Problems - Chapter 15 (with solutions)

1) What is the significance of the equilibrium constant? What does a large equilibrium constant tell us about a reaction? A small one?

The equilibrium constant tells you the relationship between product and reactant concentrations that exists, at equilibrium, in a system at some temperature T. A large equilibrium constant tells you that at equilibrium the concentrations of products will be much larger than the concentrations of reactants. A small equilibrium constant means the opposite, that the concentrations of reactants at equilibrium will be large in comparison to the concentrations of products.

2) (15.18) Write equilibrium constants for K_C, and, if applicable, for K_p, for the following processes:

a) $2 CO_2(g) \rightleftharpoons 2 CO(g) + O_2(g)$
b) $3 O_2(g) \rightleftharpoons 2 O_3(g)$
c) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
d) $H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$
e) $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$
f) $2 HgO(s) \rightleftharpoons 2 Hg(\ell) + O_2(g)$

a) $K_C = \dfrac{[CO]^2 [O_2]}{[CO_2]^2}$ $\qquad$ $K_p = \dfrac{(p_{CO})^2 (p_{O2})}{(p_{CO2})^2}$

b) $K_C = \dfrac{[O_3]^2}{[O_2]^3}$ $\qquad$ $K_p = \dfrac{(p_{O3})^2}{(p_{O2})^3}$

c) $K_C = \dfrac{[COCl_2]}{[CO] [Cl_2]}$ $\qquad$ $K_p = \dfrac{(p_{COCl2})}{(p_{CO}) (p_{Cl2})}$

d) $K_C = \dfrac{[CO] [H_2]}{[H_2O]}$ $\qquad$ $K_p = \dfrac{(p_{CO}) (p_{H2})}{(p_{H2O})}$

e) $K_C = \dfrac{[H^+] [HCOO^-]}{[HCOOH]}$ $\qquad$ $K_p =$ no expression

f) $K_C = [O_2]$ $\qquad$ $K_p = (p_{O2})$

In doing these problems recall that solids, pure liquids, and solvents do not appear in the expression for the equilibrium constant. The easiest way to decide if a value of K_p can be written is to look at the expression for K_C. If everything in K_C is a gas, then K_p can be written by substituting gas pressure for concentration in each term. Otherwise, an expression for K_p cannot be written (as in e, above).

3) The reaction below has an equilibrium constant $K_p = 2.2 \times 10^6$ at 298. K

$$2\ COF_2(g) \leftrightarrows CO_2(g) + CF_4(g)$$

Calculate K_p for each of the reactions below (at the same temperature) and predict whether reactants or products will be favored at equilibrium

a) $COF_2(g) \leftrightarrows \frac{1}{2}\ CO_2(g) + \frac{1}{2}\ CF_4(g)$
b) $6\ COF_2(g) \leftrightarrows 3\ CO_2(g) + 3\ CF_4(g)$
c) $2\ CO_2(g) + 2\ CF_4(g) \leftrightarrows 4\ COF_2(g)$

For the reaction as written, $K_p = \dfrac{(p_{CO2})\,(p_{CF4})}{(p_{COF2})^2} = 2.2 \times 10^6$. Therefore

a) $K_p = \dfrac{(p_{CO2})^{1/2}\,(p_{CF4})^{1/2}}{(p_{COF2})} = \{ (p_{CO2})(p_{CF4})/(p_{COF2})^2 \}^{1/2}$; so $K_p = (2.2 \times 10^6)^{1/2}$

$$= 1.5 \times 10^3 \ \text{(products favored)}$$

b) $K_p = \dfrac{(p_{CO2})^3\,(p_{CF4})^3}{(p_{COF2})^6} = \{ (p_{CO2})(p_{CF4})/(p_{COF2})^2 \}^3 = $; so $K_p = (2.2 \times 10^6)^3$

