Chemical Equilibrium

Problem Set: Chapter 16 questions 25, 27, 33, 35, 43, 71

Examples of Equilibrium



Water can exists simultaneously in the gas and liquid phase. The vapor pressure of H_2O at a given temperature is a property associated with an equilibrium condition. $H_2O_{(1)} \longrightarrow H_2O_{(g)}$

I₂ originally dissolved in water (left) will partition between the CCl₄ and H₂O liquids such that $[I_2]_{CCl4} / [I_2]_{H2O} = 86$. The distribution coefficient of a solute between two immiscible liquids is an equilibrium property.





 $N_2O_{4 (g) (colourless)}$ decomposes to give 2 molecules of $NO_{2(g) (brown gas)}$. At low T, we have mostly N_2O_4 . At high temperatures we have mostly NO_2 . Under a given set of conditions, the concentration of each is in equilibrium.

Dynamic Equilibrium

Equilibrium is a "dynamic" condition. Even though the system does not appear to be changing, on a microscopic level it is constantly changing.

In each case shown previously, the forward and reverse processes are occurring at equal rates, such that the macroscopic system appears to be "static".

We symbolize this equilibrium by the double arrow,

reminding us that the forward and reverse reactions are proceeding at equal rates, resulting in a balanced chemical system.

Proof of Dynamic Equilibrium





 $AgI_{(s)} \longrightarrow Ag^{+}_{(aq)} + I^{-}_{(aq)}$ $Ag^{131}I_{(s)} \longrightarrow Ag^{+}_{(aq)} + {}^{131}I^{-}_{(aq)}$

Add saturated solution made from radioactive Ag¹³¹I to saturated nonradioactive AgI

 solution is radioactive, should solid be?

 gradual appearance of radioactivity in the solid AgI is proof that ¹³¹I is incorporated into solid. That is the equilibrium is dynamic

Approach to Equilibrium

Example: Methanol production using the "synthesis" reaction



 $t_{\rm e} =$ time for equilibrium to be reached

- mol CO
- mol H₂

— mol CH₃OH

 regardless of our initial starting conditions, *change* in the system slows down and appears to come to equilibrium.

there does not appear to be a consistent final condition,
i.e. – a relationship between concentrations

....but there is!!

Final state for Synthesis reaction

TABLE 16.1 Three Approaches $CO(g) + 2 H_2(g) \implies CH_3OH(g)$	[CH ₂ OH]			
	CO(g)	H ₂ (g)	CH ₃ OH(g)	$\frac{[CO]}{[CO]}$
Experiment 1				
Initial amounts, mol	1.000	1.000	0.000	
Equilibrium amounts, mol	0.911	0.822	0.0892	14.5
Equilibrium concentrations, mol/L	0.0911	0.0822	0.00892	
Experiment 2				
Initial amounts, mol	0.000	0.000	1.000	
Equilibrium amounts, mol	0.753	1.506	0.247	N 144
Equilibrium concentrations, mol/L	0.0753	0.151	0.0247	14.4
Experiment 3				
Initial amounts, mol	1.000	1.000	1.000	
Equilibrium amounts, mol	1.380	1.760	0.620	
Equilibrium concentrations, mol/L	0.138	0.176	0.0620	→ 14.5
The concentrations printed in blue are used	in the calcula	tions in Table	e 16.2.	
^a Reaction carried out in a 10.0-L flask at 48	33 K.			Equilibrium
				constant =
				constant –
				K



- c denotes that concentrations are expressed as molarities
- the equilibrium constant is temperature dependent

• do not confuse the general expression for equilibrium with the general expression for the rate law....here the concentrations ARE raised to the stoichiometric coefficients. Remember this was not true in general for the kinetic rate law.

Thermodynamic Equilibrium Constant, K_{eq}

The thermodynamic equilibrium constant is slightly different than what we just described...

For the general reaction

 $aA + bB + cC \implies gG + hH + iI$ $K_{eq} = \frac{(a_G)^g (a_H)^h (a_I)^i}{(a_A)^a (a_B)^b (a_C)^c}$ $a_A = unitless "activiy" of A$

 $a_{\rm B}$ = unitless "activiy" of B, etc.

