

# CHEM 116 – Honors and Majors General and Analytical Chemistry I

2 Exams, 6 Quizzes, 7 Labs, 9 Weeks HWK - 595 points (1245 in course)

EII: AVE = 108 (72%) Range: 49 - 148

EI: AVE = 87 (58%)

## Class Averages

EXAM	195	65%
QZ	37	61%
LAB	118	84%
HWK	73	77%

Q1 6.0 Q5 6.5

Q3 4.2 Q6 6.1

Q4 7.8 Q7 6.1

E1 19 E5 16 L5 18

E2 17 E7 12\*\*\*

L3 18 SP 17

## Course Grade Estimate

A 75%

B 65% **class average 72.1%**

C 50% **GPA 3.1**

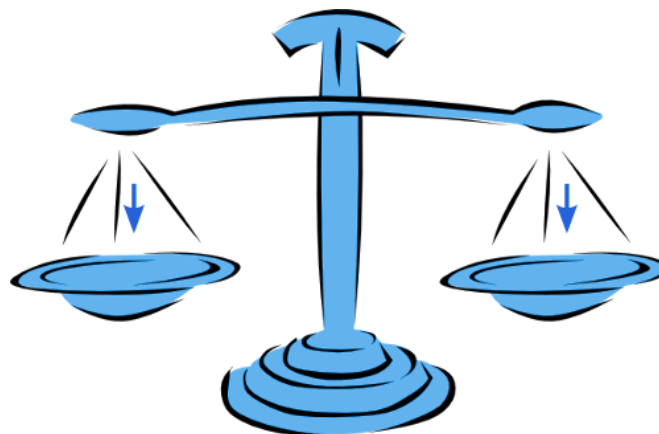
D 40% **7+**

# Chemical Equilibrium

Z Ch 6

"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."

Henri Louis Le Châtelier, 1888



**6.4, 6.9 The Concept of Activity and Equilibria  
Involving Real Gases (See Harris 8-2)**

**6.5 Heterogeneous Equilibria**

**6.6 Applications of the Equilibrium Constant**

**6.7 Solving Equilibrium Problems**

**Please check your  
grades on Blackboard  
– today is drop date –  
talk with me FIRST!**

# Arrows of Chemistry – Different Equilibrium Constants

reaction



resonance



equilibrium



## equilibrium constant, $K$

$K$  - concentration ( $K_c$ ) Zumdahl/Harris

$K_p$  - pressure

$K_a$  - ionization of weak acid

$K_b$  - ionization of weak base

$K_{sp}$  - dissolution of slightly soluble salt

# The Equilibrium Constant

## Law of Mass Action

For  $aA + bB \rightleftharpoons cC + dD$  the equilibrium constant  $K$  is

$$K = \frac{\mathcal{A}_C^c \mathcal{A}_D^d}{\mathcal{A}_A^a \mathcal{A}_B^b}$$

where  $\mathcal{A}_A^a$  is the activity (Zumdahl p. 178, 194; Harris p. 164) of species A raised to its stoichiometric coefficient a. Expression for activity depends upon how composition is expressed.

molarity ( $K$ ),  $\mathcal{A}_A = \gamma_A[A] / [\text{ref}]$

[ref] = 1 M

$\mathcal{A} = 1$  for pure liquids, solids

pressure ( $K_P$ ),  $\mathcal{A}_A = \gamma_A P_A / P_{\text{ref}}$

$P_{\text{ref}} = 1 \text{ atm (bar)}$

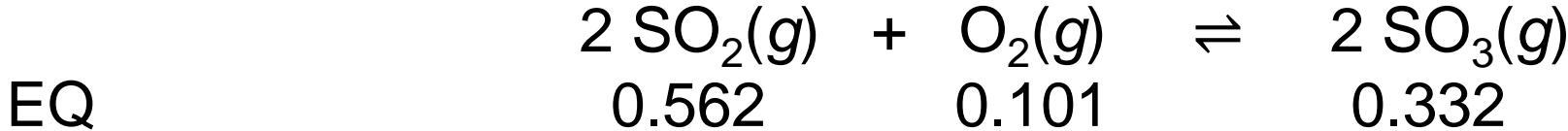
Reference composition is usually 1, insures equilibrium constant is unitless

$\gamma$  is the activity coefficient, where deviations from ideal gas or solution found

$\gamma = 1$  ideal gas, ideal solution (obeys Raoult's law)

# The Equilibrium Constant

**EX 1.** At 1000 K the equilibrium gas mixture contains 0.562 atm SO<sub>2</sub>, 0.101 atm O<sub>2</sub>, and 0.332 atm SO<sub>3</sub>. What is  $K_p$  ?

