

## LECTURE TOPICS:

TODAY'S CLASS: finish Ch.16, start Ch.17

NEXT CLASS: continue Ch.17

(1)

**CAVE FORMATIONS:  
stalactites & stalagmites**

When limestone is dissolved... Limestone  $\text{CO}_2$  present in ground-water...

$$\text{Ca}^{2+}(\text{aq}) + 2 \text{HCO}_3^{-}(\text{aq}) \rightleftharpoons \text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$$

$\text{CaCO}_3$  all dissolves once sol'n saturated with  $\text{CO}_2$

Bubble  $\text{CO}_2(\text{g})$  through  $\text{CaCO}_3$  suspension

Why does this eqm *shift right* when system is "opened" ?

## 16.6 Le Châtelier's Principle: disturbing equilibria...

"If a change is imposed on a system at eqm, the position of the eqm will shift in a direction that tends to reduce that change"

IN REALITY: the reaction mixture is NOT sentient!

- If add a substance: disturbs balance of fwd/rev rates
  - ⇒ net rxn occurs in one direction until reaches eqm again
  - ⇒ new eqm state has "shifted" to different set of [ ]'s

**Le Châtelier's Principle is a conceptual short-cut, based on:**  
 comparing actual value of REACTION QUOTIENT,  $Q$   
 with known value of EQUILIBRIUM CONSTANT,  $K$ :

$$Q = \frac{[\text{product}]_o^n}{[\text{reactant}]_o^m}$$

**THINK IT THROUGH:**

After disturbing system: if  $Q > K$ ...

- Have "more" product than at eqm
- Reverse rxn will be faster than fwd...
- Will get NET rxn in reverse direction...
- ...until  $Q = K$  again! Then rates equal.

Disturbances we'll consider...

- (3) → changes in: 1.) concentration 2.) pressure 3.) temperature

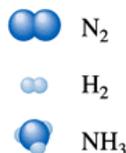
### 1. Disturbance: Change in concentration

**Response: rxn will proceed ("eqm will shift") in the direction that consumes some of the added component**

Disturb this eqm:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  Z.Fig. 13.8



(a) initial eqm mixture of:



$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Will react in 1 direction (NET!) until  $Q = K$  again...

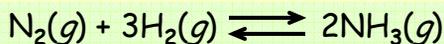


(c) New eqm position:  
 more N<sub>2</sub> (some was added...)  
 less H<sub>2</sub> (used in fwd rxn)  
 & more NH<sub>3</sub> (formed...)  
 than in original eqm position

(4)

**2. Disturbance: Change in pressure ( $\propto$  concentration...)**

**Response: If partial P of reactants/products affected, eqm will shift to counteract change in  $P_{TOTAL}$**



(a) initial eqm mixture of  $N_2$ ,  $H_2$  &  $NH_3$

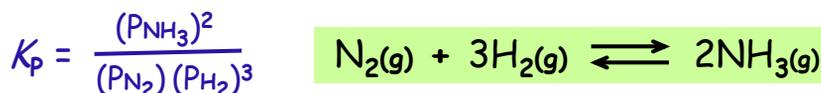
(b) Sudden  $V \downarrow \dots$   
"shifts to the right"  
(rxn proceeds fwd)  
to re-establish eqm

(c) New eqm position:  
more  $NH_3$ ;  
less  $N_2$  and  $H_2$ .

**WHY?**  $V \downarrow \Rightarrow$  all partial P's  $\uparrow$ ... so affects both rates...  
BUT: largest effect where stoich. coefficient is largest!

