

	Lectur	re 3 (9/11/20)
• Reading t	for today:	Ch2, 58-68
Problems	for today:	Ch2 (text) 5,6,9,11,14,15,17,20,22,
		24,29,35
NEXT		
• Reading:	Ch3, 75	
	Ch1, 16-20	
	Ch4, 115-110	6
• Problems:	Ch1 (text) 11	,13,16
	Ch4 (text) 12	











Type of Bond	Example	Typical Bond Energ (kJ ⋅ mol ⁻¹) (kd
Covalent	О—Н	460
	С—н С—С	⁴¹⁴ 348
Hydrogen bond	-0-H…0<	20



Hydrop	phobic Int	teractions	
Transfer of Hydrocarbons to Nonpolar Solvents Entropically Driven		nts is	
Process	$\frac{\Delta H}{(\mathbf{kJ}\cdot\mathbf{mol}^{-1})}$	$\frac{-T\Delta S}{(kJ\cdot mol^{-1})}$	$\frac{\Delta G}{(\text{kJ} \cdot \text{mol}^{-1})}$
		22.6	and a second second
CH_4 in $H_2O \Longrightarrow CH_4$ in C_6H_6	11.7	-22.6	-10.9
$\begin{array}{c} CH_4 \text{ in } H_2O \rightleftharpoons CH_4 \text{ in } C_6H_6 \\ \hline CH_4 \text{ in } H_2O \rightleftharpoons CH_4 \text{ in } CCl_4 \end{array}$	11.7 10.5	-22.6	-10.9
$\begin{array}{c} CH_4 \text{ in } H_2O \Longrightarrow CH_4 \text{ in } C_6H_6\\ \hline CH_4 \text{ in } H_2O \Longrightarrow CH_4 \text{ in } CCl_4\\ \hline C_2H_6 \text{ in } H_2O \Longrightarrow C_2H_6 \text{ in benzene} \end{array}$	11.7 10.5 9.2	-22.6 -25.1	- 10.9 - 12.1 - 15.9
$\begin{array}{c} CH_4 \text{ in } H_2O \Longrightarrow CH_4 \text{ in } C_6H_6\\ \hline CH_4 \text{ in } H_2O \Longrightarrow CH_4 \text{ in } CCl_4\\ \hline C_2H_6 \text{ in } H_2O \Longrightarrow C_2H_6 \text{ in benzene}\\ \hline C_2H_4 \text{ in } H_2O \Longrightarrow C_2H_4 \text{ in benzene}\\ \end{array}$	11.7 10.5 9.2 6.7	-22.6 -22.6 -25.1 -18.8	- 10.9 - 12.1 - 15.9 - 12.1
CH ₄ in H ₂ O \implies CH ₄ in C ₆ H ₆ CH ₄ in H ₂ O \implies CH ₄ in CCl ₄ C ₂ H ₆ in H ₂ O \implies C ₂ H ₆ in benzene C ₂ H ₄ in H ₂ O \implies C ₂ H ₄ in benzene C ₂ H ₄ in H ₂ O \implies C ₂ H ₄ in benzene	11.7 10.5 9.2 6.7 0.8	-22.6 -22.6 -25.1 -18.8 -8.8	-10.9 -12.1 -15.9 -12.1 -8.0
$\begin{array}{c} \text{CH}_4 \text{ in } \text{H}_2\text{O} \Longrightarrow \text{CH}_4 \text{ in } \text{C}_6\text{H}_6 \\\\ \hline \text{CH}_4 \text{ in } \text{H}_2\text{O} \Longrightarrow \text{CH}_4 \text{ in } \text{CCl}_4 \\\\ \hline \text{C}_2\text{H}_6 \text{ in } \text{H}_2\text{O} \Longrightarrow \text{C}_2\text{H}_6 \text{ in benzene} \\\\ \hline \text{C}_2\text{H}_4 \text{ in } \text{H}_2\text{O} \Longrightarrow \text{C}_2\text{H}_4 \text{ in benzene} \\\\ \hline \text{C}_2\text{H}_2 \text{ in } \text{H}_2\text{O} \Longrightarrow \text{C}_2\text{H}_2 \text{ in benzene} \\\\ \hline \text{Benzene in } \text{H}_2\text{O} \Longrightarrow \text{liquid benzene}^a \end{array}$	11.7 10.5 9.2 6.7 0.8 0.0	-22.6 -22.6 -25.1 -18.8 -8.8 -17.2	- 10.9 - 12.1 - 15.9 - 12.1 - 8.0 - 17.2











Bond Energies of Important Noncovalent Interactions

Type of Bond	T Example	ypical Bond Ene (kJ • mol ⁻¹)	rgy (kcal · mol ⁻¹
Covalent	О—Н С—Н С—С	${}^{460}_{414}_{348}$. 95
Noncovalent			
Ionic interaction	$-COO^{-} \cdots {}^{+}H_{3}N-$ @ ~3	Å 86	20
Hydrogen bond	-0-H…O<	20	4.7
Van der Waals interactions	H $HC - H \dots H - C -$		
	H H	0.3	0.07
Hydrophobic interactions (p	er –CH ₂ –)	26	6







Physical Properties of Water
Learning Goals: Concepts about water
 Water molecules, which are polar, can form hydrogen bonds with other molecules.
 In ice, water molecules are maximally hydrogen bonded in a crystalline array, but in liquid water, still with many
hydrogen bonds, they rapidly break and re-form in irregular networks.
 The attractive forces acting on biological molecules include ionic interactions, hydrogen bonds, and van der Waals interactions.
 Polar and ionic substances can dissolve in water.
 The hydrophobic effect explains the exclusion of nonpolar groups as a way to maximize the entropy of water molecules.
 Amphiphilic substances form micelles or bilayers that hide their hydrophobic groups while exposing their hydrophilic groups to water.











