Equilibrium Test Review:

1. The solubility of barium fluoride into water is 1.10(4) g/L. Find the Ksp of this compound.

$$\left(\frac{1.104 \text{ g } BaF_2}{Liter}\right)\left(\frac{1 \text{ mole}}{175.327 \text{ g}}\right) = 0.006297 \text{ mole } BaF_2/L$$

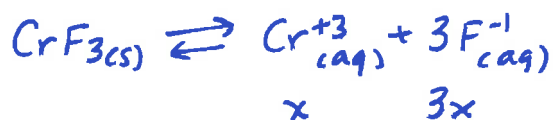$[Ba^{+2}] = .006297 \text{ M}$

$[F^-] = 2[Ba^{+2}] = 0.01259 \text{ M}$

$$BaF_{2 (s)} \rightleftharpoons Ba^{+2}_{(aq)} + 2F^{-1}_{(aq)}$$

$$Ksp = [Ba^{+2}][F^-]^2 = (.006297)(.01259)^2 = 9.987 \times 10^{-7}$$

$$\boxed{9.99 \times 10^{-7}}$$

2. At 25°C, CrF_3 has a Ksp of 6.6 x 10^{-11}.
a. Find the molar solubility of chromium (III) fluoride into water, and report the molarity of each ion in a saturated solution of chromium fluoride.

$$CrF_{3(s)} \rightleftharpoons Cr^{+3}_{(aq)} + 3F^{-1}_{(aq)}$$
$$x \qquad 3x$$

$\boxed{\text{molar solubility} = .0013 \text{ M}}$
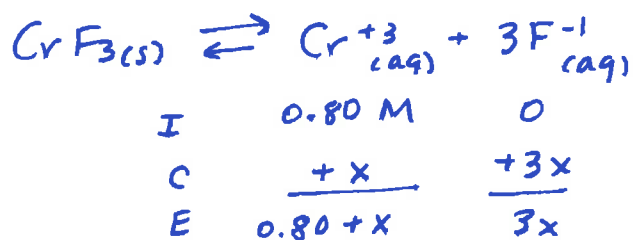
$[Cr^{+3}] = .0013 \text{ M}$

$[F^-] = 3x = .0038 \text{ M}$

$$Ksp = [Cr^{+3}][F^{-1}]^3 = x(3x)^3 = 6.6 \times 10^{-11}$$

$$27x^4 = 6.6 \times 10^{-11}$$

$$x = 0.0012504 \text{ M} \rightarrow .0013 \text{ M}$$

b. Find the molar solubility of chromium (III) fluoride, if it is dissolving into a solution of 0.80 M chromium (III) nitrate. Also report the concentration chromium and fluoride ions in this solution.

$$CrF_{3(s)} \rightleftharpoons Cr^{+3}_{(aq)} + 3F^{-1}_{(aq)}$$

I	0.80 M	0
C	+x	+3x
E	0.80+x	3x

$\boxed{\text{molar solubility} = x = .00015 \text{ M}}$

$[Cr^{+3}] = .80 + x \approx 0.80 \text{ M}$

$[F^-] = 3x = 0.00044 \text{ M}$

$$Ksp = (.80+x)(3x)^3 = 6.6 \times 10^{-11}$$

assume x << .80

$$(.80)(27 x^3) = 6.6 \times 10^{-11}$$

$$x = 0.0001451 \rightarrow .00015 M$$

c. How many grams chromium fluoride can dissolve into 100. mL of 0.80 M chromium nitrate?

$$\left(\frac{.0001451 \text{ mole } CrF_3}{Liter}\right)\left(0.100 \text{ L}\right)\left(\frac{108.9912 \text{ g}}{1 \text{ mole}}\right) = 0.001581 \rightarrow \boxed{0.0016 \text{ g}}$$
can dissolve

(#2, cont'd. CrF_3 has a Ksp of 6.6×10^{-11})

total Volume after Mixing

If 100. mL of 6.0 M Chromium (III) nitrate are mixed with 200. mL of 6.0 M NaF, $= 100.mL + 200.mL$

d. Verify that a precipitate will form. Show a calculation. $= 300.mL$

e. Find the mass of ppt that forms

f. Determine the concentrations of chromium (III) and fluoride ions after the reaction.

ⓓ To show that a ppt forms, we need to show that $Q_{sp} > K_{sp}$

$M_1 V_1 = M_2 V_2$ $M_1 V_1 = M_2 V_2$

$(6.0\ M)(100.mL) = M_2 (300.mL)$ $(6.0\ M)(200.mL) = M_2 (300.mL)$

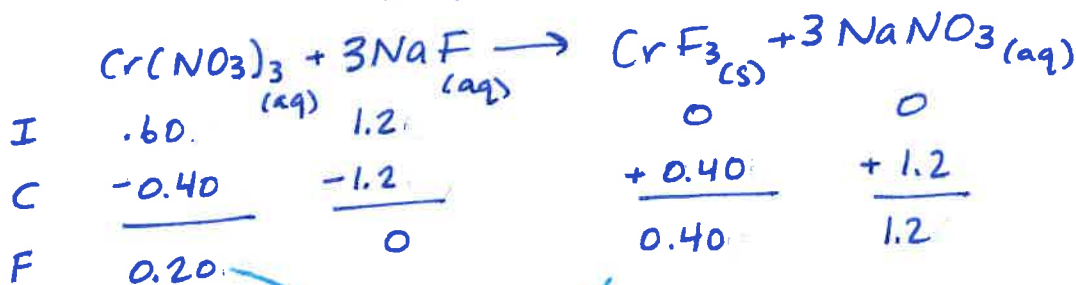$M_2 = 2.0M\ Cr^{+3}$ $M_2 = 4.0M$

$Q_{sp} = [Cr^{+3}][F^{-1}]^3 = (2.0)(4.0)^3 = \underline{128}$

$Q_{sp}\ (128) > K_{sp}(6.6 \times 10^{-11})$ So yes, a ppt will form.