**SHORT CUT:** shifts to  $\downarrow P_{total} \Rightarrow$  rxn proceeds in direction that yields fewer moles of gas (shifts to reach new eqm)

**BUT... Why do rxns shift to counteract changes in  $P_{TOT}$ ?**



**If we compress the container by 2-fold:**

- all substances' partial pressures suddenly are doubled...
- rxn quotient has exponents: larger stoich. coeff  $\Rightarrow$  larger effect
- here:  $\uparrow$  in P of  $H_2$  has huge effect  $\Rightarrow$  fwd rxn speeds up most

$$\begin{aligned} Q_p &= \frac{(2 P_{NH_3})^2}{(2 P_{N_2})(2 P_{H_2})^3} \\ &= \frac{2^2(P_{NH_3})^2}{2(P_{N_2}) \cdot 2^3(P_{H_2})^3} \\ &= \frac{1}{4} \cdot \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} \end{aligned}$$

$$\Rightarrow Q_p = \frac{1}{4} K_p$$

**Thus:  $Q_p < K_p$**

• initial driving force to proceed **RIGHT** in this case

• **BUT NOTE THE RESULT:**

for this rxn, the fwd direction leads to net consumption of gases  $\Rightarrow$  **decrease in  $P_{TOT}$**

*(system appears to "know" that it was at eqm at a lower pressure, so it reacts to reduce  $P_{TOTAL}$  a bit to achieve eqm again... but remember: it does not know anything!)*

**Impact of P  $\Delta$ s on eqm position: shifts to counter the  $\Delta$  in P**  
 shift toward more reactants (shifts left)?  
 OR more products (shifts right)?

SOME GAS PHASE RXNS...	$\Delta n_{\text{gases}}$	If $\downarrow V$ or $\uparrow P_{\text{ext}}$	If $\uparrow V$ or $\downarrow P_{\text{ext}}$
$\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$			
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$			
$\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$			

**Important:** if we change  $P_{\text{TOTAL}}$  by adding an inert gas

- inert gas = any gas not involved in rxn, & won't react other ways
- none of reactants/products partial pressures change!  
 ⇒ no effect on fwd OR reverse rxn ⇒ no shift in eqm

## Effects of Changes on the System

1. Concentration
2. Pressure

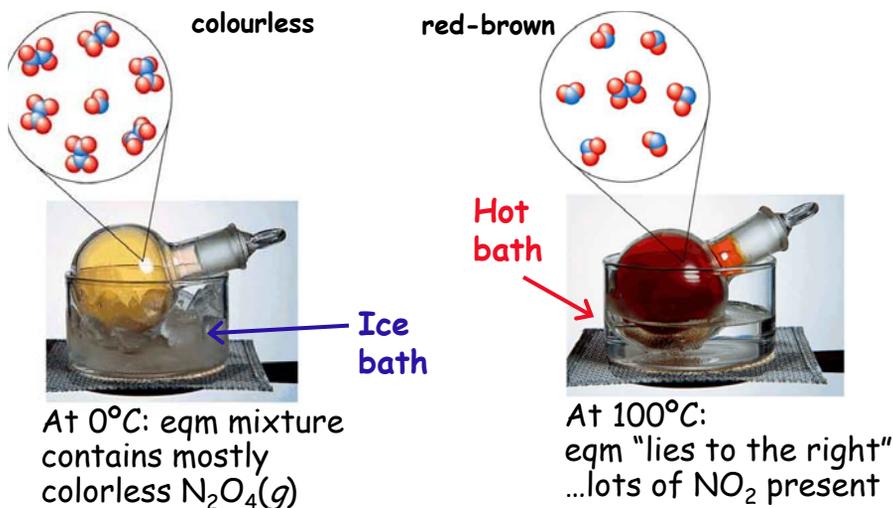
3. **Temperature:** think about fwd & reverse rxns as endothermic or exothermic (*i.e.*, which rxn requires E?)  
 → which direction's rate will change MORE?  
 → short cut: imagine energy as a reactant OR product  
 → remember: the value of  $K$  actually changes with T!

Picture energy diagram:  $E_a$ 's of fwd vs. reverse rxn...

### 3. Disturbance: Change in temperature

Response: if "energy added", rxn shifts to consume E

Shifting the  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  eqm by changing TEMP.