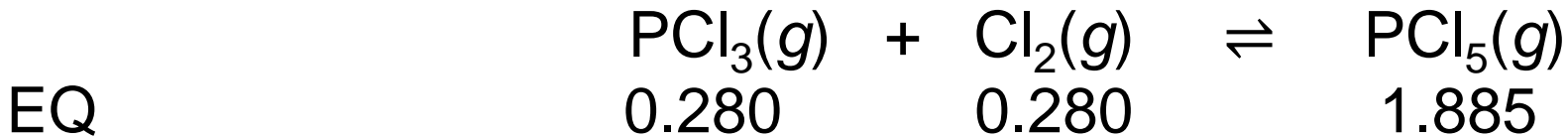


$$K_p = \frac{\mathcal{A}_{\text{SO}_3}^2}{\mathcal{A}_{\text{SO}_2}^2 \mathcal{A}_{\text{O}_2}}$$

$$= \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = (0.332)^2 / (0.562)^2(0.101) = \mathbf{3.46}$$

# The Equilibrium Constant – $K$ and $K_p$

**EX 2.** At 250°C the equilibrium concentrations are  $[\text{PCl}_3] = [\text{Cl}_2] = 0.280 \text{ M}$  and  $[\text{PCl}_5] = 1.885 \text{ M}$  for



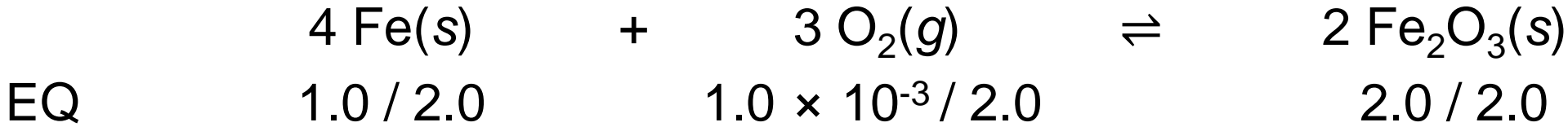
$$K = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = (1.885) / (0.280)^2 = \mathbf{24.0} \quad PV = nRT \Rightarrow P = (n/V)RT = MRT$$

$$= \frac{P_{\text{PCl}_5} / RT}{(P_{\text{PCl}_3} / RT) (P_{\text{Cl}_2} / RT)} = K_p / RT = 24.0 / (0.082)(250+273) = 0.056$$

**$K = K_p (RT)^{\Delta n}$       where  $\Delta n = n_{\text{prod}} - n_{\text{react}}$**

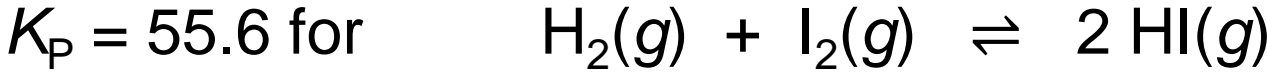
# Heterogeneous Equilibria

**EX 4.** What is the value of  $K$  if an equilibrium mixture contains 1.0 mol Fe,  $1.0 \times 10^{-3}$  mol  $O_2$ , and 2.0 mol  $Fe_2O_3(s)$  in a 2.0-L container?

