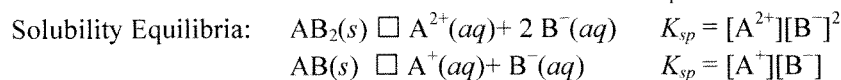**NATIONAL MATH + SCIENCE INITIATIVE**

General and Solubility Equilibrium Cheat Sheet

Relationships

Equilibrium Expression

$$K_c = \frac{[\text{Products}]^{\text{coefficients}}}{[\text{Reactants}]^{\text{coefficients}}} \qquad K_p = \frac{(\text{Products } P_{\text{atmospheres}})^{\text{coefficient}}}{(\text{Reactants } P_{\text{atmospheres}})^{\text{coefficient}}} \text{ Either setup for } Q$$

Solubility Equilibria: $AB_2(s) \ \square \ A^{2+}(aq) + 2\,B^-(aq)$ $K_{sp} = [A^{2+}][B^-]^2$

   $AB(s) \ \square \ A^+(aq) + B^-(aq)$ $K_{sp} = [A^+][B^-]$

Converting between K_p and K_c: $K_p = K_c(RT)^{\Delta n}$

Be sure to leave out any solids and liquids and realize that changing their amounts can in no way affect the position of the equilibrium – they are not variables that are included in the equilibrium expression.	Manipulating K for different versions of the same reaction: reverse rxn = $1/K$; double coefficients = K^2; ½ the coefficients = $K^{1/2}$ Adding reactions= multiply K values
If K is >1 then reaction favors products because K ratio is "top heavy"	If K is <1 then reaction favors reactants because K ratio is "bottom heavy"
LeChâtelier's Principle: If a system at equilibrium is stressed the system will shift direction until equilibrium is re-established.	A LeChâtelier's shift will result in different concentration/pressure values for the individual members of the reaction but the VALUE of K will not change without a change in the temperature.
$Q < K$ unsaturated solution is formed as the reaction has not reach the equilibrium position; no ppt $Q = K$ a saturated solutions is made; no ppt	$Q > K$ a supersaturated solution is formed the concentration of ions are greater than allowed; a ppt will form

Connections

Thermodynamics: $\Delta G = \Delta H - T\Delta S$	Electrochem: $E_{\text{cell}} = E^{\circ}_{\text{table}} - \dfrac{0.0592}{n}\log Q$
The easiest question you can be asked is "What is the value of ΔG or E_{cell} when the system is at equilibrium?" Answer: ZERO	

Potential Pitfalls

No units on K – you finally get to ignore units – just don't do it with other stuff!!!!

LeChâtelier's tricky questions:
- Only temperature will change the value of K; no shifting can affect value of K
- Amounts of solids and liquids that are not in the K expression can not change position or size of K
- Adding an inert gas (He, Ar, Ne…) to a gaseous equilibrium has NO EFFECT since it is not represented in the K expression.

In general equilibrium don't forget that these equations may have 1:2 ratios or other ratios [i.e. $(2x)^2$ terms]

Be on the lookout for "perfect squares".

Neglecting the "$-x$" will be OK. You should never have to use the quadratic equation on the AP exam. Always show the original equilibrium expression with the $-x$ first then show the approximation without the $-x$.

For solubility be aware of the COEFFICIENTS!
- Don't get confused by when to use x and $2x$ and when to apply the exponent.
- If either [X] and [Y] are given as numbers, use the number in the appropriate [ ] and remember to square/cube it if necessary. USE "x" for the unknown concentration.
- If [X] and [Y] are both unknown to you THEN apply the coefficient ratio and use "x" and "$2x$" in the appropriate [ ]. Remember to square/cube them if necessary.

NMSI Super Problem

$$2\ SO_3(g) \ \square\ 2\ SO_2(g)\ +\ O_2(g)$$
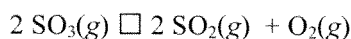
A 5.00 mol sample of sulfur trioxide, SO_3 is placed into a 5.00 L reaction vessel and allowed to decompose at 400 K according the reaction above. Once equilibrium is established, 3.00 mol of sulfur dioxide, SO_2, is present.

(a) Write the expression for the equilibrium constant, K_c, for the reaction above.