(e) $(0.100\ L)\left(\dfrac{6.0\ mole}{L}\right) = 0.60$ moles $Cr(NO_3)_3$

$(0.200\ L)\left(\dfrac{6.0\ mole}{L}\right) = 1.2$ moles NaF

$Cr(NO_3)_3 + 3NaF \longrightarrow CrF_{3(s)} + 3 NaNO_{3\ (aq)}$

I	.60	1.2	0	0
C	-0.40	-1.2	+0.40	+1.2
F	0.20	0	0.40	1.2

$(0.40$ moles $CrF_3)\left(\dfrac{108.99129}{1 mole}\right) = 43.6 g$ ppt

$[Cr^{+3}] = \dfrac{0.20\ moles}{0.300L} = .667$

$\boxed{[Cr^{+3}] = 0.67\ M}$ (f)

(e) $\boxed{44\ g\ ppt}$

now do Ksp to find $[F^-]$:

$CrF_{3(s)} \rightleftharpoons Cr^{+3}_{(aq)} + 3 F^{-1}_{(aq)}$

$\quad\quad\quad\quad .667 + x \quad\quad 3x$

$(.667)(3x)^3 = 6.6 \times 10^{-11}$

$x = 0.0001542\ M$
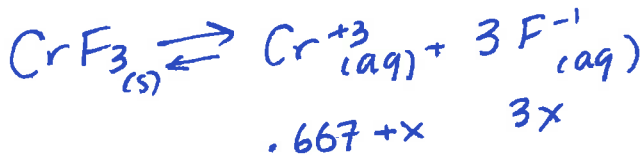
$\boxed{[F^-] = 3x = 0.00046\ M}$

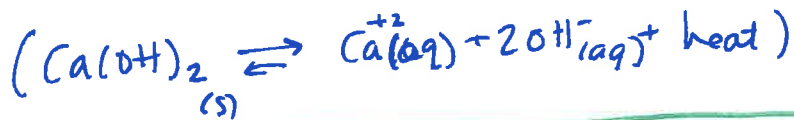$K_{sp} = (.667 + x)(3x)^3 = 6.6 \times 10^{-11}$

assume $x \ll 0.667$

(f)

3. Based on the data shown below, determine the sign of $\Delta H_{solution}$ for calcium hydroxide and barium sulfate.

$Ca(OH)_2$ Ksp = 0.000042 at 20°C
          Ksp = 0.000017 at 60°C

$BaSO_4$ Ksp = 1.1 x 10^{-10} at 20°C
          Ksp = 1.5 x 10^{-10} at 30°C

Ksp decreases as temp increases,
so ΔH_{soln} is exothermic (negative)

$(Ca(OH)_2 \;_{(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2OH^-_{(aq)} + heat)$

Ksp increases as temp increases,
so ΔH_{soln} is endothermic
(ΔH_{soln} is positive)
$(BaSO_{4(s)} + heat \rightleftharpoons Ba^{+2}_{(aq)} + SO_4^{-2}_{(aq)})$

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4. $2HI_{(g)} \longleftrightarrow H_{2(g)} + I_{2(s)}$ ΔHrxn of -51.88 kJ/mole   Kp = 2.86 at 25°C.

Which could be the Kp of this reaction at 50°C: 0.562, or 5.62?   **0.562**

Since ΔHrxn is negative (exo), Kp must decrease as temp increases

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5. $C_{(s)} + CO_{2(g)}$ $\longleftrightarrow$ $2CO_{(g)}$ ΔH rxn = + 172.5 kJ   Kc = 1.598 at 1000°C
                                                    Kc = 1 x 10^{-34} at **25** °C.

a. fill in the missing temperature: is it (25°C) or 2000 °C?   endothermic so K increases as temp increases
and vice versa.

b. If the above reaction is at equilibrium, what will happen (which way will it "shift": left, right, or no change) if the following changes are made to the reaction mixture?

Right i. Add carbon dioxide gas
Right ii. Remove carbon monoxide gas
Left iii. Add CO
no change iv. Remove $C_{(s)}$ (assume this has a negligible effect on the available container volume)
Left v. Decrease the volume of the reaction container   So all pressures will increase
no change vi. Add a catalyst
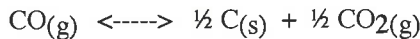**Right** vii. Increase the temperature
Left viii. Decrease temperature

$\boxed{K_p = 167}$

c. Find Kp of the above reaction at 1000 °C. $K_p = K_c(RT)^{\Delta n} = 1.598(.0821 \cdot 1273)^1 = 167.01$
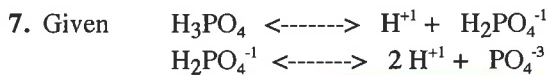
d. Find Kc of this reaction at 1000 °C: $CO_{(g)} \longleftrightarrow \frac{1}{2} C_{(s)} + \frac{1}{2} CO_{2(g)}$

This is the original rxn except reversed and cut in half. $K_c = \dfrac{1}{(1.598)^{1/2}} = \boxed{0.7911 = K_c}$

6. In i-viii, above, for which stresses/letters does Keq stay the same, and for which letters does it change?

It stays the same for i - vi . It changes in vii and viii
(Keq increases in vii and decreases in viii)

7. Given

$$H_3PO_4 \longleftrightarrow H^{+1} + H_2PO_4^{-1} \qquad Keq = 0.0075$$
$$H_2PO_4^{-1} \longleftrightarrow 2 H^{+1} + PO_4^{-3} \qquad Keq = 2.6 \times 10^{-20}$$

Add rxns: $H_3PO_4 \rightleftharpoons 3 H^{+1} + PO_4^{-3}$ $\qquad Keq = (.0075)(2.6 \times 10^{-20}) = 1.95 \times 10^{-22}$

Find the Keq for this reaction: $\qquad 3 H^{+1} + PO_4^{-3} \longleftrightarrow H_3PO_4$

this is the reverse of the "sum" rxn: $H_3PO_4 \rightleftharpoons 3 H^{+1} + PO_4^{-3}$

so $Keq = \left(\dfrac{1}{1.95 \times 10^{-22}}\right) = 5.128 \rightarrow \boxed{5.1 \times 10^{21}}$
$\times 10^{21}$

8. The Haber Process: $\qquad N_{2(g)} + 3 H_{2(g)} \longleftrightarrow 2 NH_{3(g)} \qquad \Delta H \text{ rxn} = -92 \text{ kJ}$

Temp(°C)	Kc
25	69300
300	9.6
400	0.501
500	0.058

a. What does it mean for a reaction to be at equilibrium? Discuss this in the context of this reaction.

At equilibrium, the forward rate of rxn is equal to the reverse rate of rxn. For example in the above reaction, the number of NH_3 molecules produced every second is equal to the number of NH_3 molecules consumed every second in the reverse rxn.

b. If 2.0 moles of each gas (nitrogen, hydrogen, and ammonia) are each placed into a 5.0 liter vessel at 300°C, which way will the reaction need to proceed in order to equilibrium?

$[N_2] = \dfrac{2.0 \text{ mole}}{5.0 \text{ L}} = 0.40 \text{ M}$

$([H_2]$ and $[NH_3]$ are also 0.40 M since also had 2.0 moles of those$)$

$Q = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{(.40)^2}{(.40)(.40)^3}$

$Q = 625$

$K = 9.6$ at 300 °C.