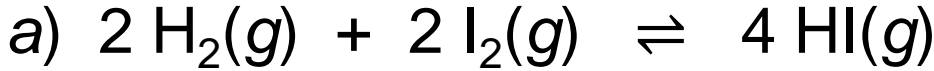


$$\begin{aligned}
 K &= 1 / [O_2]^3 = 1 / (0.50 \times 10^{-3})^3 \\
 &= \mathbf{8.0 \times 10^9}
 \end{aligned}$$

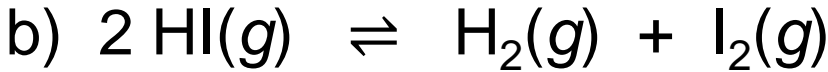
# Relationship of $K$ 's of Related Equilibria



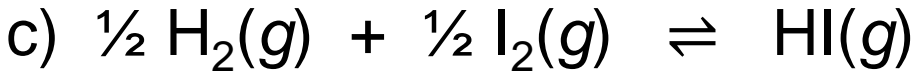
**EX 5.** For the above reaction ( $K_p = P_{\text{HI}}^2 / P_{\text{H}_2} P_{\text{I}_2}$ ) what is  $K_p$  for:



multiply all coefficients by  $n \Rightarrow K_{\text{new}} = K_o^n$



reverse reaction (multiply by -1)  $\Rightarrow K_{\text{new}} = K_o^{-1} = 1 / K_o$

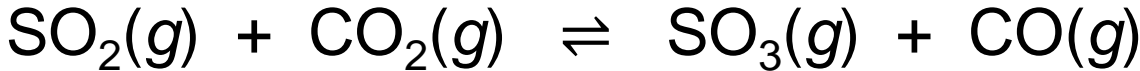


multiply all coefficients by  $n = \frac{1}{2} \Rightarrow K_{\text{new}} = K_o^{1/2} = \sqrt{K_o}$

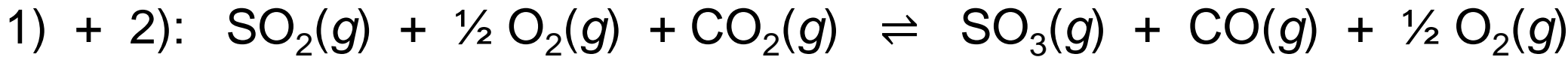
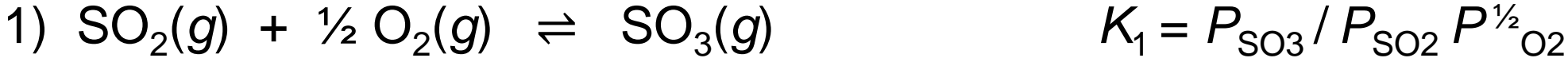


# Relationship of $K$ 's of Simultaneous Equilibria

**EX 6.** Find the equilibrium constant for



if you know the equilibrium constants for the following reactions:



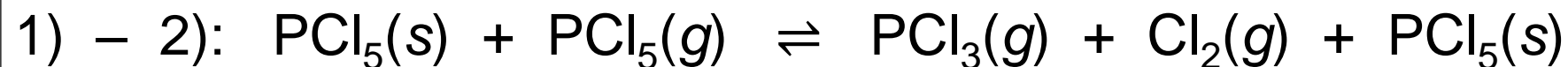
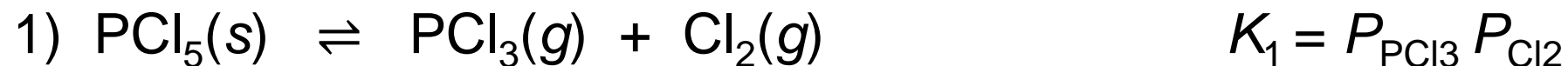
$$K = (P_{\text{SO}_3} / P_{\text{SO}_2} P^{1/2}_{\text{O}_2}) (P_{\text{CO}} P^{1/2}_{\text{O}_2} / P_{\text{CO}_2}) = K_1 K_2 \quad \text{add reactions, multiply } K\text{'s}$$

# Relationship of $K$ 's of Simultaneous Equilibria

EX 6. Find the equilibrium constant for

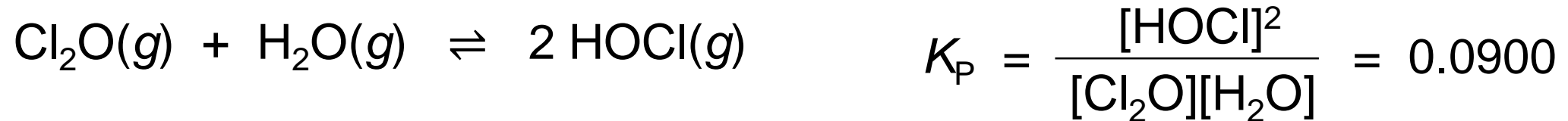


if you know the equilibrium constants for the following reactions:



$$(P_{\text{PCl}_3} P_{\text{Cl}_2}) / P_{\text{PCl}_5} = K_1 / K_2 \quad \text{subtract reactions, divide } K\text{'s}$$