$$= 1.1 \times 10^{19} \ \text{(products favored)}$$

c) $K_p = \dfrac{(p_{COF2})^4}{(p_{CO2})^2\,(p_{CF4})^2} = \{ (p_{CO2})(p_{CF4})/(p_{COF2})^2 \}^{-2}$ so $K_p = (2.2 \times 10^6)^{-2}$

$$= 2.1 \times 10^{-13} \ \text{(reactants favored)}$$

4) (15.12) The equilibrium constant for the reaction

$$2\ H_2(g) + CO(g) \leftrightarrow CH_3OH(g)$$
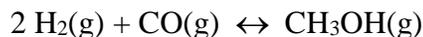
is $K_C = 1.6 \times 10^{-2}$ at a certain temperature. It is found that there are 1.17×10^{-2} moles of H_2 and 3.46×10^{-7} moles of CH_3OH in a 5.60 L system at equilibrium at this temperature. What is the concentration of CO in the system?

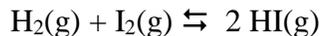$$K_C = \dfrac{[CH_3OH]}{[H_2]^2\,[CO]}$$

so $[CO] = \dfrac{[CH_3OH]}{K_C\,[H_2]^2}$ $\qquad [H_2] = \dfrac{1.17 \times 10^{-2}\ \text{mol}}{5.6\ \text{L}} = 2.09 \times 10^{-3}\ M$

$$[CH_3OH] = \dfrac{3.46 \times 10^{-7}\ \text{mol}}{5.6\ \text{L}} = 6.18 \times 10^{-8}\ M$$

$$[CO] = \dfrac{(6.18 \times 10^{-8})}{(1.6 \times 10^{-2})\,(2.09 \times 10^{-3})^2} = 0.884\ M$$

5) Consider the following reaction

$$H_2(g) + I_2(g) \leftrightarrows 2\ HI(g)$$

Complete the table below. You may assume that all concentrations are equilibrium concentrations in units of mol/L.

T(°C)	$[H_2]$	$[I_2]$	$[HI]$	K_C
25.0	0.0355	0.0388	0.922	----
340.0	----	0.0455	0.387	96.
445.0	0.0485	0.0468	----	50.2

For this reaction $K_C = \dfrac{[HI]^2}{[H_2]\,[I_2]}$

At 25 °C, missing K_C, so $K_C = \dfrac{(0.922)^2}{(0.0355)\,(0.0388)} = 617.$

At 340. °C, missing $[H_2]$

$$K_C = \frac{[HI]^2}{[H_2]\,[I_2]} \ , \text{ so } [H_2] = \frac{[HI]^2}{K_C\,[I_2]} = \frac{(0.387)^2}{(96.)\,(0.0455)} = 0.0343\ M$$

At 445. °C, missing $[HI]$

$$K_C = \frac{[HI]^2}{[H_2]\,[I_2]} \ , \text{ so } [HI] = \{K_C\,[H_2]\,[I_2]\ \}^{1/2} = \{(50.2)\,(0.0485)\,(0.0468)\}^{1/2}$$
$$= 0.338\ M$$

The final table is as follows:

T(°C)	$[H_2]$	$[I_2]$	$[HI]$	K_C
25.0	0.0355	0.0388	0.922	**(617.)**
340.0	**(0.0343)**	0.0455	0.387	96.
445.0	0.0485	0.0468	**(0.338)**	50.2

6) (15.24) What is the numerical value for K_p at T = 1273. °C for the reaction

$$2\ CO(g) + O_2(g) \leftrightarrows 2\ CO_2(g)$$
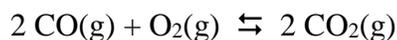
At this temperature $K_C = 2.24 \times 10^{22}$.

The general relationship to use is $K_p = K_c\,(RT)^{\Delta n}$, where Δn = change in the number of moles of gas per mole of reaction.

