

Lecture Presentation

Chapter 14 Chemical Equilibrium

14.1, 14.2, 14.3, 14.4, 14.7, 14.9, 14.10, 14.11, 14.12, 14.14, 14.15, 14.19, 14.23, 14.24, 14.25, 14.27, 14.31, 14.34, 14.50, 14.52, 14.54, 14.56, 14.58, 14.60. 14.68, 14.74, 14.88, 14.98, 14.100, 14.110

> John E. McMurry Robert C. Fay

The Equilibrium State (kinetic chapter no reversible rxn this chapter all reversible rxn)

Chemical Equilibrium: The state reached when the concentrations of reactants and products remain constant over time (dynamic equilibrium) (dynamic equilibrium: rxn to product = rxn to reactant)

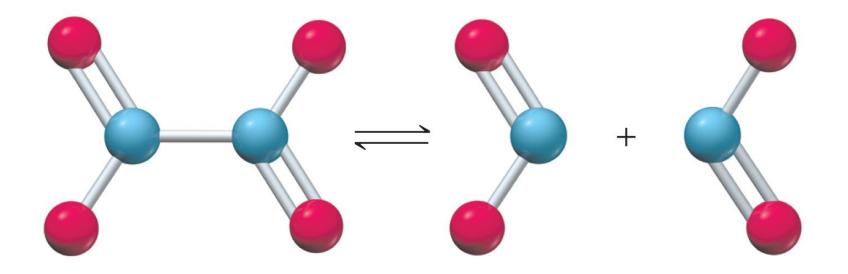
This Chapter: How far forward does the reaction go ? NOT how fast but the <u>ratio</u> of <u>products</u> and <u>reactants</u>



Liquid bromine in dynamic equilibrium with gaseous bromine.

The Equilibrium State

$N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ Colorless Brown

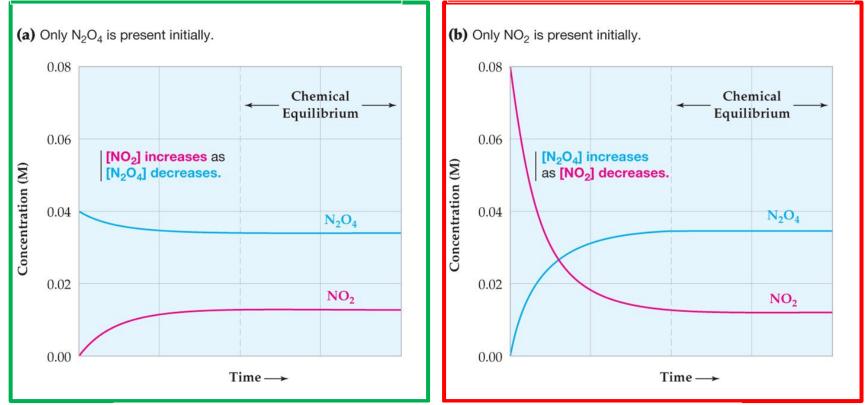


The Equilibrium State

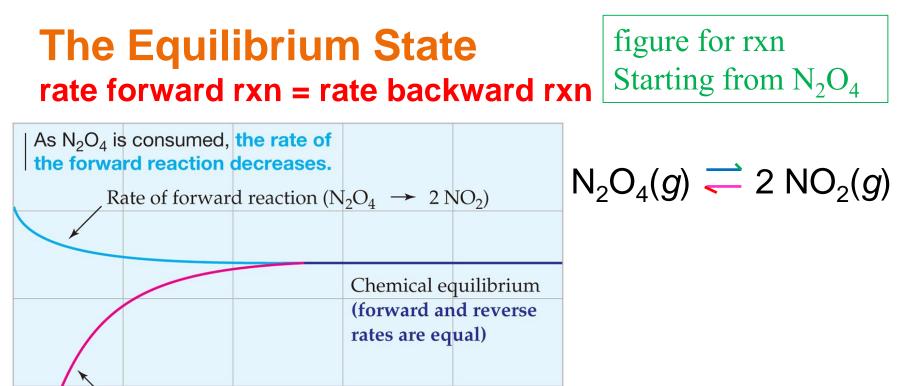
 $N_2O_4(g) \simeq 2 NO_2(g)$

Experiment 1: forward rxn start with only $N_2O_4(g)$

Experiment 2: backward rxn Start with only $NO_2(g)$



Both experiments end with exactly the same concentration of the N_2O_4 and NO_2



Rate of reverse reaction (
$$N_2O_4 \leftarrow 2 NO_2$$
)

As NO₂ is formed, the rate of the reverse reaction increases.

Time→

When the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations.

