]/[HCO_3^-] = 0.1$, which means that $[CO_3^{2-}] = 10K_2$. By adding a small amount of H_2CO_3 we shift $[H^+]$ by 0.1 and $[HCO_3^-]$ by 0.1. This leads to $[H^+]/[HCO_3^-] \approx 0.2$, which means that $[CO_3^{2-}] = 5K_2$. Note that $[CO_3^{2-}]$ has *decreased* as a result of adding H_2CO_3 to the solution.

97. **(D)** First, it is most important to get a general feel for the direction of the reaction by determining the reaction quotient:

$$Q = \frac{[C(aq)]}{[A(aq)]\cdot[B(aq)]} = \frac{0.1}{0.1\times 0.1} = 10$$

Since Q>>K, the reaction proceeds toward the reactants. Looking at the reaction in the aqueous phase only, the equilibrium can be expressed as follows:

	A(aq)	+ B(aq)	$\rightleftharpoons$ C(aq)
Initial	0.1	0.1	0.1
Change	-x	-x	+x
Equil.	0.1 - x	0.1 - x	0.1 + x

We will do part (b) first, which assumes the absence of an organic layer for extraction:

$$K = \frac{(0.1+x)}{(0.1-x)(0.1-x)} = 0.01$$

Expanding the above equation and using the quadratic formula, x = -0.0996. Therefore, the concentration of C(aq) and equilibrium is 0.1 + (-0.0996) = 4×10^{-4} M.

If the organic layer is present for extraction, we can add the two equations together, as shown below:

$$\begin{array}{lcl} A(aq) + B(aq) & \rightleftharpoons & C(aq) \\ C(aq) & \rightleftharpoons & C(or) \\ \hline A(aq) + B(aq) & \rightleftharpoons & C(or) \end{array}$$

$K = K_1 \times K_2 = 0.1 \times 15 = 0.15$.

Since the organic layer is present with the aqueous layer, and K_2 is large, we can expect that the vast portion of C initially placed in the aqueous phase will go into the organic phase.

Therefore, the initial [C] = 0.1 can be assumed to be for C(or). The equilibrium can be expressed as follows

	A(aq)	+	B(aq)	$\rightleftharpoons$	C(or)
Initial	0.1		0.1		0.1
Change	-x		-x		+x
Equil.	0.1 - x		0.1 - x		0.1 + x

We will do part (b) first, which assumes the absence of an organic layer for extraction:

$$K = \frac{(0.1+x)}{(0.1-x)(0.1-x)} = 0.15$$

Expanding the above equation and using the quadratic formula, x = -0.0943. Therefore, the concentration of C(or) and equilibrium is 0.1 + (-0.0943) = 6×10^{-4} M. This makes sense because the K for the overall reaction is < 1, which means that the reaction favors the reactants.

SELF-ASSESSMENT EXERCISES

98. **(E)**

(a) K_p: The equilibrium constant of a reaction where the pressures of gaseous reactants and products are used instead of their concentrations

(b) Q_c: The reaction quotient using the molarities of the reactants and products

(c) Δn_{gas}: The difference between the number of moles (as determined from a balanced reaction) of product and reactant gases

99. **(E)**

(a) Dynamic equilibrium: In a dynamic equilibrium (which is to say, real equilibrium), the forward and reverse reactions happen, but at a constant rate

(b) Direction of net chemical change: In a reversible reaction, if the reaction quotient $Q_c > K_c$, then the net reaction will go toward the reactants, and vice versa

(c) Le Châtelier's principle: When a system at equilibrium is subjected to external change (change in partial pressure of reactants/products, temperature or concentration), the equilibrium shifts to a side to diminish the effects of that external change

(d) Effect of catalyst on equilibrium: A catalyst does not affect the final concentrations of the reactants and products. However, since it speeds up the reaction, it allows for the equilibrium concentrations to be established more quickly

100. **(E)**

(a) Reaction that goes to completion and reversible reaction: In a reversible reaction, the products can revert back to the reactants in a dynamic equilibrium. In a reaction that goes to completion, the formation of products is so highly favored that there is practically no reverse reaction (or the reverse is practically impossible, such as a combustion reaction).