$\Delta n = 2 - 3 = -1$ $T = 1273 + 273 = 1546.\ K$

$K_p = (2.24 \times 10^{22})\ [\ (0.0826)\ (1546)\ ]^{-1} = 1.77 \times 10^{20}$

Notice that we use the value $R = 0.08206$ L·atm/mol·K in the conversion and convert temperature to K, but we do not include units for R or T, since K_p and K_C have no units.

7) (15.34) The following equilibrium constants have been determined for hydrosulfuric acid at $T = 25.0\ °C$

$H_2S(aq)\ \leftrightarrows\ H^+(aq) + HS^-(aq)$ $K_C' = 9.5 \times 10^{-8}$

$HS^-(aq)\ \leftrightarrows\ H^+(aq) + S^{2-}(aq)$ $K_C'' = 1.0 \times 10^{-19}$
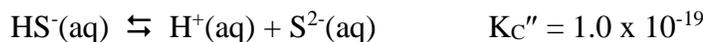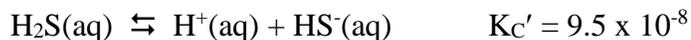
Find the equilibrium constant for the following reaction at the same temperature

$H_2S(aq)\ \leftrightarrows\ 2\ H^+(aq) + S^{2-}(aq)$ $K_C = ?$
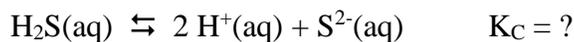
The expressions for K_C' and K_C'' are

$K_C' = \dfrac{[H^+]\ [HS^-]}{[H_2S]}$ $K_C'' = \dfrac{[H^+]\ [S^{2-}]}{[HS^-]}$

$K_C = \dfrac{[H^+]^2\ [S^{2-}]}{[H_2S]}\ =\ \dfrac{[H^+]\ [HS^-]}{[H_2S]}\ \dfrac{[H^+]\ [S^{2-}]}{[HS^-]}\ = K_C'\ K_C''$

$= (9.5 \times 10^{-8})(1.0 \times 10^{-19}) = 9.5 \times 10^{-27}$

8) For the reaction below, $K_C = 255.$ at $T = 1000.\ K$

$CO(g) + Cl_2(g) \leftrightarrows\ COCl_2(g)$
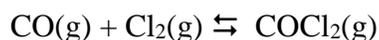
A reaction mixture (kept at $T = 1000.\ K$) initially contains no $COCl_2$. The initial concentrations of CO and Cl_2 are $[CO] = 0.1500$ M, and $[Cl_2] = 0.1750$ mol/L. What are the equilibrium concentrations of CO, Cl_2, and $COCl_2$?

$K_C = \dfrac{[COCl_2]}{[CO]\ [Cl_2]}\ = 255.$

	Initial	Change	Equilibrium
CO	0.1500	- x	0.1500 - x
Cl₂	0.1750	- x	0.1750 - x
COCl₂	0.000	+ x	x

(Note we have defined x as the concentration of $COCl_2$ that forms).

$$\frac{(x)}{(0.1500 - x)(0.1750 - x)} = 255.$$

Since it does not look like x is small compared to 0.1500, we will have to solve the above by the quadratic formula.

$$x = (0.1500 - x)(0.1750 - x)(255.) = 6.6938 - 82.875\, x + 255\, x^2$$

$$255\, x^2 - 83.875\, x + 6.6938 = 0$$

$$x = \frac{83.875 \pm [(83.875)^2 - 4\,(255)\,(6.6938)]^{1/2}}{2\,(255)} = 0.1927,\ \underline{0.1362}$$

The underlined root is correct. The other root (0.1927) would lead to a negative value for the concentration of both CO and Cl_2.