Reaction rate-

The Equilibrium Constant K_c

$$N_2O_4(g) = 2 NO_2(g)$$

TABLE 14.1 Concentration Data at 25°C for the Reaction $N_2O_4(g) \implies 2 NO_2(g)$

	Initial		Equilibrium		Equilibrium
	Concentrations (M)		Concentrations (M)		Constant Expression
Experiment	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$
1	0.0400	0.0000	0.0337	0.0125	$4.64 imes 10^{-3}$
2	0.0000	0.0800	0.0337	0.0125	$4.64 imes 10^{-3}$
3	0.0600	0.0000	0.0522	0.0156	4.66×10^{-3}
4	0.0000	0.0600	0.0246	0.0107	4.65×10^{-3}
5	0.0200	0.0600	0.0429	0.0141	4.63×10^{-3}
Elementary Reaction Mechanism Step rate = $k_1 [N_2O_4]$ rate (back) = $k_2 [NO_2]^2$					Why? Equilibrium state

The Equilibrium Constant K_c

K_c is the same at the same temperature no matter how much of each reactant or product you have

For a general reversible reaction: $aA + bB \rightleftharpoons cC + dD$

Equilibrium equation: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \leftarrow \text{Products}$ Equilibrium constant Equilibrium constant expression

For the following reaction: $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$

$$K_{\rm c} = \frac{[NO_2]^2}{[N_2O_4]} = 4.64 \times 10^{-3} \text{ (at 25 °C)}$$

End 2/26W A section

HW 14.1: The Equilibrium Constant *K*_c Write the equilibrium constant expression for the

following reactions. $(K_p = equilibrium constants with amounts given by pressure of each component)(if gas is in solution use K_c, if gas is in gas state use K_p)$

$$aA + bB \rightleftharpoons cC + dD$$
 $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

(s) or (l) leave out of K expression

(a) 2 BrCl (soln)
$$\rightarrow \underset{\leftarrow}{\rightarrow}$$
 Br₂ (soln) + Cl₂ (soln)

(b) 2 N₂(g) + 2 O₂(g)
$$\underset{\leftarrow}{\rightarrow}$$
 4 NO (g) (give K_p)

(c)
$$BaSO_4(s) \xrightarrow{} Ba^{2+}(aq) + SO_4^{2-}(aq)$$

(d) $\operatorname{Fe}_2O_3(s) + 3 \operatorname{CO}(g) \xrightarrow{}_{\leftarrow} 2 \operatorname{Fe}(s) + 3 \operatorname{CO}_2(g)$

HW 14.1: The Equilibrium Constant K_c Write the equilibrium constant expression for the following reactions. $(K_{D} = equilibrium constants with amounts are given by$ pressure of each component) (if gas is in solution use K_c , if gas is in gas state use K_p) $K_{c} = \frac{[C]^{c}[D]^{d}}{1 \text{ leave out of}}$ $aA + bB \rightleftharpoons cC + dD$ [A]^a[B]^b K expression $K_p = \frac{(P_{NO})^4}{(P_{NO})^2 (P_{OO})^2}$ (b) $2 \operatorname{N}_{2}(g) + 2 \operatorname{O}_{2}(g) \xrightarrow{} 4 \operatorname{NO}(g)$ (give K_{p}) $K_{c} = [Ba^{2+}][SO_{4}^{2-}]$ (c) $BaSO_4(s) \xrightarrow{} Ba^{2+}(aq) + SO_4^{2-}(aq)$ $K_{p} = \frac{(P_{CO2})^{3}}{(P_{CO})^{3}}$ (d) $\operatorname{Fe}_2O_3(s) + 3 \operatorname{CO}(g) \xrightarrow{} 2 \operatorname{Fe}(s) + 3 \operatorname{CO}_2(g)$ 2/28 Friday C section

The Equilibrium Constant K_c

TABLE 14.1 Concentration Data at 25°C for the Reaction $N_2O_4(g) \implies 2 NO_2(g)$

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4	0.0000	0.0600	0.0246	0.0107	$4.65 imes 10^{-3}$
5	0.0200	0.0600	0.0429	0.0141	4.63×10^{-3}

[NO ₂] ²	Experiment 1	Experiment 5	
$K_{\rm c} = \frac{1}{[N_2O_4]}$	$(0.0125)^2$ = 4.64 × 10 ⁻³	$\frac{(0.0141)^2}{} = 4.63 \times 10^{-3}$	
	0.0337	0.0429	

The Equilibrium Constant K_c

The equilibrium constant and the equilibrium constant expression are for the chemical equation as written.