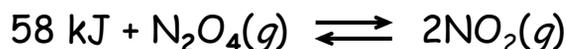


(9) IS THE FWD RXN EXOTHERMIC OR ENDOTHERMIC?

### Summary: effects of changes on an eqm system

- 1. Concentration:** the system will shift (*i.e.*, rxn will proceed in one direction) to use the added component.
  - 2. Pressure:** (partial pressures are like conc's...)
    - a.** Addition of inert gas **does not affect** eqm's position --  
→ partial P's of reactants/products unaffected!
    - b. Decreasing** volume: (↑ partial P's of ALL species...)  
→ rxn will proceed in direction that ↓ overall P...  
→ towards side with fewer moles of gas!
  - 3. Temperature:** think about fwd & reverse rxns as endothermic or exothermic (*i.e.*, which rxn requires E?)  
→ which direction's rate will change MORE?  
→ short cut: imagine energy as a reactant OR product  
→ remember: the value of  $K$  actually changes with T!
  - 4. What about adding a catalyst?**
    - Speeds up equilibration process
    - But: does not change  $\Delta G^\circ_{\text{rxn}}$
- (10) } No effect on position of equilibrium or size of  $K$

Consider disturbing an equilibrated mixture of...



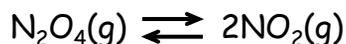
Change	Shift (rxn direction that will reestablish eqm...)
Addition of $\text{N}_2\text{O}_4(g)$	
Addition of $\text{NO}_2(g)$	
Removal of $\text{N}_2\text{O}_4(g)$	
Removal of $\text{NO}_2(g)$	
Addition of $\text{He}(g)$	
Decrease container volume	
Increase container volume	
Increase temperature	
Decrease temperature	

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Zumdahl's **TABLE 13.4**

Kotz Ch.16 #51: Dealing with gas mixtures &  $P_{\text{tot}}$

The equilibrium reaction:  
has been thoroughly studied  
(see Fig.16.6, 16.8).



- a) If the total pressure in a flask containing  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  gas at  $25^\circ\text{C}$  is 1.50 atm, and the value of  $K_p$  at this temperature is 0.148, what fraction of the  $\text{N}_2\text{O}_4$  has dissociated to  $\text{NO}_2$ ?

ANS: 0.15

- b) What happens to the fraction dissociated if the volume of the container is increased so that the total equilibrium pressure falls to 1.00 atm?

ANS: 0.189  
(eqm "shifts right")

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## Chapter 17: CHEMISTRY OF ACIDS & BASES

- Application of eqm concepts to  $H^+$ -transfer rxns in aqueous solution

### Chapter Outline

- 17.1 Acids, bases & the eqm concept
- 17.2 Brønsted concept of acids & bases
- 17.3 Water and the pH scale
- 17.4 Eqm constants for acids & bases
- 17.5 Eqm constants and acid-base rxns
- 17.6 Types of acid-base reactions
- 17.7 Calculations with eqm constants
- 17.8 Polyprotic acids & bases
- 17.9 Lewis concept of acids & bases
- 17.10 Molecular structure, bonding & acid-base behaviour

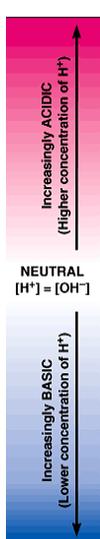
*But not in this same order...  
refer to the lecture readings.*

### Chapter Goals

- Use the Brønsted-Lowry and Lewis concepts of acids and bases
- Apply the principles of chemical equilibrium to acids and bases in aqueous solution
- Predict the outcome of reactions of acids & bases
- Understand the influence of structure and bonding on acid-base properties

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## 17.3 Water and the pH scale (review section 5.9)