$Q < K$ so the rxn needs to proceed in the forward direction to reach eqm (or "to the right" or "toward products")

c. Same question as (b), except change the temp to 400 °C

At 400 °C, $K_c = 0.501$

and Q is still 6.25

$Q > K$ so the reaction must proceed in the reverse rxn to reach eqm (or "to the left" or "toward reactants")

8. Continued: $N_{2(g)} + 3 H_{2(g)} \longleftrightarrow 2 NH_{3(g)}$

d. Suppose that nitrogen, hydrogen, and ammonia are at equilibrium at 350 °C.
If some hydrogen gas is added (at 350°C) and equilibrium is reestablished, how will the new concentrations of N_2, H_2, and NH_3 compare to the concentrations before adding the extra hydrogen?

When H_2 is added, the rxn will shift right.

When this happens, more NH_3 will form → $[NH_3]$ will be larger than before.

and when it shifts right, that means some N_2 will be consumed → $[N_2]$ will be smaller than before.

Some of the H_2 will be consumed too, but the rxn won't consume all of the H_2 we added, since the rxn won't ever go 100% in either direction. so $[H_2]$ will be larger than it was before we added it.

9. 25 grams of lead (II) iodide (molar mass 461.01 amu) are placed into a flask containing 200 mL of water and the mixture is shaken until equilibrium is established at 25°C. At this temperature, PbI_2 has a Ksp of 1.39×10^{-8}.

a. Verify (show math) that some solid lead iodide will remain undissolved in the flask.

$$PbI_{2\,(s)} \rightleftarrows Pb^{+2}_{(aq)} + 2 I^{-1}_{(aq)}$$
$$\phantom{PbI_{2\,(s)} \rightleftarrows} x \qquad\qquad 2x$$
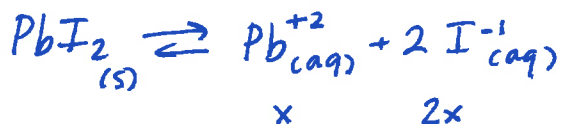
$$K_{sp} = x(2x)^2 = 1.39 \times 10^{-8}$$

$$x = .001515 \text{ M}$$

$$\left(.001515 \frac{\text{mol } PbI_2}{L}\right)(.200\,L)\left(\frac{461.01\,g}{1\,\text{mole}}\right) = 0.14\,g \; PbI_2 \text{ can dissolve}$$

$25\,g > 0.14\,g$ so not all the solid can dissolve; some solid remains undissolved.

OR you could calculate Qsp if the 25 g all did dissolve. you'd get $Q_{sp} = 0.0797$
$Q_{sp} > K_{sp}$ so solid (ppt) will be present.

b. How will the concentration of lead ion be affected (once equilibrium is reestablished) after the following changes are made? (increase, decrease, or no change)

no change 5.00 grams of lead iodide powder are added to the mixture. (The soln is already saturated so no more PbI_2 can dissolve)

decrease Solid sodium iodide is added to the mixture. *

**no change** an additional 200 mL of water are added. It will still be saturated once EQM reached

increase Solid silver nitrate is added to the mixture (The Ksp of AgI is 8.4×10^{-17} at 25°C) so some I^{-1} is consumed

increase The solution is heated to 30°C. (Lead iodide has a positive heat of solution value) as it forms AgI (solid)

increase Solid lead nitrate is added to the mixture. Rxn will shift left but not 100%

decrease Solid sodium sulfate is added to the mixture, and some lead sulfate precipitate forms.

* when NaI dissolves, $[I^-]$ will increase, so the "rxn" shifts left, using up $[Pb^{+2}]$
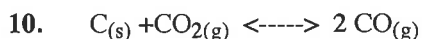
10. $C_{(s)} + CO_{2(g)} \longleftrightarrow 2\,CO_{(g)}$ $\qquad\qquad$ Kc = 1.598 at 1000°C

Suppose that 2.00 moles of carbon dioxide are added to a flask containing carbon powder and heated to 1000°C. The available volume inside the flask is 9.80 liters.

a. What will be the equilibrium concentrations of carbon dioxide and carbon monoxide, at 1000°C?

b. What will be the total pressure in the flask at equilibrium, at 1000°C?

(a)

$$[CO_2]_{original} = \frac{2.00 \text{ moles}}{9.80 \text{ L}} = 0.20408 \text{ M}$$

(b)

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2\,CO_{(g)}$$

I		0.20408	0
C		$-x$	$+2x$
E		$0.20408 - x$	$2x$

$$K_c = \frac{[CO]^2}{[CO_2]} = \frac{(2x)^2}{(0.20408-x)} = 1.598$$

$$4x^2 = 1.598(0.20408 - x) = 0.32612 - 1.598x$$

$$4x^2 + 1.598x - 0.32612 = 0$$

$$x = \frac{-1.598 \pm \sqrt{(1.598)^2 - 4(4)(-0.32612)}}{2(4)}$$

$$x = 0.148718 \quad \text{or} \quad \cancel{-0.5482}$$

x has to be positive since

$[CO] = 2x$ .. must be a positive molarity

$$[CO_2] = 0.20408 - x = 0.20408 - 0.148718 = 0.055362 \rightarrow \boxed{[CO_2] = 0.055\,M}$$

$$[CO] = 2x = 2(0.148718) = 0.2974 \rightarrow \boxed{[CO] = 0.297\,M}$$

check: $\dfrac{(0.2974)^2}{(0.055362)} = 1.598$ ✓

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$P = MRT$$

$$P_{CO_2} = (0.055362)(0.0821)(1273)$$

$$P_{CO_2} = 5.786 \text{ atm}$$

$$P_{CO} = (0.2974)(0.0821)(1273)$$
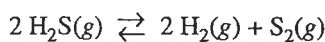
$$P_{CO} = 31.082 \text{ atm}$$

$$P_{TOTAL} = P_{CO_2} + P_{CO}$$

$$= 5.786 + 31.082$$

$$= 36.868$$

$$\boxed{P_{TOTAL} = 36.9 \text{ atm}}$$

From 2000 AP Test.
worth 10% of overall exam score
Time: about 18 minutes

$$2 H_2S(g) \rightleftarrows 2 H_2(g) + S_2(g)$$

11. 1. When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of $H_2S(g)$ is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and 3.72×10^{-2} mol of $S_2(g)$ is present at equilibrium.

(a) $K_c = \dfrac{[H_2]^2 [S_2]}{[H_2S]^2}$

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

(b) Calculate the equilibrium concentration, in mol L^{-1}, of the following gases in the container at 483 K.

  (i) $H_2(g)$

  (ii) $H_2S(g)$

(c) Calculate the value of the equilibrium constant, K_c, for the decomposition reaction at 483 K.

(d) Calculate the partial pressure of $S_2(g)$ in the container at equilibrium at 483 K.

(e) For the reaction $H_2(g) + \frac{1}{2} S_2(g) \rightleftarrows H_2S(g)$ at 483 K, calculate the value of the equilibrium constant, K_c.