$$aA + bB \rightleftharpoons cC + dD \qquad \mathcal{K}_{c} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \qquad \frac{End 2/28FA}{section}$$

$$(a) N_{2}(g) + 3 H_{2}(g) \rightleftharpoons 2 NH_{3}(g) \qquad \mathcal{K}_{c} = \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}}$$

$$(b) 2 NH_{3}(g) \rightleftharpoons N_{2}(g) + 3 H_{2}(g)$$

$$reversed rxn (a) - turn K upside down$$

$$(c) 2 N_{2}(g) + 6 H_{2}(g) \rightleftharpoons 4 NH_{3}(g) \qquad \mathcal{K}_{c} = \frac{[NH_{3}]^{4}}{[N_{2}]^{2}[H_{2}]^{6}} = \mathcal{K}_{c}^{2}$$

$$doubled rxn (a) - square all terms$$

HW 14.2: The Equilibrium Constant K_c

Give the (a) <u>equilibrium constant expression</u> and the (b) <u>numerical value of the equilibrium constant expression</u> for the following reactions given the reaction. (assume dissolved in solvent)

$$N_2(g) + O_2(g) \underset{\leftarrow}{\neq} 2 \text{ NO}(g) \qquad \text{Kc} = 7.5 \text{ x } 10^{-9} \qquad K_c = \frac{[\text{NO}]^2}{[\text{N}_2] [\text{O}_2]}$$

(1) 2 NO (g) $\underset{\leftarrow}{\rightarrow}$ N₂ (g) + O₂ (g)

(2) $2 \operatorname{N}_{2}(g) + 2 \operatorname{O}_{2}(g) \underset{\leftarrow}{\stackrel{\rightarrow}{\leftarrow}} 4 \operatorname{NO}(g)$

HW 14.2: The Equilibrium Constant *K*_c Give the (a) <u>equilibrium constant expression</u> and the (b) <u>numerical value of the equilibrium constant</u> <u>expression</u> for the following reactions given the reaction.

$$N_{2}(g) + O_{2}(g) \underset{\leftarrow}{\neq} 2 \text{ NO}(g) \qquad \text{Kc} = 7.5 \text{ x } 10^{-9} \qquad \mathcal{K}_{c} = \frac{[\text{NO}]^{2}}{[\text{N}_{2}] [\text{O}_{2}]}$$

$$(1) 2 \text{ NO}(g) \underset{\leftarrow}{\neq} N_{2}(g) + O_{2}(g) \qquad \mathcal{K}_{c} = \frac{[\text{N}_{2}] [\text{O}_{2}]}{[\text{NO}]^{2}}$$

$$(2) 2 \text{ N}_{2}(g) + 2 \text{ O}_{2}(g) \underset{\leftarrow}{\neq} 4 \text{ NO}(g) \qquad \mathcal{K}_{c} = \frac{[\text{NO}]^{4}}{[\text{N}_{2}]^{2} [\text{O}_{2}]^{2}}$$

$$(2) 2 \text{ N}_{2}(g) + 2 \text{ O}_{2}(g) \underset{\leftarrow}{\neq} 4 \text{ NO}(g) \qquad \mathcal{K}_{c} = \frac{[\text{NO}]^{4}}{[\text{N}_{2}]^{2} [\text{O}_{2}]^{2}}$$

The Equilibrium Constant K_c (K_p)

$$N_2O_4(g) \rightleftharpoons 2 NO_2(g)$$

$$K_{\rm p} = \frac{\left(P_{\rm NO_2}\right)^2}{P_{\rm N_2O_4}}$$

P is the partial pressure of that component.

HW 14.3: The Equilibrium Constant K_c (K_p)

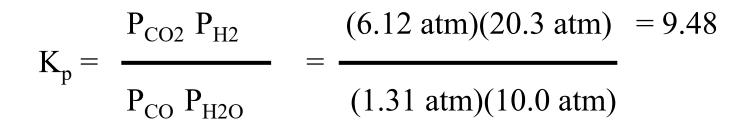
 $\begin{array}{ccc} \mathrm{CO}\,(\mathrm{g}) + \,\mathrm{H_2O}(\mathrm{g}) \, \boldsymbol{\rightarrow} & \mathrm{CO_2}\,(\mathrm{g}) \, + & \mathrm{H_2}\,(\mathrm{g}) \\ \boldsymbol{\leftarrow} \end{array}$

What is the value of K_p at 700 K if the partial pressure in an equilibrium mixture at 700 K are <u>1.31 atm of CO</u>, <u>10.0 atm of H₂O</u>, <u>6.12 atm of CO₂ and <u>20.3 atm of H₂</u>?</u>

HW 14.3: The Equilibrium Constant K_c (K_p)

 $CO(g) + H_2O(g) \underset{\leftarrow}{\rightarrow} CO_2(g) + H_2(g)$

What is the value of K_p at 700 K if the partial pressure in an equilibrium mixture at 700 K are 1.31 atm of CO, 10.0 atm of H₂O, 6.12 atm of CO₂ and 20.3 atm of H₂?