(b) K_p and K_c: K_p is the equilibrium constant using pressures of products and reactants, while K_c is the constant for reaction using concentrations.
(c) Reaction quotient (Q) and equilibrium constant expression (K): The reaction quotient Q is the ratio of the concentrations of the reactants and products expressed in the same format as the equilibrium expression. The equilibrium constant expression is the ratio of concentrations at equilibrium.
(d) Homogeneous and heterogeneous reaction: In a homogeneous reaction, the reaction happens within a single phase (either aqueous or gas). In a heterogeneous reaction, there is more than one phase present in the reaction.

101. **(E)** The answer is (c). Because the limiting reagent is I_2 at one mole, the theoretical yield of HI is 2 moles. However, because there is an established equilibrium, there is a small amount of HI which will decompose to yield H_2 and I_2. Therefore the total moles of HI created is close, but less than 2.

102. **(E)** The answer is (d). The equilibrium expression is:

$$K = \frac{P(SO_3)^2}{P(SO_2)^2 P(O_2)} = 100$$

If equilibrium is established, moles of SO_3 and SO_2 cancel out of the equilibrium expression. Therefore, if K = 100, the moles of O_2 have to be 0.01 to make K = 100.

103. **(E)** The answer is (a). As the volume of the vessel is expanded (i.e., pressure is reduced), the equilibrium shifts toward the side with more moles of gas.

104. **(E)** The answer is (b). At half the stoichiometric values, the equilibrium constant is $K^{1/2}$. If the equation is reversed, it is K^{-1}. Therefore, the $K' = K^{-1/2} = (1.8\times10^{-6})^{-1/2} = 7.5\times10^{-2}$.

105. **(E)** The answer is (a). We know that $K_p = K_c (RT)^{\Delta n}$. Since $\Delta n = (3–2) = 1$, $K_p = K_c (RT)$. Therefore, $K_p > K_c$.

106. **(E)** The answer is (c). Since the number of moles of gas of products is more than the reactants, increasing the vessel volume will drive the equilibrium more toward the product side. The other options: (a) has no effect, and (b) drives the equilibrium to the reactant side.

107. **(E)** The equilibrium expression is:

$$K = \frac{[C]^2}{[B]^2[A]} = \frac{(0.43)^2}{(0.55)^2(0.33)} = 1.9$$

108. **(E)**
(a) As more O_2 (a reactant) is added, more Cl_2 is produced.
(b) As HCl (a reactant) is removed, equilibrium shifts to the left and less Cl_2 is made.
(c) Since there are more moles of reactants, equilibrium shifts to the left and less Cl_2 is made.
(d) No change. However, the equilibrium is reached faster.
(e) Since the reaction is exothermic, increasing the temperature causes less Cl_2 to be made.

109. **(E)** SO_2 (g) will be less than SO_2 (aq), because K > 1, so the equilibrium lies to the product side, SO_2 (aq).

110. **(E)** Since K >>1, there will be much more product than reactant

111. **(M)** The equilibrium expression for this reaction is:

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = 35.5$$

(a) If $[SO_3]_{eq} = [SO_2]_{eq}$, then $[O_2] = 1/35.5 = 0.0282$ M.
moles of $O_2 = 0.0282 \times 2.05 \text{ L} = 0.0578$ moles

(b) Plugging in the new concentration values into the equilibrium expression:

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[2\times SO_2]^2}{[SO_2]^2[O_2]} = \frac{4}{[O_2]} = 35.5$$

$[O_2] = 0.113$ M

moles of $O_2 = 0.113 \times 2.05 \text{ L} = 0.232$ moles

112. **(M)** This concept map involves the various conditions that affect equilibrium of a reaction, and those that don't. Under the category of conditions that do cause a change, there is changing the partial pressure of gaseous products and reactants, which includes pressure and vessel volume. The changes that do not affect partial pressure are changing the concentration of reactants or products in an aqueous solution, through dilution or concentration. Changing the temperature can affect both aqueous and gaseous reactions. Under the category of major changes that don't affect anything is the addition of a non-reactive gas.