Activities and K_{eq}

activities are unitless

(by definition $a = \gamma \times \text{conc./stand. refer. conc.}$) stand. refer. conc. is typically chosen as 1 M

• activities are defined such that activities of dilute solutes in solution are generally numerically equivalent to their concentrations expressed as molarities ($\gamma = 1$)

• activities of gases are approximately equal to their partial pressure expressed in atmospheres.

• activities of pure solids and pure liquids are defined to be unity (i.e. $a_{pure \ liquid} = a_{pure \ solid} = 1.00$)

thermodynamic equilibrium constants are unitless.

Working with Equilibrium Constants

The equilibrium constant for a reverse reaction is given by the inverse of the forward reaction equilibrium constant...



cont'd

The equilibrium constant for a reaction that has been multiplied through by constant, x, is given by :

 $\mathbf{K_c'} = (\mathbf{K_c})^{\mathbf{x}}$

Example – multiply eq from previous example

 $N_2 + 3H_2 \longrightarrow 2 NH_3$

by 1/2 to produce only 1 mole of ammonia

$$\frac{1}{2}N_{2} + \frac{3}{2}H_{2} \longrightarrow NH_{3}$$

$$K_{c}' = \frac{[NH_{3}]}{[N_{2}]^{1/2}[H_{2}]^{3/2}} = \left(\frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}}\right)^{1/2} = (K_{c})^{1/2} = (3.6 \times 10^{8})^{1/2} = 1.9 \times 10^{4} M^{-1}$$

Equilibria with Gases

- Mixtures of gases are in many ways analogous to mixtures in solution. Concentrations of gases can be expressed as molarities OR by partial pressure due to the ideal behaviour of gases. $[G] = \frac{n_G}{V} = \frac{P_G}{RT} \quad (recall that PV = nRT)$
- Equilibrium constants for reactions involving gases are often expressed as K_p, where the subscript p denotes the use of pressure units.

For the general reaction

$$aA_{(g)} + bB_{(g)} + cC_{(g)} \rightleftharpoons gG_{(g)} + hH_{(g)} + iI_{(g)}$$
$$K_{p} = \frac{P_{G}{}^{g}P_{H}{}^{h}P_{I}{}^{i}}{P_{A}{}^{a}P_{B}{}^{b}P_{C}{}^{c}}$$

Relationship between
$$K_C$$
 and K_p
 $K_c = \frac{[G]^g [H]^h [I]^i}{[A]^a [B]^b [C]^c} = \frac{\left(\frac{P_G}{RT}\right)^g \left(\frac{P_H}{RT}\right)^h \left(\frac{P_I}{RT}\right)^i}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b \left(\frac{P_C}{RT}\right)^c} = \dots$
 $= \frac{P_G^{\ g} P_H^{\ h} P_I^{\ i}}{P_A^{\ a} P_B^{\ b} P_C^{\ c}} \left(\frac{1}{RT}\right)^{g+h+i-a-b-c} = K_p \left(\frac{1}{RT}\right)^{\Delta n}$

 $\mathbf{K}_{\mathbf{p}} = \mathbf{K}_{\mathbf{c}} (\mathbf{RT})^{\Delta \mathbf{n}}$

where:

 Δn is the difference in stoichiometric coefficients of products and reactants ($\Delta n = g+h+i-a-b-c$) R is the gas constant (0.08206 L atm mol⁻¹ K⁻¹)

Equilibria with Pure Liquids or Solids

- Equilibrium constant expressions do NOT contain terms for solids or liquid phases of a single component (not a mixture).
- Why?
 - 1) concentrations of single-component solids and liquids do not change.
 - 2) "activities" of pure liquids and solids are defined to be 1
 - Example: $C(s) + H_2O \longrightarrow CO(g) + H_2(g)$