$K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$	**1 point** for the correct equilibrium expression

(b) Calculate

       i.   the initial molar concentration of SO_3

$\dfrac{5.00\ \text{mol}}{5.00\ \text{L}} = 1.00 M = [SO_3]$	**1 point** for the correct initial concentration

       ii.   the equilibrium concentrations of O_2, SO_2, and SO_3

$[SO_2]_{eq} = \dfrac{3.00\ \text{mol}}{5.00\ \text{L}} = 0.600 M$ R $2\ SO_3$ $\rightleftarrows$ $2\ SO_2$ $+$ O_2 I 1.00 0 0 C $-2(0.300)$ $+2(0.300)$ $+(0.300)$ E 0.400 0.600 0.300 $[O_2]_{eq} = 0.300\ M$ $[SO_3]_{eq} = 0.400\ M$	**2 points** for the correct equilibrium concentration for all three species. **1 point** for the correct equilibrium concentration of any two species.

(c) Calculate the equilibrium constant, K_c for this reaction.

$K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2} = \dfrac{[0.600]^2[0.300]}{[0.400]^2} = 0.675$	**1 point** for the correct equilibrium constant consistent with part b.

(d) Calculate the equilibrium constant, K_p for this reaction.

$K_p = K_c\ (RT)^{\Delta n}$ $K_p = (0.675)(0.0821)(400)^{(3-2)}$ $K_p = (0.675)(0.0821)(400)^1 = 22.2$	**1 point** for the correct determination of Δn **1 point** for the correct equilibrium constant consistent with part c.

The reaction vessel above is cooled from 400 K to 298 K. The mixture reestablishes equilibrium with fewer moles of sulfur dioxide and oxygen gas at the new temperature.

(e) Is the forward reaction endothermic or exothermic? Justify your answer.

Endothermic; because decreasing the temperature from 400 K to 298K caused the was thermodynamically more favorable in the reverse direction (shift to have fewer products and more reactants)	**1 point** for answer with correct justification

(f) Predict the sign of the standard entropy change, $\Delta S°$, for the reaction. Explain.

$\Delta S° = (+)$; because the reaction is going from 2 moles of reactant gases to 3 moles of product gases, thus increasing the dispersal of matter.	**1 point** for correct sign with justification

(g) The value of the standard free energy change, $\Delta G°$, for the reaction is $+141.8$ kJ mol^{-1}. Calculate the value of the equilibrium constant, K, at 298 K.

$\Delta G = -RT \ln K$ $\ln K = \dfrac{\Delta G}{-RT} = \dfrac{+141.8 \text{ kJ mol}^{-1}}{-(8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = -57.3$ $K = e^{-57.3} = 1.30 \times 10^{-25}$	**1 point** for correctly using $\Delta G = -RT \ln K$ **1 point** for correct value of K

(h) Determine whether the number of moles of SO_3 will increase, decrease, or stay the same after each of the following disturbances. Justify each response.

  i. The temperature of the equilibrium mixture is decreased.

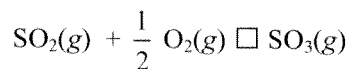|	
Since the reaction is endothermic ($\Delta H° > 0$), a decrease in the temperature will cause the reverse reaction to be thermodynamically more favorable, thus the moles of SO_3 will increase.	**1 point** for stating the number of moles will increase with justification

  ii. The volume of the reaction container is increased.

When the volume of the container is increased, the pressure is decreased causing the forward reaction to be thermodynamically more favorable (2 mol of gas to 3 mol of gas) therefore the number of moles of SO_3 will decrease.	**1 point** for stating the number of moles will decrease with justification

In a different experiment, sulfur dioxide and oxygen gases were added to a reaction vessel at 400 K and the following reaction occurred and equilibrium was established.
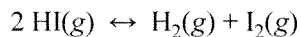
$$SO_2(g) \; + \; \frac{1}{2} \, O_2(g) \; \square \; SO_3(g)$$

(i) Calculate the equilibrium constant, K_c for this reaction at 400. K.

|	
The reaction is reversed from the one above therefore $K_2 = \dfrac{1}{K_1}$ And the coefficients are multiplied by $\dfrac{1}{2}$ therefore the equilibrium constant is raised to the $\dfrac{1}{2}$ power $K_2 = \dfrac{1}{(K_1)^{\frac{1}{2}}}$ thus $K_2 = \dfrac{1}{(K_1)^{\frac{1}{2}}} = \dfrac{1}{(0.675)^{\frac{1}{2}}} = 1.22$	**1 point** for taking the inverse of the K_c of the above reaction consistent with part (c). **1 point** for taking the square root and getting the correct value of the equilibrium constant.