# Interpreting Value of the Equilibrium Constant



$K > 1 \Rightarrow$  product-favored;  $K \gg 1 \Rightarrow$  reaction essentially complete

$K < 1 \Rightarrow$  reactant-favored;  $K \ll 1 \Rightarrow$  essentially no reaction

# Product Quotient, $Q$ (with initial concentrations, pressures)

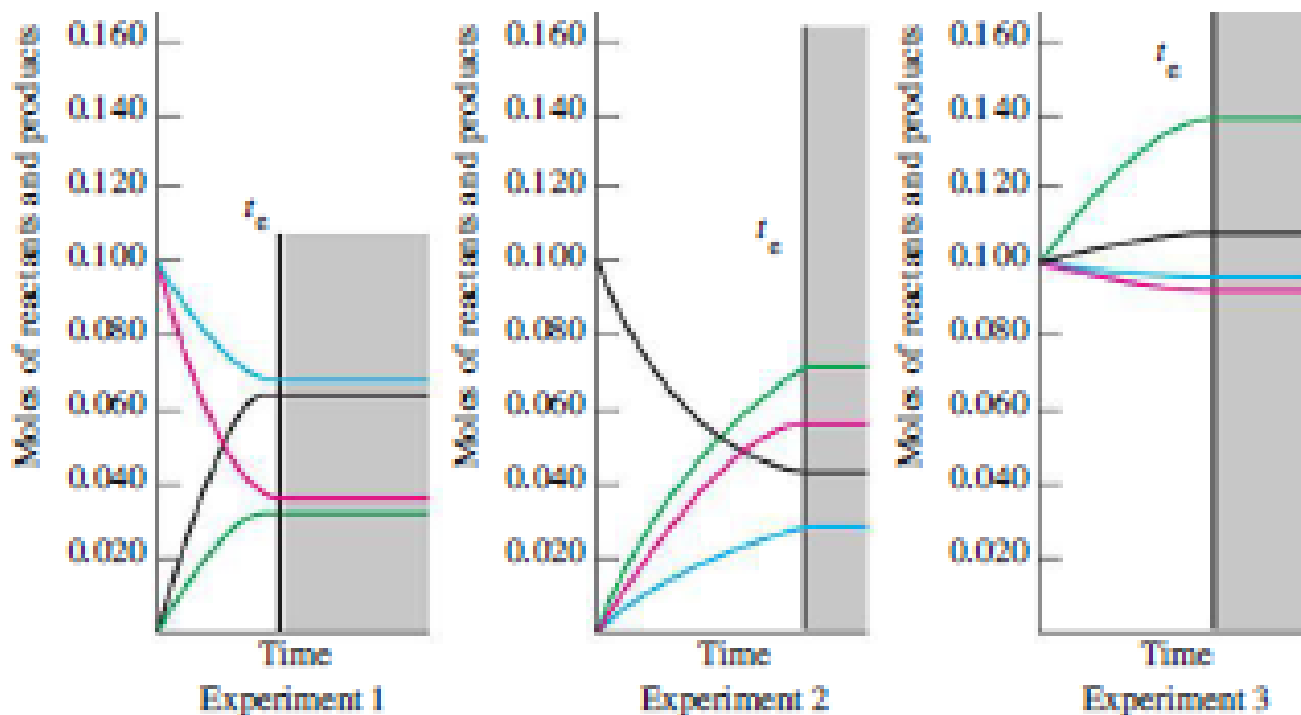
Three Approaches to Equilibrium in the Reaction



$$\frac{[\text{Cu}^{+}]^2 [\text{Sn}^{4+}]}{[\text{Cu}^{2+}]^2 [\text{Sn}^{2+}]}$$