So at equilibrium $[CO] = 0.1500 - x = 0.0138$ M
   $[Cl_2] = 0.1750 - x = 0.0388$ M
   $[COCl_2] = x = 0.1362$ M

As a check, if we substitute into our expression for K_C, we get

$$K_C = \frac{(0.1362)}{(0.0138)(0.0388)} = 254. \cong 255.$$

9) Consider the reaction

$$SO_2Cl_2(g) \leftrightarrows SO_2(g) + Cl_2(g) \qquad K_C = 2.99 \times 10^{-7} \text{ at } T = 227.\ °C$$
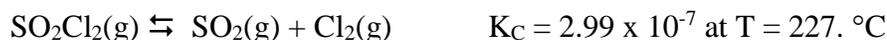
If the reaction (kept at T = 227. °C) initially contains 0.175 mol/L SO_2Cl_2 (and no SO_2 or Cl_2), what is the equilibrium concentration of Cl_2?

$$K_C = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = 2.99 \times 10^{-7}$$

	Initial	Change	Equilibrium
SO_2	0.000	+ x	x
Cl_2	0.000	+ x	x
SO_2Cl_2	0.1750	- x	0.1750 - x

(Note we have defined x as the concentration of SO_2 that forms).

$$\frac{(x)^2}{(0.1750 - x)} = 2.99 \times 10^{-7}$$

Since $K_C \ll 1$, it looks like it is worth assuming that $x \ll 0.1750$ If we make that assumption, then

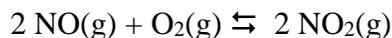$$\frac{(x)^2}{(0.1750 - x)} \cong \frac{x^2}{(0.1750)} = 2.99 \times 10^{-7}$$

So $x^2 = (2.99 \times 10^{-7})(0.1750) = 5.23 \times 10^{-8}$

$x = (5.23 \times 10^{-8})^{1/2} = 2.29 \times 10^{-4}$

Now we go back and check our assumption. Is $2.29 \times 10^{-4} \ll 0.1750$? YES, so our assumption was good.

So at equilibrium $[SO^2] = [Cl^2] = x = 2.29 \times 10^{-4}$ M
$[SO_2Cl_2] = 0.175 - x = 0.1748$ M

10) The equilibrium constant for the reaction

$$2\ NO(g) + O_2(g) \leftrightarrows 2\ NO_2(g)$$

is $K_C = 6.9 \times 10^5$ at T = 500. K. Consider a system at this temperature where the initial concentration of NO_2 is $[NO_2] = 0.1000$ mol/L, and where no NO or O_2 are initially present. What are the concentrations of NO, O_2, and NO_2 when equilibrium is reached?

$$K_C = \frac{[NO_2]^2}{[NO]^2\,[O_2]} = 6.9 \times 10^5$$

	Initial	Change	Equilibrium
NO	0.0000	+ 2x	2x
O_2	0.0000	+ x	x
NO_2	0.1000	- 2x	0.1000 - 2x

(Note we have defined x as the concentration of O_2 that forms).

$$\frac{(0.1000 - 2x)^2}{(2x)^2\,(x)} = 6.9 \times 10^5$$

Since $K_C \gg 1$, it looks like it is worth assuming that $x \ll 0.1000$ If we make that assumption, then

$$\frac{(0.1000 - 2x)^2}{(2x)^2\,(x)} \cong \frac{(0.1000)^2}{4x^3} = 6.9 \times 10^5$$

So $x^3 = \dfrac{(0.1000)^2}{4\,(6.9 \times 10^5)} = 3.62 \times 10^{-9}$

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$x = (3.62 \times 10^{-9})^{1/3} = 1.5 \times 10^{-3}$

Now we go back and check our assumption. Is $1.5 \times 10^{-3} \ll 0.1000$? YES, so our assumption was good.

So at equilibrium $[NO] = 2x = 0.0030$ M
                      $[O_2] = x = 0.0015$ M
                      $[NO_2] = 0.1000 - 2x = 0.097$ M

11) In which direction will a reaction proceed for each of the following conditions:
      a) Q < K   b) Q > K   c) Q = K

      a) If Q < K the reaction will shift from left to right (from reactants to products) as equilibrium is approached.
      b) If Q > K the reaction will shift from right to left (from products to reactants) as equilibrium is approached.
      c) If Q = K then the system is at equilibrium, and so no shifting will occur

12) Consider the reaction

      $2\ H_2S(g) \leftrightharpoons 2\ H_2(g) + S_2(g)$ $K_p = 2.4 \times 10^{-4}$ at T = 1073. K

A reaction mixture contains 0.112 atm of H_2, 0.055 atm of S_2, and 0.445 atm of H_2S. Is the reaction mixture at equilibrium? If not, in what direction will the reaction proceed?