Pofinitions of Asia	onization of Water
Deminitions of Acid	<u>is and bases.</u>
HA ≒ HB ≒	H ⁺ + A [−] If dissociation is >water: ACID → H ⁺ + B [−] If dissociation is <water: base="" ←<br="">When B[−] associates with protons, it leaves a net difference in [OH[−]]</water:>
2H ₂	$O \leftrightarrows H_3O^+ + OH^-$
In other words:	A proton donor is an Acid (HA) A proton acceptor is a Base (B ⁻)
Likewise:	The resulting anion from acid dissociation is called the conjugate base (A ⁻) The resulting protonated base is called a conjugate acid (HB)
These are Bronsted/Lo	wry definitions





Ionization of Water

Example 1:

What is the ratio of [A']/[HA] for a weak acid with a $pK_a = 6.0$ at pH 6.0? $pH = pK_a + \log [A']/[HA]$

Example 1: What is the ratio of [A:]/[HA] for a weak acid with a $pK_x = 6.0$ at pH 6.0? pH = $pK_x + \log [A']/[HA]$ $6.0 = 6.0 + \log [A']/[HA]$ $0 = \log [A']/[HA]$ antilog of 0 is 1; therefore: 1 = [A']/[HA], which means that there are equal amounts of [A'] and [HA], or [HA] is 50% disociated at a pH equal to its pK_x .

	ociation Constants and pK _a of Some Acids	
TABLE 2-4 Dissociation Constants and pK Values at 25°C of Some Acid		Some Acids
Acid	K	рK
Oxalic acid	5.37×10^{-2}	1.27 (pK ₁)
H ₃ PO ₄	7.08×10^{-3}	2.15 (pK ₁)
Formic acid	1.78×10^{-4}	3.75
Succinic acid	6.17×10^{-3}	4.21 (pK ₁)
Oxalate ⁻	5.37×10^{-5}	4.27 (pK ₂)
Acetic acid	1.74×10^{-5}	4.76
Succinate ⁻	2.29×10^{-6}	5.64 (pK2)
2-(N-Morpholino)ethanesulfonic acid (MES)	8.13×10^{-7}	6.09
H ₂ CO ₃	4.47×10^{-7}	6.35 (pK1)"
Piperazine-N,Nº-bis(2-ethanesulfonic acid) (PIPES)	1.74×10^{-7}	6.76
H ₂ PO ₄	1.51×10^{-7}	6.82 (pK ₂)
3-(N-Morpholino)propanesulfonic acid (MOPS)	$7.08 imes 10^{-8}$	7.15
N-2-Hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES)	3.39×10^{-8}	7.47
Tris(hydroxymethyl)aminomethane (Tris)	8.32×10^{-9}	8.08
Borie acid	5.75×10^{-10}	9.24
NH ⁺ ₄	5.62×10^{-10}	9.25
Glycine (amino group)	1.66×10^{-10}	9.78
HCO3	4.68×10^{-11}	10.33 (pK2)
Piperidine	7.58×10^{-12}	11.12
HPO2-	4.17×10^{-13}	12.38 (pK ₃)





Example 2: What is the ratio of [A']/[HA] for a the same weak acid with a pK₄ = 6.0 at pH 2.5? pH = pK₄ + log [A']/[HA] 2.5 = 6.0 + log [A']/[HA] -3.5 = log [A']/[HA]

Ionization of Water

Example 2:

```
What is the ratio of [A']/[HA] for a the same weak acid with a pK_x = 6.0 at pH 2.5?

pH = pK_x + \log [A']/[HA]

2.5 = 6.0 + log [A']/[HA]

-3.5 = log [A']/[HA]

antilog of -3.5 is 3.2 x 10<sup>4</sup>; therefore:

[A']/[HA] = 3.2 x 10<sup>4</sup>

[HA] is MUCH higher than [A'] (1 A' for every 3125 HA; 1/3125 = 3.2 x 10<sup>4</sup>), meaning that it is only

0.032% dissociated.

If the initial total [HA] was 0.1 M, then [HA] + [A'] = 0.1 and [A'] = 0.1 - [HA]. Substitution of this

value for [A'] into the ratio gives:

(0.1 - [HA])/[HA] = 3.2 x 10<sup>4</sup>

[HA] = 0.1/1.00032 = 0.09997 M and [A-] = 0.000032 M
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Does this make sense? Go back to the reaction:

$HA \quad \leftrightarrows \quad H^+ + A^-$

At low pH, [H+] is high, forcing the equilibrium to the left = more HA, less A-

Lonization of Water Example 3: Histidine is an important amino acid and the imidzole group can dissociate at physiological pH. There is an equilibrium with HHis* and His*; HHis* ←→ His* + H* What is the pH of a 0.1 M solution of HHis*CI'?