**Definitions:**  $[H^+] = 10^{-pH}$   $\Rightarrow$   $pH = -\log[H^+]$

**Concentrated base:**  $[H^+] = 10^{-14} M$   $\Rightarrow$   $pH = 14$

**Concentrated acid:**  $[H^+] = 10^0 M$   $\Rightarrow$   $pH = 0$

In pure water:  $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$   $\Rightarrow$   $pH + pOH = 14$

$\Rightarrow$   $pH = -\log(1.00 \times 10^{-7})$  # sig. figs in concentration  
= 7.000 = # decimal places in pH

In neutral sol'n:  $[H_3O^+] = [OH^-] = 1 \times 10^{-7} M$   $\Rightarrow$   $pH = 7$

In acidic sol'n:  $[H_3O^+] > 1 \times 10^{-7} M$ ,  $[OH^-] < 1 \times 10^{-7} M$   $\Rightarrow$   $pH < 7$

In basic sol'n:  $[H_3O^+] < 1 \times 10^{-7} M$ ,  $[OH^-] > 1 \times 10^{-7} M$   $\Rightarrow$   $pH > 7$

pH of a soft drink:  $\sim 3.30 \Rightarrow$  acidic (phosphoric & citric acids)...

Means:  $[H_3O^+] \approx 10^{-4} - 10^{-3} M$  &  $[OH^-] \approx 10^{-10} - 10^{-11} M$

$$\begin{aligned}
 -\log[H_3O^+] &= 3.30 & [OH^-] &= 10^{-(14-pH)} \\
 [H_3O^+] &= 10^{-3.30} & &= 10^{-(14-3.30)} \\
 &= 5.0 \times 10^{-4} M & &= 10^{-(10.70)} \\
 & & &= 2.0 \times 10^{-11} M
 \end{aligned}$$

Notice:  $(5.0 \times 10^{-4})(2.0 \times 10^{-11}) = 1.0 \times 10^{-14} = K_w$

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## 17.3 Water and the pH scale (review section 5.9)

Water = "amphiprotic" = can both accept & donate H<sup>+</sup>



"Auto-  
ionization"  
of water

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

*[H<sub>2</sub>O] constant since ~pure liquid ⇒ not included...  
(in advanced treatment, value → 1 & disappears...)*

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (10^{-7})(10^{-7}) = 10^{-14}$$

Reactant-favoured,  
but will have **some ions present** in "pure" H<sub>2</sub>O.

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### IN AQUEOUS SOLUTION:

**[H<sub>3</sub>O<sup>+</sup>] & [OH<sup>-</sup>] ALWAYS related.**

This eqm is always running in the background & limits pH to 0-14.

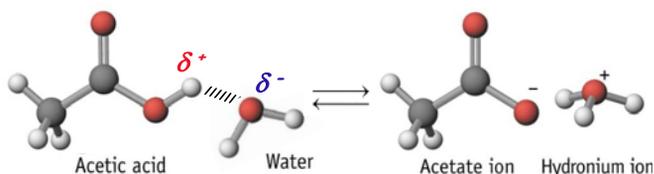
- Even if another source of H<sub>3</sub>O<sup>+</sup> (an acid) or OH<sup>-</sup> (a base) is present.
- Extra acid or base stays intact, undissociated, "on reserve"...

Acid-base reactions involve transfer of H<sup>+</sup> from acid to base.  
What we need to understand: **how it happens, and WHY ...**

## 17.1 Acids, bases & the equilibrium concept

Brønsted & Lowry's bright idea

Dissociation of acids & bases are reactions with water:

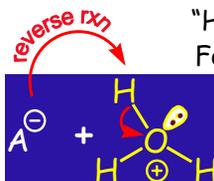
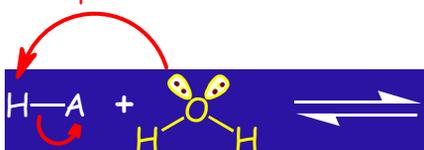


$$K = 1.8 \times 10^{-5}$$

IMPLIES: simple H-bonding dominates, but occasionally the interaction leads to full bond formation...