	$\text{Cu}^{2+}(\text{aq})$	$\text{Sn}^{2+}(\text{aq})$	$\text{Cu}^{+}(\text{aq})$	$\text{Sn}^{4+}(\text{aq})$	$Q$	$K$
<b>Experiment 1</b>						
Initial amounts, mol/L	0.100	0.100	0.000	0.000	0	
Equilibrium amounts, mol/L	0.0360	0.0680	0.0640	0.0320		1.49
<b>Experiment 2</b>						
Initial amounts, mol/L	0.000	0.000	0.100	0.100	$\infty$	
Equilibrium amounts, mol/L	0.0567	0.0283	0.0433	0.0717		1.48
<b>Experiment 3</b>						
Initial amounts, mol/L	0.100	0.100	0.100	0.100	1	
Equilibrium amounts, mol/L	0.0922	0.0961	0.1078	0.1039		1.48

# Product Quotient, Q



$t_e$  = time for equilibrium to be reached

— mol  $\text{Cu}^{2+}$   
— mol  $\text{Sn}^{2+}$       reactants

— mol  $\text{Cu}^{+}$   
— mol  $\text{Sn}^{4+}$       products

In Exp 2 green line for  $[\text{Sn}^{4+}]$  should start at 0.1 M.

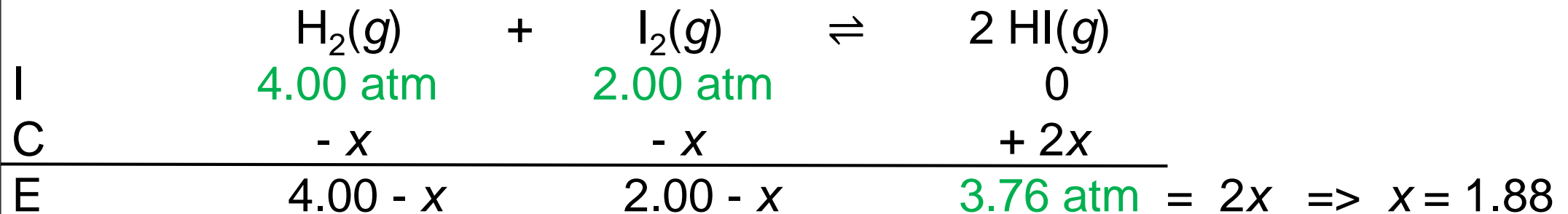
Exp	Q	K
1	0	1.49
2	$\infty$	1.48
3	1	1.48

$$\frac{[\text{Cu}^{+}]^2 [\text{Sn}^{4+}]}{[\text{Cu}^{2+}]^2 [\text{Sn}^{2+}]}$$

# Solving Equilibrium Problems

Find  $K$  given initial partial pressures and one equilibrium partial pressure.

EX 8. 4.00 atm of  $\text{H}_2(\text{g})$  and 2.00 atm of  $\text{I}_2(\text{g})$  are mixed and allowed to react. When equilibrium is reached 3.76 atm of  $\text{HI}(\text{g})$  is formed. What is  $K_p$  for the reaction?

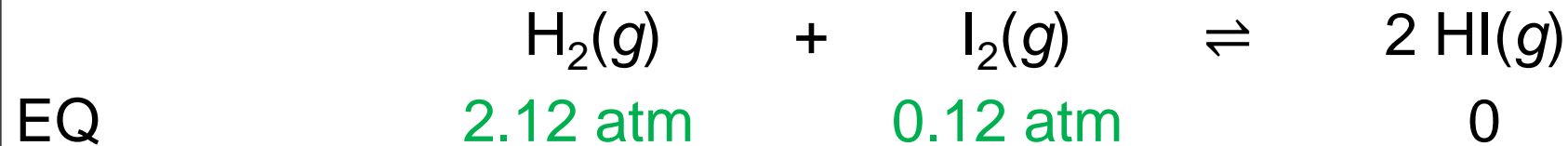


$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} = \frac{(1.88)^2}{(4.00-1.88)(2.00-1.88)} = 55.6$$

# Solving Equilibrium Problems

Given  $K$  and all equilibrium partial pressures but one, find missing pressure.