The Equilibrium Constant K_c

 $K_{\rm p} = K_{\rm c}(RT)^{\Delta n}$ **R** is the gas constant, 0.08206 $\frac{\text{L atm}}{\text{K mol}}$.

T is the absolute temperature (kelvin).

 Δn = # moles of <u>gaseous products</u> minus # moles of <u>gaseous reactants</u>. **The Equilibrium Constant** K_c $K_p = K_c (RT)^{\Delta n}$ **R** is the gas constant, 0.08206 $\frac{L \text{ atm}}{K \text{ mol}}$. $\Delta n = (c+d) - (a+b)$

 $2\text{NO}(g) + \text{O}_2(g) \xrightarrow{\rightarrow} 2\text{NO}_2(g) \xrightarrow{\leftarrow}$

If $K_c = 6.9 \times 10^5$ at 227°C, what is the value of K_p ?

 $K_p = K_c (RT)^{\Delta n}$

 $\Delta n = (2) - (2+1) = -1$

 $K_p = (6.9 \times 10^5) [(0.08206 L atm/mol K)(227+273.15)]^{-1}$

 $K_p = 16811.9 = 1.7 \text{ x } 10^4$

HW 14.4: The Equilibrium Constant K_c

 $K_{\rm p} = K_{\rm c}(RT)^{\Delta n}$ **R** is the gas constant, 0.08206 $\frac{L \text{ atm}}{K \text{ mol}}$. $\Delta n = (c+d) - (a+b)$

 $\begin{array}{c} \mathrm{H_2O}\,(\mathrm{g}) + \mathrm{CH_4}(\mathrm{g}) \xrightarrow{} \mathrm{CO}\,(\mathrm{g}) + \ 3\mathrm{H_2}\,(\mathrm{g}) \\ \xleftarrow{} \end{array}$

If $K_c = 3.8 \times 10^{-3}$ at 1000 K, what is the value of K_p ?

HW 14.4: The Equilibrium Constant K_c

 $K_{\rm p} = K_{\rm c}(RT)^{\Delta n}$ **R** is the gas constant, 0.08206 $\frac{L \text{ atm}}{K \text{ mol}}$. $\Delta n = (c+d) - (a+b)$

$$H_{2}O(g) + CH_{4}(g) \rightarrow CO(g) + 3H_{2}(g)$$

$$\leftarrow$$

End 3/2 Monday A section

If $K_c = 3.8 \times 10^{-3}$ at 1000 K, what is the value of K_p ?

 $K_p = K_c (RT)^{\Delta n}$

 $\Delta n = (1+3) - (1+1) = 2$

 $K_p = (3.8 \times 10^{-3}) [(0.08206 L atm/mol K)(1000 K)]^2$

 $K_p = 25.588 = 26$

Heterogeneous Equilibria

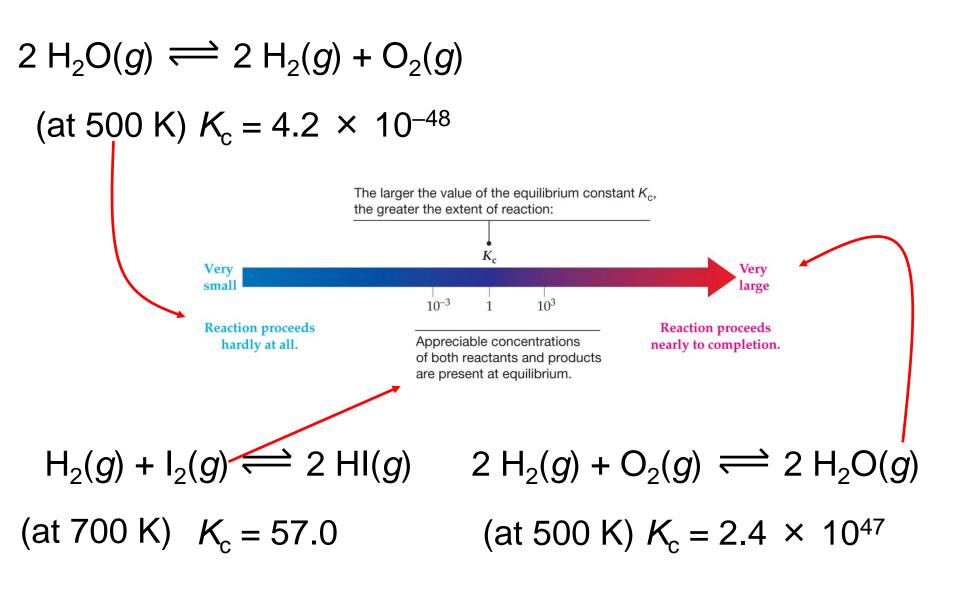
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