      $Q_p = \dfrac{(p_{H2})^2\ (p_{S2})}{(p_{H2S})^2} = \dfrac{(0.112)^2\ (0.055)}{(0.445)^2} = 3.5 \times 10^{-3}.$

      As stated in the problem, $K_p = 2.4 \times 10^{-4}$. Since $Q_p > K_p$ we need to reduce its value. Therefore the reaction will shift from right to left (more H_2S will form).

13) Consider this reaction at equilibrium

      $2\ BrNO(g) \leftrightharpoons 2\ NO(g) + Br_2(g)$
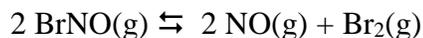
Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.
      a) NO is added to the reaction mixture.
      b) BrNO is added to the reaction mixture.
      c) Br_2 is removed from the reaction mixture.

We use Le Chatlier's principle here (we could also use the reaction quotient, but that takes longer and will give the same result).

     a) System will shift from right to left (to get rid of some of the added NO).

     b) System will shift from left to right (to get rid of some of the added BrNO).

     c) System will shift from left to right (to replace some of the Br_2 that was removed).

14) Each of the following reactions is allowed to come to equilibrium, and the volume is then changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

     a) $CO(g) + H_2O(g) \leftrightarrows CO_2(g) + H_2(g)$ volume is decreased

     b) $PCl_3(g) + Cl_2(g) \leftrightarrows PCl_5(g)$ volume is increased

     c) $CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$ volume is increased

     a) Since volume is decreased all of the pressures will increase. The system will respond by trying to reduce the total pressure. However, since there are the same number of moles of reactants and products, there will be no shift in the reaction.

     b) Since volume is increased all of the pressures will decrease. The system will respond by trying to increase the total prssure. Since there are more moles of reactants than products, the system will shift from right to left.

     c) Since volume is increased the pressure of CO_2 will decrease. Note we don't have to consider the "pressure" of solids, since they don't enter into the expression for the equilibrium constant. The system will respond by increasing the pressure of CO_2. Therefore the reaction will shift from left to right.

15) (15.86) Consider the following reaction

     $A(g) \leftrightarrows 2 B(g)$
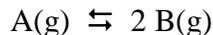
Data for this reaction for systems at equilibrium are given below.

T(°C)	[A] (M)	[B] (M)
200.0	0.0125	0.843
300.0	0.171	0.764
400.0	0.250	0.724

     a) Find the value for K_C and K_p at each of the above temperatures.

     b) Is the above reaction exothermic or endothermic? Justify your answer.

     a) $K_C = \dfrac{[B]^2}{[A]}$ $K_p = K_C (RT)^{\Delta n}$ $\Delta n = 2 - 1 = 1$

At T = 200. °C = 473. K $K_C = \dfrac{(0.843)^2}{(0.0125)} = 56.9$

$$K_p = (56.9) [(0.08206) (473.)] = 2210.$$

At T = 300. °C = 573. K $\quad K_C = \dfrac{(0.764)^2}{(0.171)} = 3.41$

$$K_p = (3.41) [(0.08206) (573.)] = 161.$$

At T = 400. °C = 673. K $\quad K_C = \dfrac{(0.724)^2}{(0.250)} = 2.09$

$$K_p = (2.09) [(0.08206) (673.)] = 116.$$

b) K (either K_C or K_p) gets smaller as temperature increases. By Le Chatlier's principle we would expect that to occur if heat were a product of the reaction, since at higher temperatures there is more heat, so the reaction will shift from right to left to reduce the heat in the system. Therefore the reaction is <u>exothermic</u>.