EX 9. At 425°C  $K_p = 55.6$  for the following reaction. If  $P_{\text{H}_2} = 2.12 \text{ atm}$  and  $P_{\text{I}_2} = 0.12 \text{ atm}$  at 425°C what is the equilibrium partial pressure of HI?

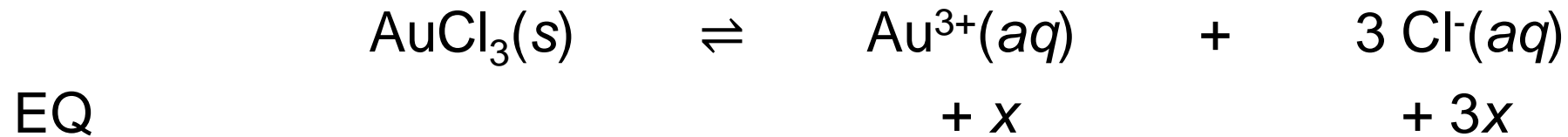


$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}} \Rightarrow P_{\text{HI}} = \sqrt{(K_p P_{\text{H}_2} P_{\text{I}_2})} = \sqrt{55.6 (2.12)(0.12)}$$
$$= 3.76 \text{ atm}$$

# Solving Equilibrium Problems

Given  $K_{sp}$  for dissolution of a solid, find ion concentrations.

EX 11. What are the equilibrium concentration of the ions at 25°C if  $K_{sp} = 3.2 \times 10^{-25}$ ?



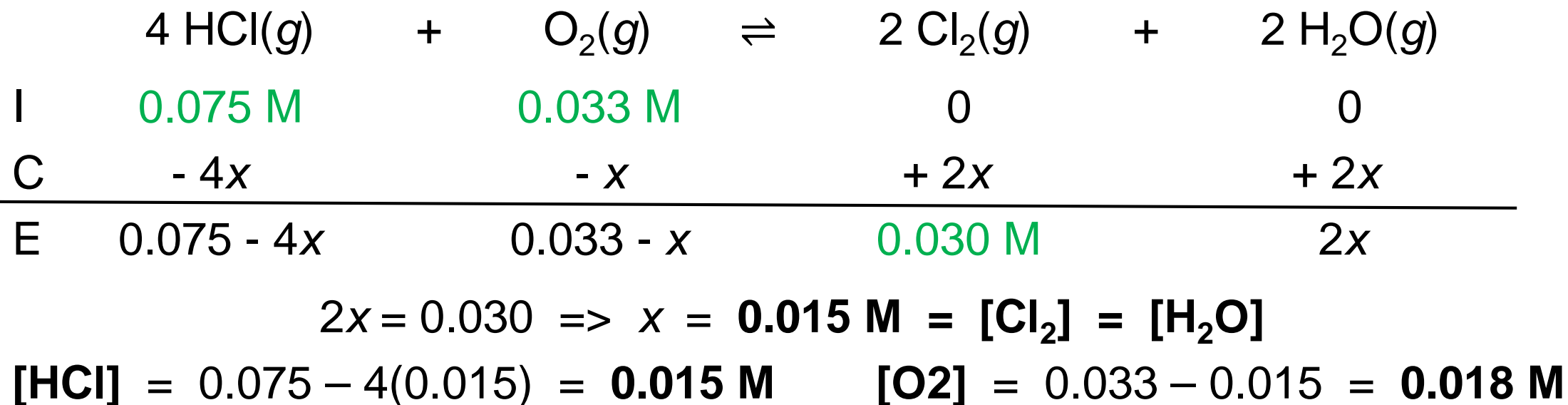
$$\begin{aligned} K_{sp} &= x(3x)^3 = 27x^4 \Rightarrow x = (K_{sp}/27)^{1/4} \\ &= [(3.2 \times 10^{-25})/27]^{1/4} \\ &= 3.3 \times 10^{-7} = [\text{Au}^{3+}] \\ &9.9 \times 10^{-7} = [\text{Cl}^-] \end{aligned}$$



# Solving Equilibrium Problems

Given all initial concentrations and one equilibrium concentration, find others.