AP® CHEMISTRY
2003 SCORING GUIDELINES (Form B)

Question 1

Total Score 10 points

$$2\,HI(g) \leftrightarrow H_2(g) + I_2(g)$$

1. After a 1.0 mole sample of $HI(g)$ is placed into an evacuated 1.0 L container at 700. K, the reaction represented above occurs. The concentration of $HI(g)$ as a function of time is shown below.
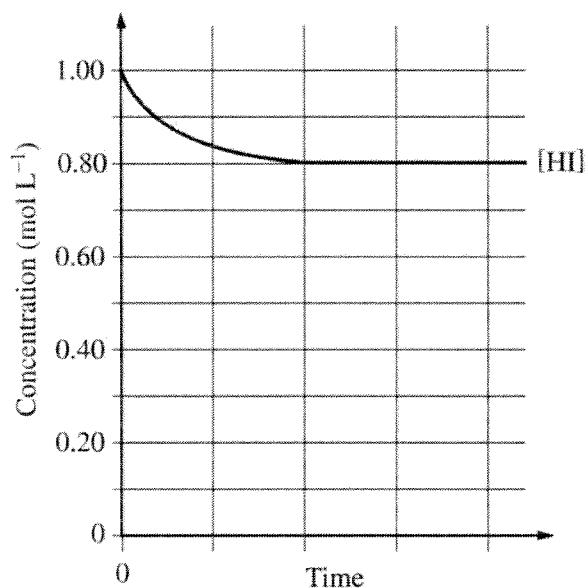
(a) Write the expression for the equilibrium constant, K_c, for the reaction.

$K_c = \dfrac{[H_2][I_2]}{[HI]^2}$	1 point for correct expression

(b) What is $[HI]$ at equilibrium?

From the graph, $[HI]_{eq}$ is 0.80 M	1 point for equilibrium $[HI]$

Question 1 (cont'd.)

(c) Determine the equilibrium concentrations of $H_2(g)$ and $I_2(g)$.

		$2\,HI(g) \;\rightarrow\; H_2(g) \;+\; I_2(g)$		1 point for stoichiometric relationship between HI reacting and $H_2(g)$ or $I_2(g)$ forming
I	1.0 M	0	0	
C	−0.20 M	+0.10 M	+0.10 M	
E	0.80 M	0.10 M	0.10 M	
	$[I_2] = [H_2] = 0.10\,M$			1 point for $[H_2]_{eq}$ and $[I_2]_{eq}$

(d) On the graph above, make a sketch that shows how the concentration of $H_2(g)$ changes as a function of time.

From the graph, $[H_2]_{eq}$ is $0.10\,M$ The curve should have the following characteristics: - start at $0\,M$; - increase to $0.1\,M$; - reach equilibrium at the same time [HI] reaches equilibrium	1 point for any two characteristics 2 points for all three characteristics

(e) Calculate the value of the following equilibrium constants for the reaction at 700. K.

   (i) K_c

$K_c = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{[0.10][0.10]}{[0.80]^2} = 0.016$	1 point for correct substitution (must agree with parts (b) and (c))

   (ii) K_p

$K_p = K_c = 0.016$ The number of moles on the product side is equal to the number of moles on the reactant side $K_p = K_c(RT)^{\Delta n}$ $\Delta n = 2 - 2 = 0$ $K_p = K_c(RT)^0$ $K_p = K_c$	1 point for $K_p = K_c$ (with verification)

Question 1 (cont'd.)

(f) At 1,000 K, the value of K_c for the reaction is 2.6×10^{-2}. In an experiment, 0.75 mole of HI(g), 0.10 mole of $H_2(g)$, and 0.50 mol of $I_2(g)$ are placed in a 1.0 L container and allowed to reach equilibrium at 1,000 K. Determine whether the equilibrium concentration of HI(g) will be greater than, equal to, or less than the initial concentration of HI(g). Justify your answer.