(b)

Initial moles of H_2S = $(3.40 \text{ g})\left(\dfrac{1 \text{ mole}}{34.081 \text{ g}}\right)$ = 0.099763 moles H_2S

	$2 H_2S$	$\rightleftarrows$	$2 H_2$	+	S_2
I	0.099763		0		0
C	−2(.0372)		+2(.0372)		+.0372
E	.025363		.0744		.0372 mole (given)

$[H_2S]_{eqm}$ = $\dfrac{.025363 \text{ moles}}{1.25 \text{ L}}$ = 0.02029 → (b) $\boxed{[H_2S]_{eqm} = 0.0203 \text{ M}}$

$[H_2]_{eqm}$ = $\dfrac{0.0744 \text{ mole}}{1.25 \text{ L}}$ = 0.05952 → $\boxed{[H_2]_{eqm} = 0.0595 \text{ M}}$

(c) $[S_2]_{eqm}$ = $\dfrac{0.0372 \text{ mole}}{1.25 \text{ L}}$ = 0.02976 M

$K_c = \dfrac{[H_2]^2 [S_2]}{[H_2S]^2} = \dfrac{(.05952)^2 (.02976)}{(.02029)^2}$ = 0.25609

$\boxed{K_c = 0.256}$

(d) and (e) are on next page
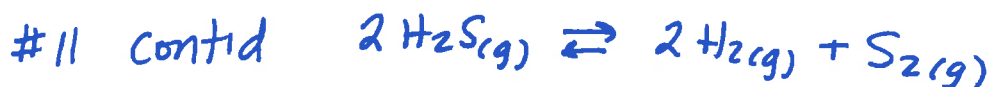
#11 cont'd $\quad 2\,H_2S_{(g)} \rightleftarrows 2\,H_{2(g)} + S_{2(g)}$

(d) Calculate the partial pressure of $S_2(g)$ in the container at equilibrium at 483 K.

(e) For the reaction $H_2(g) + \frac{1}{2}\,S_2(g) \rightleftarrows H_2S(g)$ at 483 K, calculate the value of the equilibrium constant, K_c.

(d) given: .0372 moles of S_2 were present
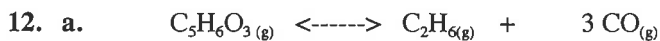at eqm in the 1.25 L flask at 483 K

$$P_{S2} = \frac{n_{S2}\,RT}{V} = \frac{(.0372\,mole)(.0821\,\frac{L\cdot atm}{mol\cdot k})(483\,k)}{1.25\,L}$$

$$\boxed{P_{S2} = 1.18\,atm}$$

(e) The rxn in (e) is what you get if you
cut the original equation in half,
and reverse the reactants and products.

$$K_c = \left(\frac{1}{(0.25609)^{1/2}}\right) = 1.98$$

$$\boxed{K_c = 1.98}$$

12. a. $C_5H_6O_{3\,(g)}$ <-----> $C_2H_{6(g)}$ + $3\,CO_{(g)}$

5.63 grams of $C_5H_6O_3$ gas are placed into an evacuated 2.50 Liter flask and heated to 200. °C.

i. Calculate the initial pressure of $C_5H_6O_3$ in the container, before any reaction occurs.
ii. The total pressure in the container gradually rose to an equilibrium value of 1.63 atm.
Calculate Kp and Kc for the reaction at 200.°C.

$\boxed{0.766\ atm}$

(i) $P = \dfrac{nRT}{V} = \dfrac{(5.63g)\left(\dfrac{1\,mole}{114.1006g}\right)\left(.0821\,\dfrac{L\cdot atm}{mol\cdot K}\right)(473K)}{2.50\ L} = 0.76646$

(ii) $C_5H_6O_3 \rightleftharpoons C_2H_6 + 3\,CO$
     $.76646-x \qquad\quad x \qquad\quad 3x$

$P_{TOTAL} = 1.63\ atm = (0.76646-x) + x + 3x$
   at
EQM $x = 0.28785\ atm$

$P_{C5H6O5} = .76646-x = 0.4786\ atm$
$P_{C2H6} = x = .28785\ atm$
$P_{CO} = 3x = 0.86355\ atm$

$K_p = \dfrac{P_{C2H6}\cdot P_{CO}^3}{P_{C5H6O3}}$

$K_p = \dfrac{(.28785)(.86355)^3}{(0.4786)}$

$K_p = 0.38731 \longrightarrow \boxed{K_p = 0.387}$

$K_c = \dfrac{K_p}{(RT)^{\Delta n}} = \dfrac{.38731}{(.0821\cdot473)^3} = \boxed{6.61\times10^{-6}}$
                                                                    K_c
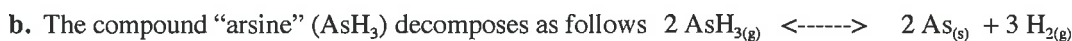
b. The compound "arsine" (AsH_3) decomposes as follows $2\,AsH_{3(g)}$ <-----> $2\,As_{(s)} + 3\,H_{2(g)}$
Some AsH_3 is added to an empty container so that it is present at 0.516 atm. After sitting for a couple of days, the
reaction mixture reached a final equilibrium pressure of 0.642 atm.   Calculate Kp for the reaction.

$2\,AsH_{3(g)} \rightleftharpoons 2\,As_{(s)} + 3\,H_{2(g)}$

I	.516	0	0
C	-2x	+2x	+3x
E	.516-2x	2x	3x

$P_{AsH3} = .516-2x = 0.264\ atm$
$P_{H2} = 3x = 0.378\ atm$

$K_p = \dfrac{(P_{H2})^3}{(P_{AsH3})^2} = \dfrac{(.378)^3}{(.264)^2}$

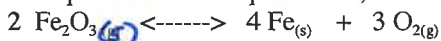$P_{TOTAL} = P_{AsH3} + P_{H2}$ (only include gases)
$0.642 = .516-2x +3x \qquad\qquad x = 0.126$

$K_p = 0.77493$
$\boxed{K_p = 0.775}$

c. Some solid ferric oxide is placed into an evacuated flask at high temperature, and the following reaction is allowed
to come to equilibrium. At equilibrium, the total gas pressure is 0.084 atm.   Calculate Kp.
     $2\,Fe_2O_{3(s)}$ <-----> $4\,Fe_{(s)} + 3\,O_{2(g)}$

$P_{TOTAL} = P_{O2}$ (since O_2 is the only gas present)

$P_{O2} = .084\ atm$

$K_p = (P_{O2})^3 = (.084)^3 = \boxed{0.00059}$
                                              K_p

13. Ag_2CrO_4 has a Ksp of 1.2×10^{-12}
Ag_2CO_3 has a Ksp of 8.1×10^{-12}
AgCl has a Ksp of 1.8×10^{-10}

A dilute solution of silver nitrate is slowly added to a solution containing CrO_4^{-2} ion dissolved at 0.20 M, CO_3^{-2} dissolved at 0.10 M, and Cl^{-1} dissolved at 0.010 M.

a. For each silver compound, calculate the maximum concentration of Ag^{+1} ion that can be present in solution without a precipitate forming. (neglect volume changes; assume that adding the silver nitrate solution won't significantly affect the 3 given molarities.)