EX 12. The equilibrium concentration of gaseous chlorine is **0.030 M** when **0.075** and **0.033 M** hydrogen chloride and oxygen gas, respectively, are initially placed in a reaction vessel. How much hydrogen chloride and oxygen gas are left unreacted at equilibrium?



# Solving Equilibrium Problems

Treating systems with a small equilibrium constant

EX 13. If 2.00 mol of HBr were placed in a 1.00 L vessel at 1495 K what would be the equilibrium concentration of all species if  $K = 2.86 \times 10^{-5}$ ?

	$2 \text{ HBr(g)}$	$\rightleftharpoons$	$\text{H}_2\text{(g)}$	+	$\text{Br}_2\text{(g)}$
I	2.00 M		0		0
C	- 2x		+ x		+ x
<hr/>					
E	$2.00 - 2x$		x		x

$$K = \frac{x^2}{(2.00 - 2x)^2} \Rightarrow \sqrt{K} = x / (2.00 - 2x)$$

ignore 2x since K small  $\Rightarrow$  x small  
(not ignored then  $x = 0.01058$ )

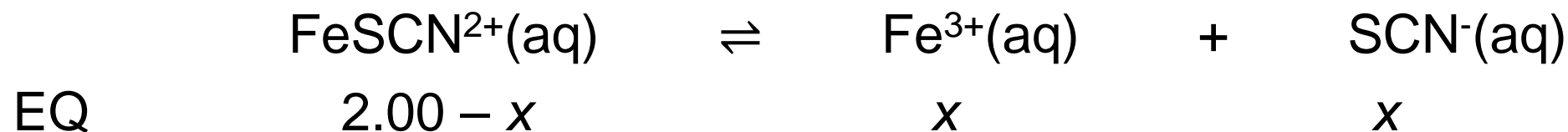
$$x = 2 \sqrt{K} = 2 \sqrt{(2.86 \times 10^{-5})} = 0.01069$$

$$[\text{HBr}] = 2.00 - 2(0.01069) = 1.9786 \Rightarrow \mathbf{1.98 \text{ M}} \quad [\text{H}_2] = [\text{Br}_2] = \mathbf{0.01 \text{ M}}$$

# Solving Equilibrium Problems

Systems requiring a quadratic equation

EX 14. At a particular temperature  $K = 9.1 \times 10^{-4}$ . Determine the concentration of all ions in a solution that is initially 2.0 M  $\text{FeSCN}^{2+}$ .



$$K = \frac{x^2}{2.00 - x} \quad \text{or} \quad x^2 + xK - 2K = 0$$

for  $ax^2 + bx + c = 0$

$$x = -9.1 \times 10^{-4} \pm \sqrt{(9.1 \times 10^{-4})^2 - 4(2)(9.1 \times 10^{-4})}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= 0.042 \text{ M} = [\text{Fe}^{3+}] = [\text{SCN}^{-}]$$

$$[\text{FeSCN}^{2+}] = 2.0 \text{ M}$$

$$- 0.043 \text{ M} \quad \text{unphysical}$$

if  $x$  ignored in denominator then  $[\text{Fe}^{3+}] = 0.043 \text{ M}$

# Le Châtelier's Principle

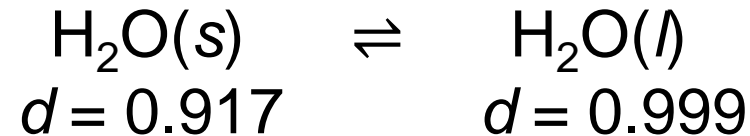
"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other actors involved in this shift, it would lead to a change of opposite sign in the parameter involved."

**Henri Louis Le Châtelier, 1888**

- I. change of **temperature** at constant pressure
- II. change of **total pressure** at constant temperature
  - a) add or remove gaseous reactant or product at constant volume
  - b) change volume of container
  - c) add inert gas (one not involved in the reaction) at constant volume
- III. change of **concentration/partial pressure** at constant volume (same as II a)

# Le Châtelier's Principle – Change $P$ ( $T$ Constant)

## 1) Pressure induced phase transition



Density =  $m/V$  => liquid water has a larger volume available to a given mass of molecules than ice does. Therefore, ice melts under pressure (remember that the phase diagram for water has a negative slope for the solid/liquid coexistence line).