$Q = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{[0.10][0.50]}{[0.75]^2} = 8.9 \times 10^{-2}$ $K_c = 2.6 \times 10^{-2}$	1 point for calculating Q and comparing to K_c
$Q > K_c$ To establish equilibrium, the numerator must decrease and the denominator must increase. Therefore, [HI] will increase.	1 point for predicting correct change in [HI]

AP® CHEMISTRY
2008 SCORING GUIDELINES (Form B)

Question 1

Answer the following questions regarding the decomposition of arsenic pentafluoride, $AsF_5(g)$.

(a) A 55.8 g sample of $AsF_5(g)$ is introduced into an evacuated 10.5 L container at 105°C.

(i) What is the initial molar concentration of $AsF_5(g)$ in the container?

$\text{mol AsF}_5 = 55.8 \text{ g AsF}_5 \times \dfrac{1 \text{ mol AsF}_5}{169.9 \text{ g AsF}_5} = 0.328 \text{ mol}$ $[AsF_5]_i = \dfrac{0.328 \text{ mol AsF}_5}{10.5 \text{ L}} = 0.0313 \, M$	One point is earned for the correct molar mass. One point is earned for the correct concentration.

(ii) What is the initial pressure, in atmospheres, of the $AsF_5(g)$ in the container?

$PV = nRT$ $P = \dfrac{0.328 \text{ mol} \times 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 378 \text{ K}}{10.5 \text{ L}} = 0.969 \text{ atm}$	One point is earned for the correct substitution. One point is earned for the correct pressure.

At 105°C, $AsF_5(g)$ decomposes into $AsF_3(g)$ and $F_2(g)$ according to the following chemical equation.

$$AsF_5(g) \rightleftarrows AsF_3(g) + F_2(g)$$
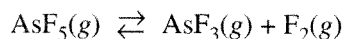
(b) In terms of molar concentrations, write the equilibrium-constant expression for the decomposition of $AsF_5(g)$.

$K = \dfrac{[AsF_3] \, [F_2]}{[AsF_5]}$	One point is earned for the correct equation.

(c) When equilibrium is established, 27.7 percent of the original number of moles of $AsF_5(g)$ has decomposed.

(i) Calculate the molar concentration of $AsF_5(g)$ at equilibrium.

$100.0\% - 27.7\% = 72.3\%$ $[AsF_5] = 0.723 \times 0.0313 \, M = 0.0226 \, M$	One point is earned for the correct concentration.

(ii) Using molar concentrations, calculate the value of the equilibrium constant, K_{eq}, at 105°C.

$[AsF_3] = [F_2] = 0.277 \times [AsF_5]_i$ $\qquad = 0.277 \times 0.0313 \, M = 0.00867 \, M$ $K_{eq} = \dfrac{[AsF_3][F_2]}{[AsF_5]} = \dfrac{[0.00867][0.00867]}{[0.0226]} = 0.00333$	One point is earned for setting $[AsF_3] = [F_2]$. <u>Note</u>: the point is not earned if the student indicates that $[AsF_3] = [F_2] = [AsF_5]$. One point is earned for the correct calculation of $[AsF_3]$ and $[F_2]$. One point is earned for the correct calculation of K_{eq}.

(d) Calculate the mole fraction of $F_2(g)$ in the container at equilibrium.

$mol \, AsF_5 = 0.0226 \, M \times 10.5 \, L = 0.237 \, mol$ $mol \, F_2 = mol \, AsF_3 = 0.00867 \, M \times 10.5 \, L = 0.0910 \, mol$ $mol \, fraction \, F_2 = \dfrac{mol \, F_2}{mol \, F_2 + mol \, AsF_3 + mol \, AsF_5}$ $\qquad = \dfrac{0.0910}{0.0910 + 0.0910 + 0.237} = 0.217$ OR $mol \, fraction \, F_2 = \dfrac{0.00864}{0.00864 + 0.00864 + 0.0226} = 0.217$	One point is earned for the correct calculation of the mole fraction of $F_2(g)$.

Question 1
(10 points)

Several reactions are carried out using AgBr, a cream-colored silver salt for which the value of the solubility-product-constant, K_{sp}, is 5.0×10^{-13} at 298 K.

(a) Write the expression for the solubility-product constant, K_{sp}, of AgBr.

$K_{sp} = [Ag^+][Br^-]$	One point is earned for the correct expression (ion charges must be present; parentheses instead of square brackets not accepted).

(b) Calculate the value of $[Ag^+]$ in 50.0 mL of a saturated solution of AgBr at 298 K.