16) (15.47) Find $\Delta G°$ and K for the following equilibrium reaction at T = 25. °C

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

Also find ΔG for the reaction if $p(PCl_5) = 0.0029$ atm, $p(PCl_3) = 0.27$ atm, and $P(Cl_2) = 0.40$ atm.

$$\Delta G°_{rxn} = [\Delta G°_f(PCl_3(g)) + \Delta G°_f(Cl_2(g))] - [\Delta G°_f(PCl_5(g))]$$
$$= [(-269.6) + (0)] - [-305.0] = 35.4 \text{ kJ/mol}$$

$$\ln K = -\frac{\Delta G°_{rxn}}{RT} = \frac{-35400. \text{ J/mol})}{(8.314 \text{ J/mol.K})(298.2 \text{ K})} = -14.28$$
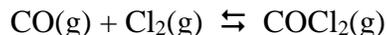
$$K = e^{-14.28} = 6.3 \times 10^{-7}$$

For the nonstandard conditions we may use the equation

$$\Delta G_{rxn} = \Delta G°_{rxn} + RT \ln Q$$

$$Q = \frac{(p(PCl_3))(p(Cl_2))}{(p(PCl_5))} = \frac{(0.27)(0.40)}{(0.0029)} = 37.2$$

$$\Delta G_{rxn} = 35.4 \text{ kJ/mol} + (8.314 \times 10^{-3} \text{ kJ/mol·K})(298.2 \text{ K}) \ln(37.2) = 44.4 \text{ kJ/mol}$$

17) (15.50) The equilibrium constant for the reaction

$$CO(g) + Cl_2(g) \leftrightarrows COCl_2(g)$$

is 5.62 x 10^{35} at T = 25. °C. Using only this information find the value for $\Delta G°_{rxn}$ for this process at this temperature.

$$\Delta G°_{rxn} = - RT \ln K = - (8.314 \text{ x } 10^{-3} \text{ kJ/mol·K})(298.2 \text{ K}) \ln(5.62 \text{ x } 10^{35})$$

$$= - 204.1 \text{ kJ/mol}$$

18) The gas phase reaction of sulfur dioxide (SO_2) with molecular oxygen (O_2) can produce sulfur trioxide (SO_3). The balanced equation for the reaction is

$$2 SO_2(g) + O_2(g) \leftrightarrows 2 SO_3(g)$$
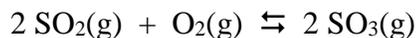
Thermodynamic data for the reactants and products are given below, at T = 25. °C.

Substance	$\Delta H°_f$ (kJ/mol)	$\Delta G°_f$ (kJ/mol)	S° (J/mol·K)
$O_2(g)$	0.0	0.0	205.2
$SO_2(g)$	- 296.8	- 300.1	248.2
$SO_3(g)$	- 395.7	- 371.1	256.8

Based on this information find $\Delta G°_{rxn}$ and K for the above reaction at T = 25. °C

$$\Delta G°_{rxn} = [2 \Delta G°_f(SO_3(g))] - [2 \Delta G°_f(SO_2(g)) + \Delta G°_f(O_2(g))]$$

$$= [2 (- 371.1)] - [2 (- 300.1) + 0.00] = - 142.0 \text{ kJ/mol}$$

$$\ln K = - \frac{\Delta G°_{rxn}}{RT} = \frac{142000. \text{ J/mol}}{(8.314 \text{ J/mol·K) (298.2 K)}} = 57.27$$

$$K = e^{57.27} = 7.5 \text{ x } 10^{24}$$

19) The equilibrium constant for the reaction

$$ClF_3(g) \leftrightarrows ClF(g) + F_2(g)$$

is $K_p = 0.14$ at T = 700. K.

A system initially has $p_{ClF3} = p_{ClF} = 0.200$ atm. There is initially no F_2 in the system. Find the values for p_{ClF3}, p_{ClF}, and p_{F2} that will be present when equilibrium is reached.