Ag_2CrO_4 :

$$K_{sp} = [Ag^{+1}]^2 [CrO_4^{-2}]$$

$$1.2 \times 10^{-12} = [Ag^{+1}]^2 (0.20)$$

$$\boxed{[Ag^{+1}]_{max} = 0.0000024 \text{ M}}$$

$\alpha \ 2.4 \times 10^{-6}$ M

to prevent precipitation of Ag_2CrO_4 (solid)

(if $[Ag^{+1}]$ is larger than this, $Q_{sp} > K_{sp}$ so preciptation would occur)

Ag_2CO_3 :

$$K_{sp} = [Ag^{+1}]^2 [CO_3^{-2}]$$

$$8.1 \times 10^{-12} = [Ag^{+1}]^2 (0.10)$$

$$\boxed{[Ag^{+1}]_{max} = 9.0 \times 10^{-6} \text{ M}}$$
to prevent precipitation
of Ag_2CO_3 (solid)

AgCl :

$$K_{sp} = [Ag^{+1}][Cl^-]$$

$$1.8 \times 10^{-10} = [Ag^{+1}](0.010)$$

$$[Ag^+]_{max} = \boxed{1.8 \times 10^{-8} \text{ M to prevent formation of AgCl (solid)}}$$

**b.** Which silver compound will precipitate first, as the $AgNO_3$ solution is added?

AgCl. it has the lowest value of $[Ag^{+1}]_{max}$.

once $[Ag^{+1}]$ exceeds 1.8×10^{-8} M, AgCl (solid) will precipitate out.

14. Consider a beaker containing a saturated solution of CaF_2 in equilibrium with undissolved CaF_2 (s).
If solid $CaCl_2$ is added to this solution,
a. will the amount of solid CaF_2 at the bottom of the beaker increase, decrease, or remain the same?
b. will the concentration of Ca^{+2} ions in solution increase or decrease?
c. will the concentration of F^{-1} ions in solution increase or decrease?
(For a, b, and c, assume that the mixture immediately reestablishes equilibrium.)

$$CaF_{2(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F^{-1}_{(aq)}$$
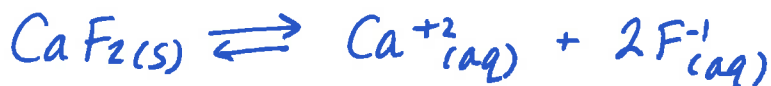
(a) if $CaCl_2$ is added, it will dissolve, so $[Ca^{+2}_{(aq)}]$
will increase. So the "rxn" above will shift **left**
to consume some of the $Ca^{+2}_{(aq)}$ that was added.

So More CaF_2(solid) will form;

the amt of $CaF_{2(s)}$ in the beaker will increase.

(b) $[Ca^{+2}]$ will increase (will be larger than it was before.)

when $Ca^{+2}_{(aq)}$ was added, the rxn shifted left to
consume some of the $Ca^{+2}_{(aq)}$, but not all of it.

(c) $[F^-]$ will decrease. (will be less than it was before.)

when the rxn shifts left, some of the $[F^-_{(aq)}]$
is consumed.

If numbers help, K_{sp} of $CaF_2 = 3.9 \times 10^{-11}$

So the original solution, $[Ca^{+2}] = .00021 M$ and $[F^-] = .00042 M$.
Ca^{+2} and F^{-1} were present in a 1:2 ratio.

but since we added Ca^{+2} ion and **not** F^{-1} ion when
we added $CaCl_2$, we now have More than a 1:2 ratio:

$[Ca^{+2}_{(aq)}]$ will now be More than .00021 M

and $[F^-]$ will now be less than .00042 M.

15. Consider a beaker containing a saturated solution of PbI_2 in equilibrium with undissolved PbI_2 (s).
If solid KI is added to this solution,
a. will the amount of solid PbI_2 at the bottom of the beaker increase, decrease, or remain the same?
b. will the concentration of Pb^{+2} ions in solution increase or decrease?
c. will the concentration of I^{-1} ions in solution increase or decrease?
(For a, b, and c, assume that the mixture immediately reestablishes equilibrium.)

$$PbI_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2I^{-1}_{(aq)}$$
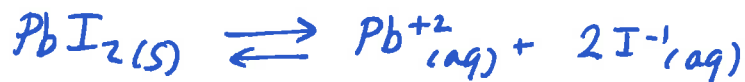
(a) if KI is added, it will dissolve, so $[I^-_{(aq)}]$ increases.
So the rxn will shift left, so some PbI_2 solid will form.

> So the amt of PbI_2 (solid) in the beaker increases.

(b) $[Pb^{+2}_{(aq)}]$ will decrease.
when the rxn shifts left, some $Pb^{+2}_{(aq)}$ will be
consumed as it turns into solid PbI_2.
↑↗
(becomes part of)

(c) $[I^-]$ will increase.
we added $I^-_{(aq)}$ to the solution.
the rxn will shift left to consume some of
the $I^{-1}_{(aq)}$, but not all of it.

(At equilibrium originally,
there were twice as many $I^-_{(aq)}$ as $Pb^{+2}_{(aq)}$
now there are more than twice as many,
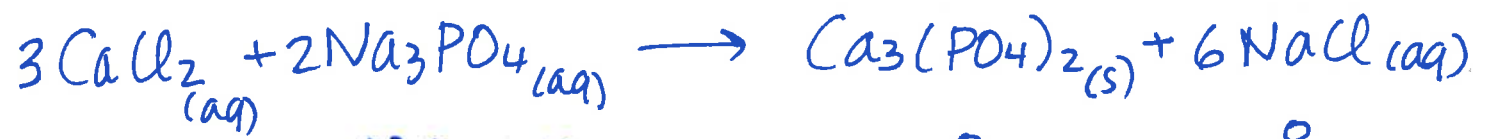so $[I^-]$ is more than it was,
and $[Pb^{+2}]$ is less than it was)