Let x = equilibrium concentration of Ag^+ (and of Br^-). Then $K_{sp} = 5.0 \times 10^{-13} = x^2 \Rightarrow x = 7.1 \times 10^{-7} M$	One point is earned for the correct value with supporting work (units not necessary).

(c) A 50.0 mL sample of distilled water is added to the solution described in part (b), which is in a beaker with some solid AgBr at the bottom. The solution is stirred and equilibrium is reestablished. Some solid AgBr remains in the beaker. Is the value of $[Ag^+]$ greater than, less than, or equal to the value you calculated in part (b) ? Justify your answer.

The value of $[Ag^+]$ after addition of distilled water is equal to the value in part (b). The concentration of ions in solution in equilibrium with a solid does <u>not</u> depend on the volume of the solution.	One point is earned for the correct answer with justification.

(d) Calculate the minimum volume of distilled water, in liters, necessary to completely dissolve a 5.0 g sample of AgBr(s) at 298 K. (The molar mass of AgBr is 188 g mol^{-1}.)

$5.0 \text{ g AgBr} \times \dfrac{1 \text{ mol AgBr}}{188 \text{ g AgBr}} = 0.0266 \text{ mol AgBr}$ $\dfrac{0.0266 \text{ mol}}{V} = 7.1 \times 10^{-7} \text{mol L}^{-1} \Rightarrow V = 3.7 \times 10^4 \text{ L}$	One point is earned for the calculation of moles of dissolved AgBr. One point is earned for the correct answer for the volume of water

(e) A student mixes 10.0 mL of 1.5×10^{-4} M AgNO$_3$ with 2.0 mL of 5.0×10^{-4} M NaBr and stirs the resulting mixture. What will the student observe? Justify your answer with calculations.

$[\text{Ag}^+] = \dfrac{(10.0 \text{ mL})(1.5 \times 10^{-4} M)}{12.0 \text{ mL}} = 1.3 \times 10^{-4} M$ $[\text{Br}^-] = \dfrac{(2.0 \text{ mL})(5.0 \times 10^{-4} M)}{12.0 \text{ mL}} = 8.3 \times 10^{-5} M$ $Q = [\text{Ag}^+][\text{Br}^-] = (1.3 \times 10^{-4} M)(8.3 \times 10^{-5} M) = 1.1 \times 10^{-8}$ $1.1 \times 10^{-8} > 5.0 \times 10^{-13}$, $\therefore$ a precipitate will form.	One point is earned for calculation of concentration of ions. One point is earned for calculation of Q and conclusion based on comparison between Q and K_{sp}. One point is earned for indicating the precipitation of AgBr.

(f) The color of another salt of silver, AgI(s), is yellow. A student adds a solution of NaI to a test tube containing a small amount of solid, cream-colored AgBr. After stirring the contents of the test tube, the student observes that the solid in the test tube changes color from cream to yellow.

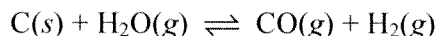   (i) Write the chemical equation for the reaction that occurred in the test tube.

$\text{AgBr}(s) + \text{I}^-(aq) \rightarrow \text{AgI}(s) + \text{Br}^-(aq)$ **OR** $\text{AgBr}(s) + \text{NaI}(aq) \rightarrow \text{AgI}(s) + \text{NaBr}(aq)$	One point is earned for the correct equation.

   (ii) Which salt has the greater value of K_{sp}: AgBr or AgI ? Justify your answer.

AgBr has the greater value of K_{sp}. The precipitate will consist of the less soluble salt when both I$^-$(aq) and Br$^-$(aq) are present. Because the color of the precipitate in the test tube turns yellow, it must be AgI(s) that precipitates; therefore K_{sp} for AgBr must be greater than K_{sp} for AgI. **OR** K_{eq} for the displacement reaction is $\dfrac{K_{sp} \text{ of AgBr}}{K_{sp} \text{ of AgI}}$. Because yellow AgI forms, $K_{eq} > 1$; therefore K_{sp} of AgBr $> K_{sp}$ of AgI.	One point is earned for the correct choice with justification.