Examples of Equilibrium Constants

TABLE 16.3 Equilibrium Constants of Some Common Reactions

Reaction	Equilibrium constant, K_p
$\begin{array}{l} 2 \operatorname{H}_{2}(g) + \operatorname{O}_{2}(g) \rightleftharpoons 2 \operatorname{H}_{2}O(l) \\ \operatorname{CaCO}_{3}(s) \rightleftharpoons \operatorname{CaO}(s) + \operatorname{CO}_{2}(g) \end{array}$	1.4×10^{83} at 298 K 1.9×10^{-23} at 298 K
$2 \operatorname{SO}_{2}(g) + \operatorname{O}_{2}(g) \rightleftharpoons 2 \operatorname{SO}_{3}(g)$ C(s) + H ₂ O(g) \leftarrow CO(g) + H ₂ (g)	3.4 at 1000 K $1.6 \times 10^{-21} \text{ at } 298 \text{ K}$ 10.0 at about 1100 K

 A reaction is often said to go to completion if the numerical value of the equilibrium constant is very large (i.e. K > 10¹⁰)

Note: that large K is consistent with a large value in the numerator (products) and/or a small value in the denominator (reactants).

$$2 H_{2(g)} + O_{2(g)} \rightarrow 2 H_2O_{(l)}$$
 (written with single arrow)

Example

A few liters of liquid water are added to the largest experimental container that can be found in the chemistry department at York (CAC smog chamber; 9.0 m³) at 298K. If we waited a large period of time such that the system comes to equilibrium (or add a hypothetical catalyst to speed up the reaction), what would be the equilibrium concentration of H₂ and O₂? How many molecules of H₂ and O₂ would exist?

$$2 H_2 0_{(1)} \longrightarrow 2 H_{2(g)} + O_{2(g)} \qquad K_p = \frac{P_{H_2}^2 P_{O_2}}{1} = (1.4 \times 10^{83})^{-1} =$$
Let $P_{O2} = x; P_{H2} = 2x \qquad = 7.1 \times 10^{-84} \text{ atm}^3$

$$K_p = (2x)^2 x = 4x^3 = 7.1 \times 10^{-84} \qquad x = 1.21 \times 10^{-28} \text{ atm}$$

$$n = \frac{PV}{RT} = \frac{(1.21 \times 10^{-28} \text{ atm})(9000 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298\text{ K})} = 4.46 \times 10^{-26} \text{ mol}$$

$O_2 = n \times N_A = (4.46 \times 10^{-26} \text{ mol})(6.022 \times 10^{23} \text{ mol}^{-1}) = 0.027 \text{ molecules}$

Conclusion – at equilibrium, only a fraction of a molecule of O_2 will exist. Since this is physically impossible, we conclude the reaction lies completely to the right and does not proceed to the left to any meaningful extent.

$$2 H_2 0_{(l)} \implies 2 H_{2(g)} + O_{2(g)}$$

The Reaction Quotient (kwo:shent)

- Often we would like to predict the direction of chemical change for a system that is not at equilibrium.
- This prediction is trivial for the cases of systems in which we have only reactants or only products. But what about an intermediate case in which we start with a mixture of reactants and products?
- To make this prediction, we use the reaction quotient, Q_c or Q_p or Q_{eq} . For the 'general reaction' :

 $\mathbf{Q}_{c} = \frac{\left[\mathbf{G}\right]_{init}^{g} \left[\mathbf{H}\right]_{init}^{h} \left[\mathbf{I}\right]_{init}^{i}}{\left[\mathbf{A}\right]_{init}^{a} \left[\mathbf{B}\right]_{init}^{b} \left[\mathbf{C}\right]_{init}^{c}}$

where "init" implies initial concentrations for the nonequilibrium system

Note: we can also write analogous equations for Q_p *using partial pressures and* Q_{eq} *using activities*

Predicting the Direction of Change

- We compare the reaction **CALCULATED** quotient to the **KNOWN** equilibrium constant to predict the direction of chemical change in a reaction.
- If Q_c < K_c the reaction will proceed to the right
- If $Q_c > K_c$ the reaction will proceed to the left
- If $Q_c = K_c$ the reaction is at equilibrium



Le Chatelier's Principle

When an equilibrium system is subject to some change in conditions, the system will respond by minimizing the effect of that change.