a) $(.100L)(.80 \frac{mol}{L}) = 0.080$ mole $CaCl_2$ # 16a

$(.150 L)(.20 \text{ mol/L}) = .030$ moles Na_3PO_4

$$3 CaCl_{2(aq)} + 2 Na_3 PO_4{}_{(aq)} \longrightarrow Ca_3(PO_4)_{2(s)} + 6 NaCl_{(aq)}$$
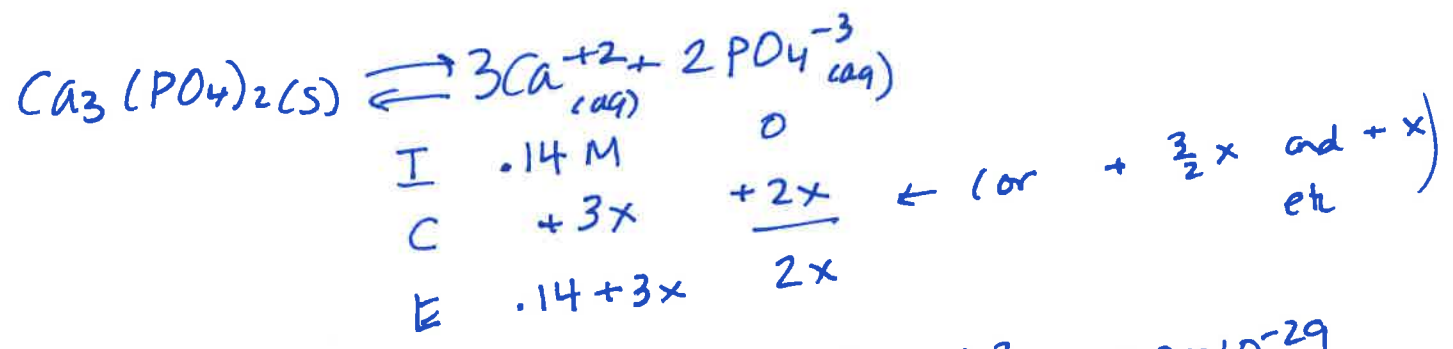
I .080 moles   .030 moles   0   0

C -.045   -.030   +.015

F .035   0   .015 moles

$(.015 \text{ moles})(310.183 \frac{1}{mole}) = 4.7 g$ precipitate

$[Ca^{+2}] = \dfrac{.035 \text{ mole}}{(.100 L + .150 L)} = $ 0.14 M Ca^{+2}

$[PO_4{}^{-3}] = ??$ need to do K_{sp}

$$Ca_3(PO_4)_2{}_{(s)} \rightleftharpoons 3 Ca^{+2}{}_{(aq)} + 2 PO_4{}^{-3}{}_{(aq)}$$

I   .14 M   0

C   +3x   +2x   ← (or   + $\frac{3}{2}$x and + x) etc

E   .14 + 3x   2x

$K_{sp} = [Ca^{+2}]^3 [PO_4{}^{-3}]^2 = (.14 + 3x)^3 (2x)^2 = 2.0 \times 10^{-29}$
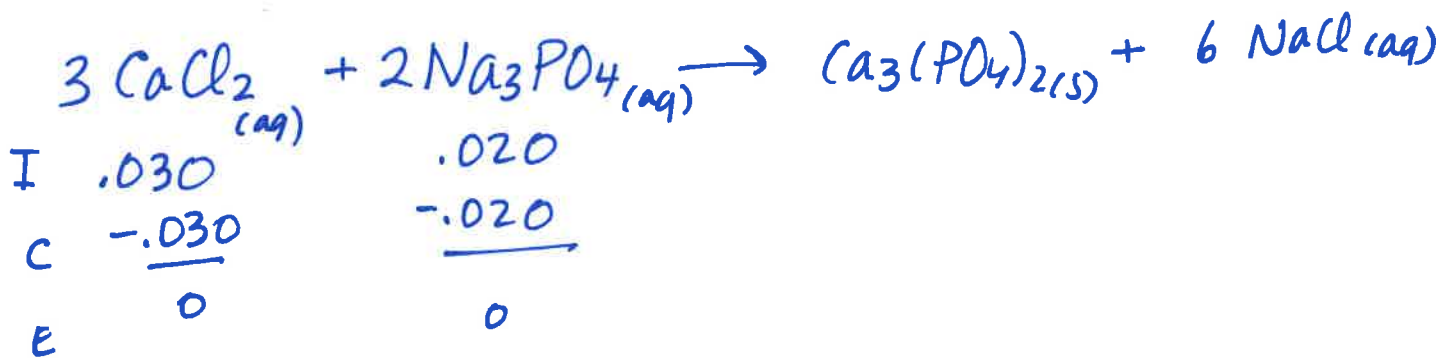
↑ assume 3x ≪ .14

$(.14)^3 (2x)^2 = 2.0 \times 10^{-29}$

$x = 4.2687 \times 10^{-14}$

$[PO_4{}^{-3}] = 2x = 8.5 \times 10^{-14} M$

b) $(.100L)(.30m) = .030$ moles $CaCl_2$

$(.200L)(.10m) = .020$ moles Na_3PO_4

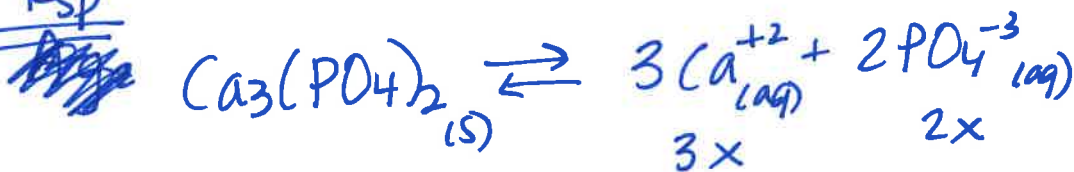$$3\ CaCl_{2\ (aq)} + 2\ Na_3PO_{4\ (aq)} \longrightarrow Ca_3(PO_4)_{2\ (s)} + 6\ NaCl_{(aq)}$$

I	.030	.020
C	−.030	−.020
E	0	0

Both went to zero,
so we'll need to solve for
both of the molarities using a K_{sp}

Do K_{sp}

$$Ca_3(PO_4)_{2\ (s)} \rightleftharpoons 3\ Ca^{+2}_{(aq)} + 2\ PO_4^{-3}{}_{(aq)}$$

$3x \qquad 2x$

or x and $\frac{2}{3}x$, etc.

$$[Ca^{+2}]^3\ [PO_4^{-3}]^2 = K_{sp}$$

$$(3x)^3 (2x)^2 = 2.0 \times 10^{-29}$$

$$108\ x^5 = 2.0 \times 10^{-29}$$

$$x = 7.137 \times 10^{-7}\ M$$

$$[Ca^{+2}] = 3x = 2.1 \times 10^{-6}\ M$$

$$[PO_4^{-3}] = 2x = 1.4 \times 10^{-6}\ M$$

c) $(.200 L)(.40 \frac{mole}{L}) = .080$ moles $CaCl_2$

$(.350 L)(.20 \frac{mole}{L}) = .070$ moles Na_3PO_4

$$3 CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_{2(S)} + 6 NaCl_{(aq)}$$

I	.080	.070
C	−.080	−(.080)($\frac{2}{3}$)
	0	.0166 moles

$[PO_4^{-3}] = \dfrac{.0166 \text{ moles}}{(.200 + .350) L} = 0.0303$ M $\boxed{[PO_4^{-3}] = .030 \text{ M}}$