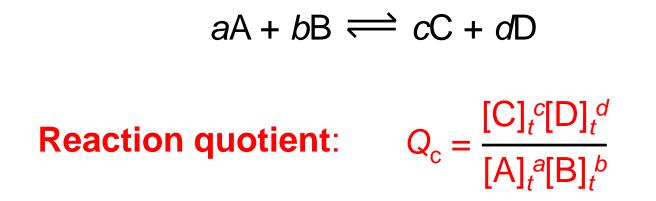
Limestone Lime

$$K_{c} = \frac{[CaO][CO_{2}]}{[CaCO_{3}]} = \frac{(1)[CO_{2}]}{(1)} = [CO_{2}]$$

<u>Pure solids</u> and <u>pure liquids</u> are not included in equilibrium expression.

$$K_c = [CO_2]$$
 $K_p = P_{CO_2}$ MolarityPressureIf dissolved.If just gas - no solvent.





The reaction quotient, Q_c , is defined in the same way as the equilibrium constant, K_c , except that the concentrations in Q_c are not necessarily equilibrium values. (value of mixed reaction before equilibrium)

- If $Q_c < K_c$ net reaction goes from left to right (*reactants to products*, \rightarrow).
- If $Q_c > K_c$ net reaction goes from right to left (*products to reactants,* \leftarrow).
- If $Q_c = K_c$ no net reaction occurs. (at equilibrium)

End 3/3 Tuesday C section

HW 14.5: Using the Equilibrium Constant

- If $Q_c < K_c$ net reaction goes from left to right (*reactants to products*, \rightarrow).
- If $Q_c > K_c$ net reaction goes from right to left (*products to reactants,* \leftarrow).
- If $Q_c = K_c$ no net reaction occurs. (at equilibrium)

If the equilibrium constant $K_c = 2.78 \times 10^{-10}$ and you have a reaction $A + 2 B \rightarrow 3 C + D$ and $[A] = 1.78 \times 10^{-4}$, $[B] = 1.1 \times 10^{-5}$ and $[C] = 1.23 \times 10^{-6}$, $[D] = 7.8 \times 10^{-8}$ does the reaction go forward to produce more products or backwards to produce more reactant or stay in equilibrium ?

HW 14.5: Using the Equilibrium Constant

- If $Q_c < K_c$ net reaction goes from left to right (*reactants to products*, \rightarrow).
- If $Q_c > K_c$ net reaction goes from right to left (*products to reactants,* \leftarrow).
- If $Q_c = K_c$ no net reaction occurs. (at equilibrium)

If the equilibrium constant $K_c = 2.78 \times 10^{-10}$ and you have a reaction $A + 2 B \rightarrow 3 C + D$ and $[A] = 1.78 \times 10^{-4}$, $[B] = 1.1 \times 10^{-5}$ and $[C] = 1.23 \times 10^{-6}$, $[D] = 7.8 \times 10^{-8}$ does the reaction go forward to produce more products or backwards to produce more reactant or stay in equilibrium ?

End 3/2/20

Monday

section A

Kc =
$$\frac{[C]^{3}[D]}{[A][B]^{2}}$$
 Q = $\frac{[1.23 \times 10^{-6}]^{3}[7.8 \times 10^{-8}]}{[1.78 \times 10^{-4}][1.1 \times 10^{-5}]^{2}}$

 $Q = 6.74 \text{ x } 10^{-12} \text{ \& } 6.74 \text{ x } 10^{-12} < 2.78 \text{ x } 10^{-10}$

Reaction goes forward until equilibrium is reached.