**Mechanism of H<sup>+</sup> transfer(s):** simple bimolecular process

lone pair attacks δ<sup>+</sup> H

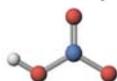


"HYDRONIUM" ion  
Formal charge on O  
= 6 - (2 + ½(6))  
= +1

## 17.2 Brønsted concept of acids & bases

**ACIDS** defined as  
**H<sup>+</sup> donors**

**Strong:** HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>  
**Weak:** CH<sub>3</sub>COOH, NH<sub>4</sub><sup>+</sup> & all others in 206...



⇒ solution's pH < 7

**BASES** defined as  
**H<sup>+</sup> acceptors**

**Strong:** OH<sup>-</sup> (others discussed later)  
**Weak:** CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, ...NH<sub>3</sub>, amines  
accept H<sup>+</sup> by sharing a lone pair, to form bond



⇒ solution's pH > 7

- more general than Arrhenius' definitions (acid<sub>(aq)</sub> ⇌ H<sup>+</sup>; base<sub>(aq)</sub> ⇌ OH<sup>-</sup>)
  - not restricted to aqueous solutions
  - based on how the reaction occurs!
- (17) → via base attacking acid to remove an H<sup>+</sup>

### Polyprotic acids/bases: can lose/gain more than one H<sup>+</sup>

**Table 17.1**

Acid Form	Amphiprotic Form	Base Form
H <sub>2</sub> CO <sub>3</sub> (carbonic acid)	HCO <sub>3</sub> <sup>-</sup> (hydrogen carbonate ion or bicarbonate ion)	CO <sub>3</sub> <sup>2-</sup> (carbonate ion)
H <sub>3</sub> PO <sub>4</sub> (phosphoric acid)	$\left\{ \begin{array}{l} \text{H}_2\text{PO}_4^- \text{ (dihydrogen phosphate ion)} \\ \text{HPO}_4^{2-} \text{ (hydrogen phosphate ion)} \end{array} \right\}$	PO <sub>4</sub> <sup>3-</sup> (phosphate ion)

↔ = amphoteric: can BOTH donate & accept H<sup>+</sup>

**Conjugate acid-base pairs:** HA + H<sub>2</sub>O ⇌ A<sup>-</sup> + H<sub>3</sub>O<sup>+</sup>  
Structures differ by ONE H<sup>+</sup> B + H<sub>2</sub>O ⇌ BH<sup>+</sup> + OH<sup>-</sup>

**Table 17.2**

	ACID	Base		CONJUGATE BASE	Conjugate acid
Hydrochloric acid	HCl	+ H <sub>2</sub> O	→	Cl <sup>-</sup>	+ H <sub>3</sub> O <sup>+</sup>
Hydrogen carbonate	HCO <sub>3</sub> <sup>-</sup>	+ H <sub>2</sub> O	⇌	CO <sub>3</sub> <sup>2-</sup>	+ H <sub>3</sub> O <sup>+</sup>
Carbonate ion	H <sub>2</sub> O	+ CO <sub>3</sub> <sup>2-</sup>	⇌	OH <sup>-</sup>	+ HCO <sub>3</sub> <sup>-</sup>
Ammonia	H <sub>2</sub> O	+ NH <sub>3</sub>	⇌	OH <sup>-</sup>	+ NH <sub>4</sub> <sup>+</sup>
Water	H <sub>2</sub> O	+ H <sub>2</sub> O	⇌	OH <sup>-</sup>	+ H <sub>3</sub> O <sup>+</sup>

## ASSIGNED READINGS:

### BEFORE NEXT CLASS:

**Read:** 16.6-16.7  
5.9 (pH review) & 17.1-17.3

**+ WORK ON Problems from Ch.16 & 17.1-3**

(don't wait until assigned for tutorial homework!)