__now do K_{sp} to find $[Ca^{+2}]$__

$$Ca_3(PO_4)_{2(S)} \rightleftharpoons 3 Ca^{+2}_{(aq)} + 2 PO_4^{-3}_{(aq)}$$

I	0	.030
C	+x	+$\frac{2}{3}$x
E	x	.030 + $\frac{2}{3}$x

← or 3x and 2x etc

$K_{sp} = x^3 (.030 + \frac{2}{3}x)^2 = 2.0 \times 10^{-29}$

assume $\frac{2}{3}$x ≪ .030

$x^3 (.030)^2 = 2.0 \times 10^{-29}$

$x = \boxed{2.8 \times 10^{-9} \text{ M} = [Ca^{+2}]}$

Equilibrium MC practice!

$$2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g)$$
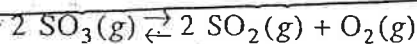
41. After the equilibrium represented above is established, some pure $O_2(g)$ is injected into the reaction vessel at constant temperature. After equilibrium is reestablished, which of the following has a lower value compared to its value at the original equilibrium?

will shift left
so SO_2 will
turn into SO_3
(some SO_2 will
be consumed)

(A) K_{eq} for the reaction

(B) The total pressure in the reaction vessel

(C) The amount of $SO_3(g)$ in the reaction vessel

(D) The amount of $O_2(g)$ in the reaction vessel

(E) The amount of $SO_2(g)$ in the reaction vessel

$$H_2(g) + Br_2(g) \rightleftharpoons 2 HBr(g)$$
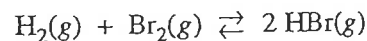
42. At a certain temperature, the value of the equilibrium constant, K, for the reaction represented above is 2.0×10^5. What is the value of K for the reverse reaction at the same temperature?

(A) -2.0×10^{-5}

(B) 5.0×10^{-6}

(C) 2.0×10^{-5}

(D) 5.0×10^{-5}

(E) 5.0×10^{-4}

$$\frac{1}{2.0 \times 10^5} =$$

$$\frac{1}{2} \cdot \frac{1}{10^5} = 0.5 \times 10^{-5}$$

$$= 5 \times 10^{-6}$$

$$Ag_2CrO_4 \rightleftharpoons 2 Ag^{+1} + CrO_4^{-2}$$

67. What is the molar solubility in water of Ag_2CrO_4?

(The K_{sp} for Ag_2CrO_4 is 8×10^{-12}.)

(A) $8 \times 10^{-12} M$

(B) $2 \times 10^{-12} M$

(C) $\sqrt{4 \times 10^{-12}} M$

(D) $\sqrt[3]{4 \times 10^{-12}} M$

(E) $\sqrt[3]{2 \times 10^{-12}} M$

$$(2x)^2(x) = 8 \times 10^{-12}$$

$$4x^3 = 8 \times 10^{-12}$$

$$x = (2 \times 10^{-12})^{1/3}$$

---

75. In a saturated solution of $Zn(OH)_2$ at $25°C$, the value of $[OH^-]$ is $2.0 \times 10^{-6} M$. What is the value of the solubility-product constant, K_{sp}, for $Zn(OH)_2$ at $25°C$?

(A) 4.0×10^{-18}

(B) 8.0×10^{-18}

(C) 1.6×10^{-17}

(D) 4.0×10^{-12}

(E) 2.0×10^{-6}

$$[Zn^{+2}] = \frac{[OH^-]}{2} = 1.0 \times 10^{-6}$$

$$(1.0 \times 10^{-6})(2.0 \times 10^{-6})^2$$

$$= 4 \times 10^{-18}$$

---

21. Which of the systems in equilibrium represented below will exhibit a shift to the left (toward reactants) when the pressure on the system is increased by reducing the volume of the system? (Assume that temperature is constant.)

(A) $2 Mg(s) + O_2(g) \rightleftharpoons 2 MgO(s)$ $\Delta n = -1$

(B) $SF_4(g) + F_2(g) \rightleftharpoons SF_6(g)$ $\Delta n = -1$

(C) $H_2(g) + Br_2(g) \rightleftharpoons 2 HBr(g)$ $\Delta n = 0$

(D) $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ $\Delta n = -2$

(E) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ $\Delta n = +1$

fewer moles gas on left

---

36. Which of the following changes to a reaction system in equilibrium would affect the value of the equilibrium constant, K_{eq}, for the reaction? (Assume in each case that all other conditions are held constant.)

(A) Adding more of the reactants to the system

(B) Adding a catalyst for the reaction to the system

(C) Increasing the temperature of the system

(D) Increasing the pressure on the system

(E) Removing some of the reaction products from the system

you can only change K_{eq} by changing temperature.

Questions 29-33 refer to the following.

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$$
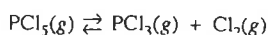
$PCl_5(g)$ decomposes into $PCl_3(g)$ and $Cl_2(g)$ according to the equation above. A pure sample of $PCl_5(g)$ is placed in a rigid, evacuated 1.00 L container. The initial pressure of the $PCl_5(g)$ is 1.00 atm. The temperature is held constant until the $PCl_5(g)$ reaches equilibrium with its decomposition products. The figures below show the initial and equilibrium conditions of the system.
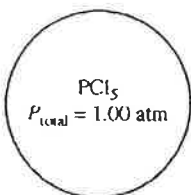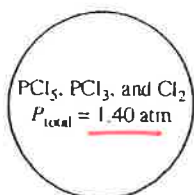
PCl₅
P_{total} = 1.00 atm

PCl₅, PCl₃, and Cl₂
P_{total} = 1.40 atm

Figure 1: Initial   Figure 2: Equilibrium

29. Which of the following is the most likely cause for the increase in pressure observed in the container as the reaction reaches equilibrium?

(A) A decrease in the strength of intermolecular attractions among molecules in the flask
(B) An increase in the strength of intermolecular attractions among molecules in the flask
(C) An increase in the number of molecules, which increases the frequency of collisions with the walls of the container
(D) An increase in the speed of the molecules that then collide with the walls of the container with greater force

gaseous

1 mole PCl_5 → 2 mole products
number of gas molecules increases
so pressure increases.

30. As the reaction progresses toward equilibrium, the rate of the forward reaction

(A) increases until it becomes the same as the reverse reaction rate at equilibrium
(B) stays constant before and after equilibrium is reached
(C) decreases to become a constant nonzero rate at equilibrium
(D) decreases to become zero at equilibrium

the underlined part is true, but the fwd rate will decrease as the PCl_5 is consumed

31. If the decomposition reaction were to go to completion, the total pressure in the container would be

(A) 1.4 atm
(B) 2.0 atm
(C) 2.8 atm
(D) 3.0 atm

1 mole PCl_5 → 2 moles gas
moles of gas would double, so pressure would double

$$2(1.00 \, atm) = 2.00 \, atm$$

32. Which of the following statements about K_p, the equilibrium constant for the reaction, is correct?

(A) $K_p > 1$
(B) $K_p < 1$
(C) $K_p = 1$
(D) It cannot be determined whether $K_p > 1$, $K_p < 1$, or $K_p = 1$ without additional information.