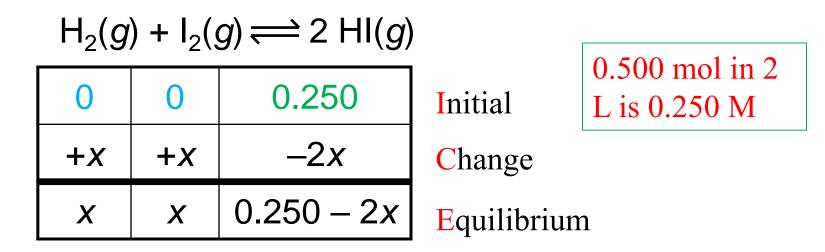
Using the Equilibrium Constant – ICE method [Initial, Change, Equilibrium] (given K & initial concentrations, calculate equilibrium concentrations)

At 700 K, 0.500 mol of HI is added to a 2.00 L container and allowed to come to equilibrium. Calculate the equilibrium concentrations of H₂, I₂, and HI . K_c is 57.0 at 700 K. Initial: Zero

of reactants

$$H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$$

Set up a table: Initial, Change, Equilibrium



Substitute values into the equilibrium expression:

$$K_{c} = \frac{[HI]^{2}}{[H_{2}][I_{2}]}$$
 57.0 = $\frac{(0.250 - 2x)^{2}}{x^{2}}$

Solve for "x":

$$\sqrt{57.0} = \sqrt{\frac{(0.250 - 2x)^2}{x^2}}$$
 $x = 0.0262$
 $7.55 = \frac{0.250 - 2x}{x}$ $7.55 = 0.250 - 2x$
 $9.55 = 0.250$ $x = 0.250 - 2x$
 $x = 0.250 - 2x$

Determine the equilibrium concentrations:

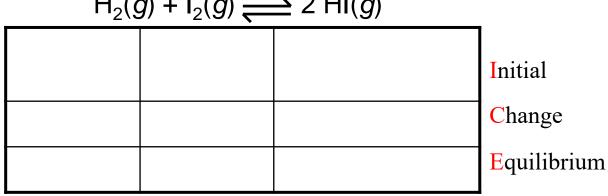
$$H_2 = x = 0.0262 \text{ M}$$

 $I_2 = x = 0.0262 \text{ M}$
 $HI = 0.250 - 2x = 0.250 - 2(0.0262) = 0.198 \text{ M}$

HW 14.6: Using the Equilibrium Constant

For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, for initial concentrations of $H_2(0.00623 M)$, I_2 (0.00414 M) and HI (0.0224 M). Calculate the concentrations at equilibrium given K_c (54.3) assuming forward rxn.

- (a) Set up the ICE table. (where $x = change of H_2$)
- (b) show the expression for Kc
- (c) If your solution to Kc gives x = 0.00156, calculate the concentration of HI.



 $H_2(g) + I_2(g) \longrightarrow 2 HI(g)$

Kc =

Solution x = 0.00156

HW 14.6: Using the Equilibrium Constant

For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, for initial concentrations of $H_2(0.00623 M)$, I_2 (0.00414 M) and HI (0.0224 M). Calculate the concentrations at equilibrium given K_c (54.3) assuming forward rxn.

(a) Set up the ICE table. (where $x = change of H_2$)

(b) show the expression for Kc

(c) If your solution to Kc gives x = 0.00156, calculate the concentration of HI.

	$\Box_2(g) + \Box_2(g) \rightleftharpoons Z \Box \Box(g)$					
	0.00623	0.00414	0.0224	Initial		
	-X	-X	+2 <i>x</i>	Change		
	0.00623-x	0.00414-x	0.0224 + 2x	Equilibrium		
1				-		

$$H_2(g) + I_2(g) \Longrightarrow 2 HI(g)$$

 $[0.0224+2x]^2 = 54.3$ Kc = [0.00623 - x][0.00414 - x]

Solution x = 0.00156[HI] = 0.0224 + 2(0.00156) = 0.0255 M Using the Equilibrium Constant – showing the math not responsible for on exam – too long for quiz/exam Step 2: The equilibrium constant is

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

$$54.3 = \frac{5.02 \times 10^{-4} + 0.0448x + 0.0448x + 4x^2}{(2.58 \times 10^{-5} - 0.00623 \times -0.00414 \times x + x^2)}$$

 $54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$

 $1.40 \ge 10^{-3} - 0.56472 \ge 54.3 \ge 5.02 \ge 10^{-4} + 0.089 \ge 4x^2$

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

Using the Equilibrium Constant – showing the math not responsible for on exam – too long for quiz/exam

For equation: $50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 4) is

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

Here we have a = 50.3, b = -0.654, and $c = 8.98 \times 10^{-4}$

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

x = 0.0114 M or x = 0.00156 M

The first solution is physically impossible because the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for x is easy.

At equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156) M = 0.00467 M$$
$$[I_2] = (0.00414 - 0.00156) M - 0.00258 M$$
$$[HI] = (0.0224 + 2 \times 0.00156) M = 0.0255 M$$

Le Châtelier's Principle

Le Châtelier's Principle: If a stress is applied to a reaction mixture *at equilibrium*, net reaction occurs in the direction that relieves the stress. (possible changes) (equilibrium shifts to undo stress applied to system)

- concentration of reactants or products
- pressure and volume

only effect for rxn with gases, otherwise not much effect of P & V for liquid & solids

 temperature can be changed. (can predict only if given enthalpy) (-∆H exo → lower T)

Altering an Equilibrium Mixture: Changes in Concentration

In general, when an equilibrium is disturbed by the addition or removal of any reactant or product, Le Châtelier's principle predicts that

- the concentration stress of an *added* reactant or product is relieved by net reaction in the direction that *consumes* the added substance.
- the concentration stress of a *removed* reactant or product is relieved by net reaction in the direction that *replenishes* the removed substance.

Altering an Equilibrium Mixture: Changes in Concentration

 $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ at 700 K, $K_c = 0.291$

An equilibrium mixture of 0.50 M N₂, 3.00 M H₂, and 1.98 M NH₃ is disturbed by increasing the N₂ concentration to 1.50 M.

$$Q_{\rm c} = \frac{[{\rm NH}_3]^2}{[{\rm N}_2][{\rm H}_2]^3} = \frac{(1.98)^2}{(1.50)(3.00)^3} = 0.0968 < K_{\rm c}$$

Since $Q_c < K_c$, more reactants will be *consumed* and the net reaction will be from *left* to *right*.

Altering an Equilibrium Mixture: Changes in Concentration Red Pale yellow Colorless End 3/4/20 $Fe^{3+}(aq) + SCN^{-}(aq) \Longrightarrow FeNCS^{2+}(aq)$ A section, C section subtract Add subtract (b) Alter adding FeCla (c) After dding KSCN (d) After adding (a) Original solution: (e) After adding HgCl₂ to (a): [FeNCS2+1 Fe³⁺(pale yellow), to (a): [FeNCS²⁺] to (a): [FeNCS2+] $H_2C_2O_4$ to (a): [FeNCS²⁺] decreases SCN⁻(colorless), decreases as increases. increases. and FeNCS²⁺(red). as [Fe(C₂O₄)₃³⁻] $[Hq(SCN)_4^{2-1}]$ ncreases. increases. PYRE)

add reactant, rxn goes \rightarrow add product, rxn goes \leftarrow

subtract reactant, rxn goes \leftarrow subtract product, rxn goes \rightarrow

End Quiz 6 End Test 3

Altering an Equilibrium Mixture: Changes in Pressure & Volume

 $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$

(a) A mixture of gaseous N₂, H₂, and NH₃ at equilibrium $(Q_c = K_c)$.



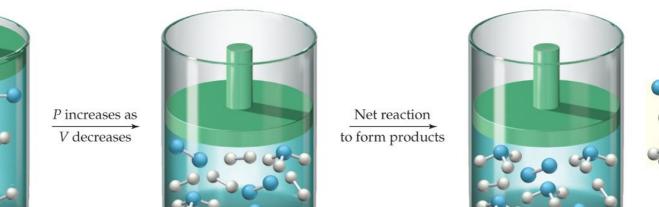
(b) When the pressure is increased by decreasing the volume, the mixture is no longer at equilibrium ($Q_c < K_c$).

(c) Net reaction occurs from reactants to products, decreasing the total number of gaseous molecules until equilibrium is re-established $(Q_c = K_c)$.

 $= N_2$

 $= NH_3$

 $= H_2$



<u>4 moles gas reactant → 2 moles gas product (this example)</u>
* increase P or decrease V rxn goes → (toward side w less moles gas)
* decrease P or increase V rxn goes ← (toward side w more moles gas)

Altering an Equilibrium Mixture: Changes in Pressure and Volume

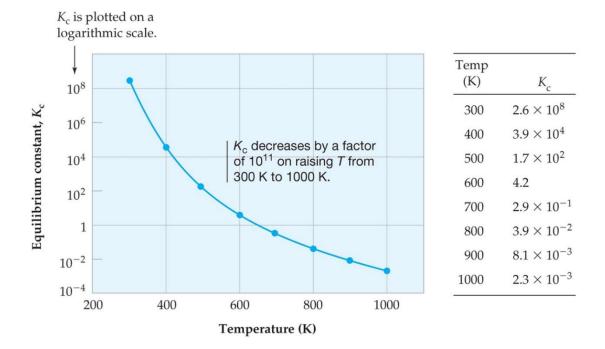
In general, when an equilibrium is disturbed by a change in volume that results in a corresponding change in pressure, Le Châtelier's principle predicts that

- an <u>increase in P (reducing V)</u> rxn goes toward side with less moles gas
- a <u>decrease in P (increasing V)</u> rxn goes toward side with more moles gas