Petrucci states it as:

When an equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that partially offsets the impact of the change.

Effect of Change in Amount

If the amount of one species in an equilibrium system is increased, the system will try to decrease it according to the Le Chatelier's Principle

- Indeed the equilibrium will shift in the direction that favours the removal of that species.
- Alternatively, if the amount of the species is decreased, the equilibrium shifts in the direction that increases the amount of that species.

Example: recall the synthesis reaction

 $CO_{(g)} + 2 H_{2(g)} \longrightarrow CH_3OH_{(g)} K_c = 14.5$

What would happen to the equilibrium system if we added a cold finger to the reaction vessel, allowing us to condense out methanol? Let us presume that we can remove 80% of the gaseous methanol as liquid, in each of several condensation steps. Start with experiment 1 conditions.

Effect of Incremental removals of CH₃OH

	[CO] _g mol/ L	[H ₂] _g mol/ L	[CH ₃ OH] _g mol/L	Q _c	-CH ₃ OH moles*	Comment
Exp 1 Start	.0911	.0822	.00892	14.5		Q _c = K _c , equilib
Condense 80%	.0911	.0822	.00178	2.90	-0.0714	Q _c < K _c ; must shift right
Shift right	.0863	.0726	.00659	14.5		$Q_c = K_c$, equilib.
Condense 80%	.0863	.0726	.00132	2.90	-0.0527	Q _c < K _c ; must shift right again
Shift right	.0825	.0651	.00507	14.5		$Q_c = K_c$, equilib.
Condense 80%	.0825	.0651	.00101	2.90	-0.0405	Q _c < K _c ; must shift right again
Shift right	.0795	.0591	.00402	14.5		Q _c = K _c , equilib.

Each time we condense liquid methanol, we remove gaseous methanol, making $Q_c < K_c$. The equilibrium condition is re-established by a shift of the reaction to the right, such that $Q_c = K_c$ again.

*Incremental amount of liquid methanol removed in moles (calculated).



Effect of Change in Pressure

If the total pressure of a chemical system is increased (or decreased) by changing the volume, the equilibrium will shift in a direction that favours a reduction (or increase) in the total pressure.

 $K_c = 280 (1000K)$ $2 \text{ SO}_{2(g)} + \text{O}_{2(g)} \Longrightarrow 2 \text{ SO}_{3(g)}$ **Example:** A decrease in volume increases the partial pressure of all gases 0.68 mol SO₃ in the system. The equilibrium is shifted 0.32 mol SO₂ in a direction that 0.16 mol O2 reduces the total Mo pressure, in this case 0.83 mol SO₃ 10.0 L 1.00 L to the right, since 0.17 mol SO there are fewer moles of gases on the right. ∠0.085 mol O₂ (a) (b)

Another Explanation

$$2 \text{ SO}_{2(g)} + \text{O}_{2(g)} \implies 2 \text{ SO}_{3(g)} \qquad \text{K}_{c} = 280 \text{ (1000 K)}$$
$$\text{K}_{c} = \frac{[\text{SO}_{3}]^{2}}{[\text{SO}_{2}]^{2}[\text{O}_{2}]} = \frac{[0.068]^{2}}{[.032]^{2}[.016]} = 282$$

After compression to 1.0L, and before the system can respond we have all concentration increased 10 fold: [SO₃] = 0.68 M; [SO₂] = 0.32 M; [O₂] = 0.16M

$$Q_{c} = \frac{[SO_{3}]^{2}}{[SO_{2}]^{2}[O_{2}]} = \frac{[0.68]^{2}}{[.32]^{2}[.16]} = 28.2$$

Since $Q_c < K_c$, *equilibrium will shift to the right*. Note that for every "x" moles of O_2 consumed, "2x" moles of SO_2 are consumed and "2x" moles of SO_3 are produced. Thus, when equilibrium is reached we must have:

$$\mathbf{K}_{c} = \frac{[\mathbf{SO}_{3}]^{2}}{[\mathbf{SO}_{2}]^{2}[\mathbf{O}_{2}]} = \frac{[\mathbf{0.68} + 2\mathbf{x}]^{2}}{[.32 - 2\mathbf{x}]^{2}[.16 - \mathbf{x}]} = 282$$