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$
$$1.00-x \qquad x \qquad x$$
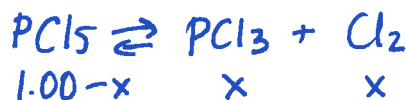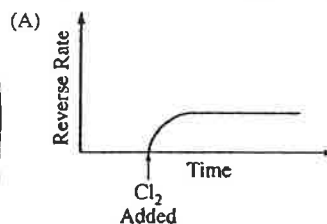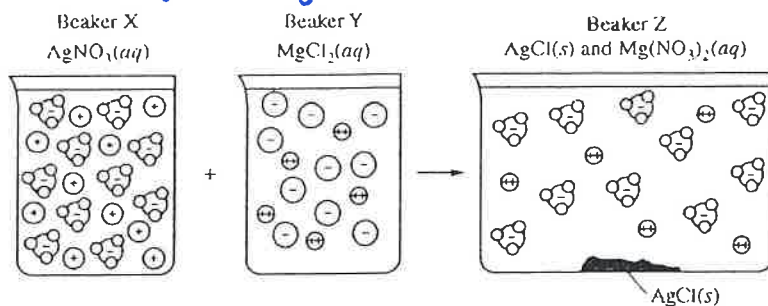
$$K_p = \frac{x^2}{1.00-x}$$

$$P_{TOTAL} = 1.40 \, atm = 1.00-x + x + x$$
e EQM
$$x = 0.40 \, atm$$

$$K_p = \frac{(.40)^2}{(60)} < 1$$

33. Additional $Cl_2(g)$ is injected into the system at equilibrium. Which of the following graphs best shows the rate of the reverse reaction as a function of time? (Assume that the time for injection and mixing of the additional $Cl_2(g)$ is negligible.)

(A)
Reverse Rate / Time
Cl₂ Added

(B)
Reverse Rate / Time
Cl₂ Added
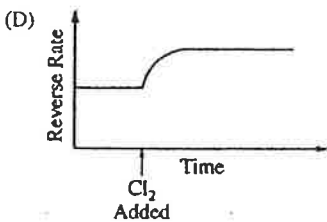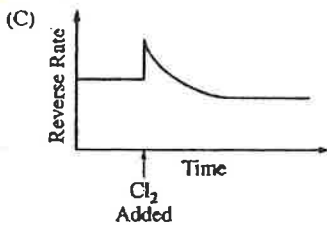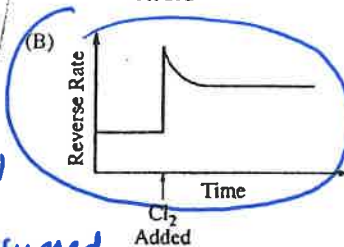
← the new rate will be higher (both the fwd and reverse rates will increase, since more molecules are present in the same volume.

(C)
Reverse Rate / Time
Cl₂ Added

(D)
Reverse Rate / Time
Cl₂ Added

$$2\,AgNO_{3(aq)} + MgCl_{2(aq)} \rightarrow 2\,AgCl_{(s)} + Mg(NO_3)_{2(aq)}$$

Beaker X	Beaker Y	Beaker Z
$AgNO_3(aq)$	$MgCl_2(aq)$	$AgCl(s)$ and $Mg(NO_3)_2(aq)$

AgCl(s)

← only Mg^{+2} and NO_3^{-1} ions are left in solution, so ≈ all the Ag^{+1} and Cl^{-1} went into ppt.

Since there is no excess Ag^{+1} or Cl^-, they must have been mixed in a 2:1 ratio

56. Beaker X and beaker Y each contain 1.0 L of solution, as shown above. A student combines the solutions by pouring them into a larger, previously empty beaker Z and observes the formation of a white precipitate. Assuming that volumes are additive, which of the following sets of solutions could be represented by the diagram above?

|	Beaker X	Beaker Y	Beaker Z
(A)	2.0 M $AgNO_3$	2.0 M $MgCl_2$	4.0 M $Mg(NO_3)_2$ and $AgCl(s)$
(B)	2.0 M $AgNO_3$	2.0 M $MgCl_2$	2.0 M $Mg(NO_3)_2$ and $AgCl(s)$
(C)	2.0 M $AgNO_3$	1.0 M $MgCl_2$	1.0 M $Mg(NO_3)_2$ and $AgCl(s)$
(D)	2.0 M $AgNO_3$	1.0 M $MgCl_2$	0.50 M $Mg(NO_3)_2$ and $AgCl(s)$

the $[Mg(NO_3)_2]$ will dilute to half of its original concentration. none is consumed, but the 1.00 L volume doubled to 2.0 L when mixed.

both c and d had the 2:1 (stoichiometric) ratio of $AgNO_3$ to $MgCl_2$

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$
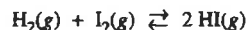
7. At 450°C, 2.0 moles each of $H_2(g)$, $I_2(g)$, and HI(g) are combined in a 1.0 L rigid container. The value of K_c at 450°C is 50. Which of the following will occur as the system moves toward equilibrium?

(A) More $H_2(g)$ and $I_2(g)$ will form.
(B) More HI(g) will form.
(C) The total pressure will decrease.
(D) No net reaction will occur, because the number of molecules is the same on both sides of the equation.

) so all are 2.0 M

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2.0)^2}{(2.0)(2.0)} = 1$$

$Q_c < K_c$ so the rxn must shift right, so more HI will form.

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

60. $COCl_2(g)$ decomposes according to the equation above. When pure $COCl_2(g)$ is injected into a rigid, previously evacuated flask at 690 K, the pressure in the flask is initially 1.0 atm. After the reaction reaches equilibrium at 690 K, the total pressure in the flask is 1.2 atm. What is the value of K_p for the reaction at 690 K?
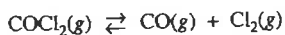
(A) 0.040
(B) 0.050
(C) 0.80
(D) 1.0

$$COCl_2 \rightleftharpoons CO + Cl_2$$
$$1.0-x \qquad x \qquad x$$
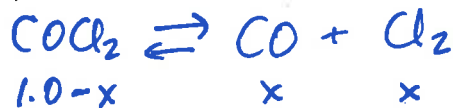
$$K_p = \frac{x^2}{(1.0-x)} = \frac{(0.2)^2}{(1.0-0.2)} = \frac{(0.2)^2}{(0.8)} = 0.05$$

$$P_{Total} = (1.0-x) + x + x = 1.2\,atm$$
$$x = 0.2$$