Altering an Equilibrium Mixture: Changes in Temperature

 $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$

 $\Delta H^{\circ} = -2043$ kJ means + heat (heat is product)



As the temperature increases, the equilibrium shifts from products to reactants.

exothermic reaction $(-\Delta H^{\circ})$ rxn releases heat higher T = add heat rxn goes \leftarrow (to more reactant)

Altering an Equilibrium Mixture: Changes in Temperature

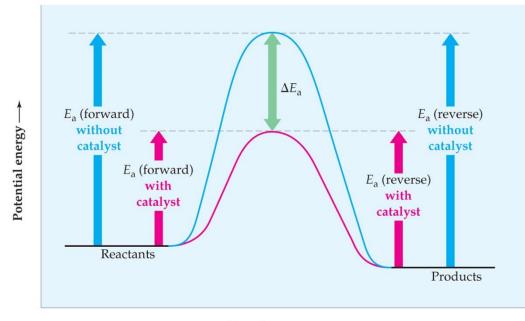
In general, when an equilibrium is disturbed by a change in temperature, Le Châtelier's principle predicts that

- the equilibrium constant (K = product /reactant) for an <u>exothermic reaction (negative ∆H^e)</u> decreases (get more reactant) as the temperature increases.
- the equilibrium constant for an <u>endothermic reaction</u> (positive ΔH^e) increases (get more product) as the temperature increases.

End 3/6 A, C section

The Effect of a Catalyst on Equilibrium

The activation energy for the **catalyzed pathway** (red curve) is lower than that for the **uncatalyzed pathway** (blue curve) by an amount ΔE_a .



A catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount. The catalyst therefore accelerates the forward and reverse reactions by the same factor, and the composition of the equilibrium mixture is unchanged.

catalysis – no effect on equilibrium

activation energy for catalyzed path is lower that for uncatalyzed -

same activation energy for both \rightarrow (forward) and \leftarrow (backward) reactions

HW 14.7: Le Châtelier's Principle: If a stress is applied to a reaction mixture *at equilibrium*, net reaction occurs in the direction that relieves the stress. (equilibrium shifts to undo stress applied to system)

 $2 A(g) + B(g) \rightarrow 3 C(g) + 2 D(g) \Delta H = negative (circle one parenthesis under which direction will equilibrium shift each letter)$ $hint: <math>\Delta H$ negative is exothermic = (+ heat, heat is product)

- (a) add A $\operatorname{rxn goes} [(\rightarrow) \text{ or } (\leftarrow)]$
- (b) remove B $\operatorname{rxn goes} [(\rightarrow) \text{ or } (\leftarrow)]$
- (c) add C $\operatorname{rxn goes} [(\rightarrow) \text{ or } (\leftarrow)]$
- (d) remove C rxn goes $[(\rightarrow) \text{ or } (\leftarrow)]$
- (e) higher T rxn goes $[(\rightarrow) \text{ or } (\leftarrow)]$ end Test 3 (c) & below

(f) higher P rxn goes $[(\rightarrow) \text{ or } (\leftarrow)]$ (assume all reactants & products in reaction are gases)

(g) higher V rxn goes $[(\rightarrow) \text{ or } (\leftarrow)]$ (assume all reactant & products in reaction are gases) **HW 14.7:** Le Châtelier's Principle: If a stress is applied to a reaction mixture *at equilibrium*, net reaction occurs in the direction that relieves the stress. (equilibrium shifts to undo stress applied to system)

 $2 A (g) + B(g) \rightarrow 3 C(g) + 2 D(g) \Delta H =$ negative (circle one parenthesis under which direction will equilibrium shift each letter) hint: ΔH negative is exothermic = (+ heat, heat is product)

- (a) add A $\operatorname{rxn goes} [(\rightarrow) \text{ or } (\leftarrow)]$
- (b) remove B $\operatorname{rxn goes} [(\rightarrow) \operatorname{or} (\leftarrow)]$
- (c) add C $\operatorname{rxn goes} [(\rightarrow) \text{ or } (\leftarrow)]$
- (d) remove C $\operatorname{rxn goes} [(\rightarrow) \operatorname{or} (\leftarrow)]$

(e) higher T rxn goes [(→) or (←)] end Test 3 (e) & below (higher T = add heat)
(f) higher P rxn goes [(→) or (←)] (assume all reactants & products in reaction are gases) (moves to fewer moles gas)

(g) higher V rxn goes $[(\rightarrow) \text{ or } (\leftarrow)]$ (assume all reactant & products in reaction are gases) (moves to fewer moles gas)