1998 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

Question 7 - Adapted for a Short Response

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad\qquad \Delta H° = +131 \text{ kJ mol}^{-1}$$

A rigid container holds a mixture of graphite pellets ($C(s)$), $H_2O(g)$, $CO(g)$, and $H_2(g)$ at equilibrium. State whether the number of moles of $CO(g)$ in the container will increase, decrease, or remain the same after each of the following disturbances is applied to the original mixture. For each case, assume that all other variables remain constant except for the given disturbance. Explain each answer with a short statement.

(a) Additional $H_2(g)$ is added to the equilibrium mixture at constant volume.

The number of moles of CO will decrease because adding H_2 will shift the reaction to the left, (one point) or adding H_2 will make the reaction quotient larger than K, thus the reaction shifts to the left.	**1 point** is earned for the correct response with justification.

(b) The temperature of the equilibrium mixture is increased at constant volume.

The number of moles of CO will increase. Since the reaction is endothermic, the adding of heat (as a reactant) will drive the reaction to the right.	**1 point** is earned for the correct response with justification.

(c) The volume of the container is decreased at constant temperature.

The number of moles of CO will decrease. because there are more moles of gas (2) on the right than on the left (1), thus decreasing the volume which increases the pressure causing the reaction to shift to the left.	**1 point** is earned for the correct response with a correct explanation.

(d) The graphite pellets are pulverized.

The number of moles of CO will stay the same because solids are not involved in the equilibrium expression OR Solids have no effect on the equilibrium mixture.	**1 point** is earned for the correct response with a correct explanation.

Question 1

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$$
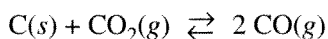
Solid carbon and carbon dioxide gas at 1,160 K were placed in a rigid 2.00 L container, and the reaction represented above occurred. As the reaction proceeded, the total pressure in the container was monitored. When equilibrium was reached, there was still some $C(s)$ remaining in the container. Results are recorded in the table below.

Time (hours)	Total Pressure of Gases in Container at 1,160 K (atm)
0.0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

(a) Write the expression for the equilibrium constant, K_p, for the reaction.

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}}$$	One point is earned for the correct expression.

(b) Calculate the number of moles of $CO_2(g)$ initially placed in the container. (Assume that the volume of the solid carbon is negligible.)

$$n = \frac{PV}{RT} = \frac{(5.00\ \text{atm})(2.00\ \text{L})}{(0.0821\ \frac{\text{L atm}}{\text{mol K}})(1{,}160\ \text{K})} = 0.105\ \text{mol}$$	One point is earned for the correct setup. One point is earned for the correct answer.

(c) For the reaction mixture at equilibrium at 1,160 K, the partial pressure of the $CO_2(g)$ is 1.63 atm. Calculate

   (i) the partial pressure of $CO(g)$, and

$$P_{CO_2} + P_{CO} = P_{total}$$ $$P_{CO} = P_{total} - P_{CO_2} = 8.37\ \text{atm} - 1.63\ \text{atm} = 6.74\ \text{atm}$$	One point is earned for the correct answer supported by a correct method.

(ii) the value of the equilibrium constant, K_p.

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(6.74 \text{ atm})^2}{1.63 \text{ atm}} = 27.9$$	One point is earned for a correct setup that is consistent with part (a). One point is earned for the correct answer according to the setup.

(d) If a suitable solid catalyst were placed in the reaction vessel, would the final total pressure of the gases at equilibrium be greater than, less than, or equal to the final total pressure of the gases at equilibrium without the catalyst? Justify your answer. (Assume that the volume of the solid catalyst is negligible.)

The total pressure of the gases at equilibrium with a catalyst present would be equal to the total pressure of the gases without a catalyst. Although a catalyst would cause the system to reach the same equilibrium state more quickly, it would not affect the extent of the reaction, which is determined by the value of the equilibrium constant, K_p.	One point is earned for the correct answer with justification.

In another experiment involving the same reaction, a rigid 2.00 L container initially contains 10.0 g of C(s), plus CO(g) and CO_2(g), each at a partial pressure of 2.00 atm at 1,160 K.

(e) Predict whether the partial pressure of CO_2(g) will increase, decrease, or remain the same as this system approaches equilibrium. Justify your prediction with a calculation.

$$Q = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(2.00 \text{ atm})^2}{2.00 \text{ atm}} = 2.00 < K_p \ (= 27.9),$$ therefore P_{CO_2} will decrease as the system approaches equilibrium.	One point is earned for a correct calculation involving Q or ICE calculation. One point is earned for a correct conclusion based on the calculation.