We will later discuss how to solve these problems. For now the solution is: "x" = 0.0751 moles; $[SO_3]_{final}$ = 0.830M, $[SO_2]_{final}$ = 0.1697M, $[O_2]_{final}$ = 0.0849M,

What We Learned So Far

$$K_{c} = \frac{[G]^{g}_{eq}[H]^{h}_{eq}[I]^{i}_{eq}}{[A]^{a}_{eq}[B]^{b}_{eq}[C]^{c}_{eq}}$$

$$Q_{c} = \frac{[G]_{init}^{g} [H]_{init}^{h} [I]_{init}^{i}}{[A]_{init}^{a} [B]_{init}^{b} [C]_{init}^{c}}$$

$$\boldsymbol{K}_{c} = \frac{P_{G}^{\ g} P_{H}^{\ h} P_{I}^{\ i}}{P_{A}^{\ a} P_{B}^{\ b} P_{C}^{\ c}} \left(\frac{1}{RT}\right)^{g+h+i-a-b-c} = K_{p} \left(\frac{1}{RT}\right)^{\Delta n}$$

Effect of Increased Total pressure using "spectator" gases

If we increase the total pressure at constant volume by adding an inert gas or another gas not involved in the equilibrium, the partial pressure of each species in the equilibrium will not change...therefore the reaction quotient will not change.

The system will not respond to changes in total pressure achieved by adding inert gases at constant volume.

Note: In solution, dilution of a mixture by addition of water WOULD change the total volume, WOULD change the concentration of each species in an equilibrium, and therefore the reaction quotient WOULD change in general. We should expect a shift in equilibrium in this case

Effect of Change in Temperature

To predict the effect that temperature has on an equilibrium system, we can invoke Le Chatelier's principle. If we increase the temperature, the equilibrium system responds by trying to lower the temperature (utilize the excess energy). It would do this by shifting in the direction of the endothermic reaction. If the temperature is decreased, the equilibrium shifts in the direction of the reaction that provides excess heat (ie- the exothermic reaction)

 $N_2O_{4(g)}$ \implies 2 $NO_{2(g)}$ $\Delta H = +57.2 \text{ kJ mol}^{-1}$

- **Q:** Will the amount of $NO_{2(g)}$ formed be greater at high or low temperature?
- A: The forward reaction as written is endothermic. An increase in temperature will favour a shift to the right in equilibrium. $NO_{2(g)}$ will be higher at higher temperature.

Effect of a Catalyst

- For a given set of reaction conditions, the equilibrium amounts of reactants and products in a reversible reaction are independent of whether the reaction is homogeneous, heterogeneous or otherwise catalysed.
- A catalyst does not change the position of equilibrium
- The catalyst only acts to decrease the amount of time it takes to get to equilibrium
- Since we know that catalysts can provide alternate reaction mechanisms, *our conclusion must be that the equilibrium condition is independent of the process by which the system moves from initial to final conditions.* We will learn more about this in the section on Free Energy

Equilibrium Calculations: Example 1

Practice Example 16.10 B:

0.100 moles SO_2 and 0.100 moles O_2 are introduced into an evacuated 1.52 L flask at 900K. When equilibrium is achieved, the amount of SO_3 measured is 0.0916 moles. Use this data to determine K_p for the reaction:

 $2 SO_{3(g)} \leftarrow \rightarrow 2 SO_{2(g)} + O_{2(g)}$

Solution Approach:

we will use an ICE table to relate the initial and equilibrium (final) conditions. It will be convenient to start working in units of moles. Our equilibrium concentrations can then be expressed as moles L^{-1} . We can then calculate K_c , and finally relate it to K_p through the known relationship; $K_p = K_c (RT)^{\Delta n}$.

