Equilibrium. These problems are from your textbook. More can be found in chapter 19.

1. (19.5) Write the equilibrium-constant expression (Kc) for each of the following reactions.
   a. SO_2Cl_2 (g) ⇌ SO_2 (g) + Cl_2 (g)
   b. 2 H_2O_2 (g) ⇌ 2 H_2O (l) + O_2 (g)

2. (19.11) Phosgene, $COCl_2$ (g), a toxic gas used in the synthesis of a variety of organic compounds, decomposes according to

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

   A sample of phosgene gas at an initial concentration of 0.500 M is heated at 527 °C in a reaction vessel. At equilibrium, the concentration of CO (g) was found to be 0.046 M. Calculate the equilibrium constant for the reaction at 527 °C.

3. (19.14) Nitrogen dioxide decomposes at high temperatures according to the equation:

   $$2\quad NO_2\ (g) \rightleftharpoons 2\ NO\ (g) + O_2\ (g)$$

   Suppose initially we have pure NO_2 (g) at 1000 K and 0.500 bar. If the total pressure is 0.732 bar when equilibrium is reached, what is the value of Kp (make sure to include the correct units)?

4. (19.17) Given that [Ni(CO)$_4$] = 0.85 M at equilibrium for the reaction below, calculate the concentration of CO (g) at equilibrium.

   $$Ni(s) + 4\ CO\ (g) \rightleftharpoons Ni(CO)_4\ (g) \qquad Kc = 5.0 \times 10^4\ M^{-3}$$

5. (19.24) Sodium bicarbonate decomposes according to the equation below. Given that Kp = 0.26 bar^2 at 125 °C, calculate the partial pressures of CO_2 (g) and H_2O (g) at equilibrium when $NaHCO_3$ (s) is heated to 125 °C in a closed vessel.

   $$2\ NaHCO_3\ (s) \rightleftharpoons Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g)$$

6. (19.25) For the reaction below, calculate the equilibrium concentrations of ICl (g), I_2 (g), and Cl_2 (g) when 0.65 moles of I_2 (g) and 0.33 moles of Cl_2 (g) are mixed in a 1.5 liter reaction vessel.

   $$2\ ICl\ (g) \rightleftharpoons I_2\ (g) + Cl_2\ (g) \qquad Kc = 0.11$$

7. (19.37) Consider the chemical equilibrium described below. Predict the way in which the equilibrium will shift in response to each of the following changes.

   $$C\ (s) + 2\ H_2\ (g) \rightleftharpoons CH_4\ (g) \qquad \Delta H^o_{rxn} = -74.6\ kJ\ mol^{-1}$$

   a. The temperature is decreased
   b. The volume is decreased
   c. Decrease in the pressure of H_2
   d. Increase in the pressure of CH_4
   e. Adding C (s) to the flask

8. (19.50) If 0.20 bar H_2 and 3.0 bar CH_4 (g) are mixed in the presence of 4 grams of carbon at 500 °C, determine if the reaction is at equilibrium. If it is not, determine if products or reactants will be formed

   $$C\ (s) + 2\ H_2\ (g) \rightleftharpoons CH_4\ (g) \qquad Kp = 2.69 \times 10^3\ bar^{-1}\ (at\ 500\ °C)$$

1a. $K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$

1b. $K_c = \frac{[O_2]}{[H_2O_2]^2}$

2. $K_c = \frac{[CO][Cl_2]}{[COCl_2]}$

	$COCl_2$ ⇌	CO +	Cl_2
I	0.5 M	Ø	Ø
C	$-x$	$+x$	$+x$
E	$0.5-x$	x	x

↳ [CO] @ Equilibrium = 0.046 M

$x = 0.046\ M$

$K_c = \frac{(0.046\ M)(0.046\ M)}{(0.5-0.046\ M)}$

$K_c = 4.66 \times 10^{-3}\ M$

3.

	$2NO_2$ ⇌	$2NO$ +	O_2
I	0.5 bar	Ø	Ø
C	$-2x$	$+2x$	$+x$
E	$0.5-2x$	$2x$	x
	0.036 bar	0.464 bar	0.232 bar

$P_{TOT} = 0.732\ bar = P_{NO_2} + P_{NO} + P_{O_2}$

$0.732\ bar = 0.5 - 2x + 2x + x$

$0.732\ bar = 0.5 + x$

$x = 0.232\ bar$

$K_p = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2} = \frac{(0.464\ bar)^2(0.232\ bar)}{(0.036\ bar)^2} = 38.54\ bar$

4. $K_c = \frac{[Ni(CO)_4]}{[CO]^4}$

$5.0 \times 10^4\ M^{-3} = \frac{0.85\ M}{[CO]^4}$

$5.0 \times 10^4\ M^{-3}\ [CO]^4 = 0.85\ M$

$[CO]^4 = 1.7 \times 10^{-5}\ M^4$

$[CO] = 0.0642\ M$

5. $K_p = P_{CO_2} P_{H_2O}$

	$2NaHCO_3(s)$ ⇌	$Na_2CO_3(s)$ +	$CO_2(g)$ +	$H_2O(g)$
I	4	Ø	Ø	Ø
C	$-2x$	$+x$	$+x$	$+x$
E	$4-2x$	x	x	x

$0.26\ bar^2 = (x)(x) = x^2$

$x = 0.51\ bar$

6. $2\,ICl \rightleftharpoons I_2 + Cl_2$ $K_c = 0.11$

	$2\,ICl$	I_2	Cl_2
I	Ø	0.43	0.22
C	+2x	−x	−x
E	2x	0.43 − x	0.22 − x

$[Cl_2] = \frac{0.33\text{ mol}}{1.5\text{ L}} = 0.22\text{ M}$

$[I_2] = \frac{0.65}{1.5} = 0.43\text{ M}$

$$K_c = \frac{[I_2][Cl_2]}{[ICl]^2} = \frac{(0.43-x)(0.22-x)}{(2x)^2} = 0.11$$

$$0.0953 - 0.65x + x^2 = 0.11(2x)^2 = 0.44x^2$$

$$0.56x^2 - 0.65x + 0.0953 = Ø$$

a = 0.56
b = −0.65
c = 0.0953

$$\frac{0.65 \pm \sqrt{(0.65)^2 - 4(0.56)(0.0953)}}{2(0.56)} = x$$

$x = \frac{0.65 + 0.457}{1.12} = 0.988$ ← Not possible

$x = \frac{0.65 - 0.457}{1.12} = 0.172$

$[ICl] = 2x = 2(0.172) = 0.345\text{ M}$
$[I_2] = 0.43 - 0.172 = 0.258\text{ M}$
$[Cl_2] = 0.22 - 0.172 = 0.048\text{ M}$

7. $C(s) + 2H_2(g) \rightleftharpoons CH_4(g) + \text{heat}$ $\Delta H = -74.6$ kJ/mol → exothermic

a. ↓T = ↓ heat shift to products

b. decreasing the volume will increase the pressure of ALL gases by the same factor ($P \propto \frac{1}{V}$). But, since the P_{H_2} weighs more (because squared), the reaction will shift toward products.

General rule: ↓ volume favors the side with the fewest moles of gas

↑ volume favors the side with the highest moles of gas

c. ↓ P_{H_2} = reactants favored

d. ↑ CH_4 = reactants favored

e. No change (solids don't influence equilibrium)

8. $Q = \frac{P_{CH_4}}{P_{H_2}^{2}} = \frac{3.0 \text{ bar}}{(0.2 \text{ bar})^2} = 75 \text{ bar}^{-1}$

$K > Q$

products favored