Question 1
(10 points)

Answer the following questions about the solubility of some fluoride salts of alkaline earth metals.

(a) A student prepares 100. mL of a saturated solution of MgF_2 by adding 0.50 g of solid MgF_2 to 100. mL of distilled water at 25°C and stirring until no more solid dissolves. (Assume that the volume of the undissolved MgF_2 is negligibly small.) The saturated solution is analyzed, and it is determined that $[F^-]$ in the solution is $2.4 \times 10^{-3}\ M$.

   (i) Write the chemical equation for the dissolving of solid MgF_2 in water.

$MgF_2(s) \rightleftarrows Mg^{2+}(aq) + 2\,F^-(aq)$	1 point is earned for the correct equation.

   (ii) Calculate the number of moles of MgF_2 that dissolved.

$\dfrac{2.4 \times 10^{-3}\,\text{mol F}^-}{1.0\ \text{L}} \times 0.100\ \text{L} \times \dfrac{1\ \text{mol MgF}_2}{2\ \text{mol F}^-} = 1.2 \times 10^{-4}\ \text{mol MgF}_2$	1 point is earned for the correct calculation moles from concentration. 1 point is earned for the correct stoichiometry.

   (iii) Determine the value of the solubility-product constant, K_{sp}, for MgF_2 at 25°C.

$[Mg^{2+}] = \dfrac{1}{2}\,[F^-] = \dfrac{1}{2}\,(2.4 \times 10^{-3}\ M) = 1.2 \times 10^{-3}\ M$ $K_{sp} = [Mg^{2+}][F^-]^2 = (1.2 \times 10^{-3})(2.4 \times 10^{-3})^2$ $\qquad = 6.9 \times 10^{-9}$	1 point is earned for the correct setup for determining the value of K_{sp}. 1 point is earned for the correct value of $[Mg^{2+}]$. 1 point is earned for the correct value of K_{sp}.

(b) A beaker contains 500. mL of a solution in which both $Ca^{2+}(aq)$ and $Ba^{2+}(aq)$ are present at a concentration of $0.10\ M$ at 25°C. A student intends to separate the ions by adding $0.20\ M$ NaF solution one drop at a time from a buret. At 25°C the value of K_{sp} for CaF_2 is 3.5×10^{-11}; the value of K_{sp} for BaF_2 is 1.8×10^{-6}.

   (i) Which salt will precipitate first, CaF_2 or BaF_2? Justify your answer.

CaF_2 will precipitate first. Its K_{sp} value is smaller, thus the ion-concentration product $[Ca^{2+}][F^-]^2$ will be the first to exceed the K_{sp} value.	1 point is earned for the correct choice with its justification.

Question 1 (continued)

For parts (b)(ii) and (b)(iii) below, assume that the addition of the NaF solution does not significantly affect the total volume of the liquid in the beaker.

(ii) Calculate the minimum concentration of $F^-(aq)$ necessary to initiate precipitation of the salt selected in part (b)(i).

$K_{sp} = 3.5 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (0.10)[F^-]^2$ $3.5 \times 10^{-10} = [F^-]^2$ $[F^-] = \sqrt{3.5 \times 10^{-10}} = 1.9 \times 10^{-5} M$	1 point is earned for the correct value of $[F^-]$.

(iii) Calculate the minimum volume of 0.20 M NaF that must be added to the beaker to initiate precipitation of the salt selected in part (b)(i).

Assuming that the volume of added $NaF(aq)$ is negligible, the total volume of the solution at the point of precipitation is 500. mL. Then $(0.20\,M)(V) = (1.9 \times 10^{-5}\,M)(0.500\,L)$ $V = 4.7 \times 10^{-5}\,L$ (or $4.8 \times 10^{-5}\,L$) $\quad = 4.7 \times 10^{-2}\,mL$ (or $4.8 \times 10^{-2}\,mL$)	1 point is earned for the correct volume.

(c) There are several ways to dissolve salts that have limited solubility. Describe one procedure to redissolve the precipitate formed in part (b).

Valid procedures include adding water, adding acid (H^+), heating (i.e., increasing the temperature), and any valid statement that implies a shifting of the equilibrium toward the products side of the dissolution equation.	1 point is earned for a description of a valid procedure.