$K_p = \dfrac{(p_{ClF}) \, (p_{F2})}{(p_{ClF3})} = 0.14$

	Initial	Change	Equilibrium
ClF	0.200	x	0.200 + x
F_2	0.	x	x
ClF_3	0.200	- x	0.200 - x

$\dfrac{(0.200 + x) \, (x)}{(0.200 - x)} = 0.14$

$x^2 + 0.200 \, x = 0.028 - 0.14 \, x$

$x^2 + 0.340 \, x - 0.028 = 0$

$x = -\,\dfrac{0.340 \pm [\,(0.340)^2 - 4\,(1)\,(-0.028)\,]^{1/2}}{2\,(1)} = \underline{+\,0.069}, \, -0.408$

The root - 0.408 would give a negative partial pressure for ClF and F_2 and so can be discarded. Using x = 0.069 gives

$\quad p_{ClF} = 0.269$ atm $\qquad\qquad p_{F2} = 0.069$ atm $\qquad\qquad p_{ClF3} = 0.131$ atm
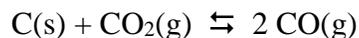
As a check, if we insert these values into the expression for K_p, we get

$\quad K_p = \dfrac{(0.269)\,(0.069)}{(0.131)} = 0.142$, within roundoff error of the correct value.

Note that if we assumed x << 0.200, we would get x = 0.14, which would clearly violate the assumption that x is small. So in this problem we have to solve the quadratic.

20) The equilibrium constant for the reaction

$\quad C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$

measured at T = 850. °C, is $K_p = 1.2 \times 10^{14}$.
$\qquad$ A system initially has $p_{CO} = 0.400$ atm and $p_{CO2} = 0.300$ atm. What are the pressures of CO and CO_2 when the system reaches equilibrium?

This is a trickier problem than it looks. If we set up our calculation using the ICE method, we get the following result

$$K_p = \frac{(p_{CO})^2}{p_{CO2}} = 1.2 \times 10^{14}$$

	Initial	Change	Equilibrium
CO	0.400	+ 2x	0.400 + 2x
CO$_2$	0.300	- x	0.300 – x

$$\frac{(0.400 + 2x)^2}{(0.300 - x)} = 1.2 \times 10^{14}$$

The assumption that x << 0.300 does not work, and there is difficulty with roundoff error if we try to solve this problem using the quadratic equation. So…what do we do?

Based on the large value for K_p we expect that at equilibrium most of the gas will be CO. That suggests that as a starting condition we use the pressures that would be present if all of the gas was CO, and then find the equilibrium pressures.

	Initial	If all CO	Change	Equilibrium
CO	0.400	1.000	+ 2x	1.000 + 2x
CO$_2$	0.300	0.000	- x	− x

then $$\frac{(1.000 + 2x)^2}{(- x)} = 1.2 \times 10^{14}$$

If we assume that |x| << 1.000, then

$$\frac{(1.000)^2}{(- x)} = 1.2 \times 10^{14}$$

$$x = - \frac{(1.000)^2}{1.2 \times 10^{14}} = - 8.3 \times 10^{-15} \qquad \text{Is } |x| << 1.000? \text{ YES, so our assumption that x is small is good.}$$

Therefore the equilibrium pressures are

$$p_{CO} = 1.000 + 2 (- 8.3 \times 10^{-15}) = 1.000 \text{ atm}$$
$$p_{CO2} = - (- 8.3 \times 10^{-15}) = 8.3 \times 10^{-15} \text{ atm}$$

As a check, $$K_p = \frac{(1.000)^2}{(8.3 \times 10^{-15})} = 1.2 \times 10^{14}$$

the correct value for K_p.

Note that this "trick" of using different conditions than those given in the problem has no effect on the equilibrium pressures we find. In fact, this method is often used to do problems when it is difficult to find the equilibrium pressures directly from the initial conditions.