Solution: example 1

Amounts and Concentrations	2 SO ₃	\leftrightarrow	2 SO ₂	O ₂
I _{nitial} (mol)	0		0.100	0.100
C _{hange} (mol)	+2x		-2x	-X
E _{quilibrium} (mol)	0+2x		0.1–2x	0.1 –x
Conc. mol L ⁻¹	2x/V		(0.1-2x)/V	(0.1-x)/V
Conc. mol L ⁻¹	.06026		.00553	.03566

We are given that the equilibrium amount of $SO_3 = 0.0916$ mole

2x = 0.0916 moles \rightarrow x = 0.0458 moles

Knowing that V= 1.52 L, we can complete the last line in the table.

Solution 1, cont'd

 $K_{c} = \frac{[SO_{2}]^{2}[O_{2}]}{[SO_{3}]^{2}} = \frac{[.00553]^{2}[.03566]}{[0.06026]^{2}} = 3.00 \times 10^{-4}$ $\Delta n = (2 + 1) - 2 = 1$ $K_{p} = K_{c} (RT)^{\Delta n}$ $K_{p} = 3.00 \text{ x } 10^{-4} (0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (900 \text{ K})$ $K_{p} = 0.022$

Equilibrium Calculations: Example 2

Practice Example 16.12 A:

If 0.150 moles $H_{2(g)}$ and 0.200 moles $I_{2(g)}$ are introduced into a 15.0 L flask at 445 °C and allowed to come to equilibrium, how many moles of HI will be present?

 $H_{2(g)} + I_{2(g)} \leftrightarrow 2 HI_{(g)} \qquad K_c = 50.2 (445^{\circ}C)$

Solution Approach:

We will again use ICE table to relate the initial and equilibrium (final) conditions. In this case though, we will not know the equilibrium concentrations, but we know K_c . We use "x" as the variable of change, write the equilibrium expression in terms of x, and then solve for x. We must solve a quadratic to get x.

Example 2 – solution

Amounts and	H ₂	I ₂	\leftrightarrow	2 HI
Concentrations				
I _{nitial} (mol)	0.150	0.200		0
C _{hange} (mol)	-X	-X		+2x
E _{quilibrium} (mol)	0.150-x	0.200-x		2 x
Conc. mol L ⁻¹	(0.150-x)/V	(0.200-x)/V		2x/V
	$(2\mathbf{x})^2$			

$$K_{c} = \frac{[HI]^{2}}{[H_{2}][I_{2}]} = \frac{(V)}{(\frac{0.150 - x}{V})(\frac{0.200 - x}{V})} = \frac{(2x)^{2}}{(0.150 - x)(0.20 - x)} = 50.2$$

This can be algebraically arranged to give:

 $-46.2 x^2 + 17.57 x - 1.506 = 0$

This is a quadratic equation...a=-46.2, b=17.57, c-1.506

Solution 2, cont'd

$$\mathbf{x} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-17.57 \pm \sqrt{(17.57)^2 - 4(-46.2)(-1.506)}}{2(-46.2)}$$

x = 0.1305 OR 0.2498

taking the + and – root respectively. Only one solution is physically realistic; x = 0.1305. For x = 0.25 moles we would end up with negative amounts of H₂ and I₂.

Thus x = 0.1305 moles and at equilibrium we have 2x moles of HI,

At equilibrium we have 0.261 moles of HI

Complex Formation $A + B \stackrel{k_1}{\leftarrow} AB$

The equilibrium constant for complex formation is often called the association constant:



Even more often we operate with the dissociation constant:

$$\boldsymbol{K}_{d} = \frac{[A]_{eq}[B]_{eq}}{[AB]_{eq}} \boldsymbol{M}$$



Mass Conservation Principle for Complex Formation

 $[A]_{tot} = [A] + [AB]$ and $[B]_{tot} = [B] + [AB]$

Relationship between the Equilibrium Constant and the Rate Constants

At equilibrium the rate of forward reaction is equal to the rate of reverse reaction:

 $k_1[A]_{eq}[B]_{eq} = k_{-1}[AB]_{eq} \implies k_{-1}/k_1 = [A]_{eq}[B]_{eq}/[AB]_{eq} = K_d$

$$\boldsymbol{K}_{\mathrm{d}} = \frac{\boldsymbol{k}_{-1}}{\boldsymbol{k}_{1}}$$