

**HANDOUT SET**

**GENERAL CHEMISTRY II**

## Periodic Table of the Elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA												IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 <b>H</b> 1.00794																	2 <b>He</b> 4.00262
2	3 <b>Li</b> 6.941	4 <b>Be</b> 9.0122											5 <b>B</b> 10.811	6 <b>C</b> 12.011	7 <b>N</b> 14.0067	8 <b>O</b> 15.9994	9 <b>F</b> 18.9984	10 <b>Ne</b> 20.179
3	11 <b>Na</b> 22.9898	12 <b>Mg</b> 24.305											13 <b>Al</b> 26.98154	14 <b>Si</b> 28.0855	15 <b>P</b> 30.97376	16 <b>S</b> 32.066	17 <b>Cl</b> 35.453	18 <b>Ar</b> 39.948
4	19 <b>K</b> 39.0983	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.9559	22 <b>Ti</b> 47.88	23 <b>V</b> 50.9415	24 <b>Cr</b> 51.9961	25 <b>Mn</b> 54.9380	26 <b>Fe</b> 55.847	27 <b>Co</b> 58.9332	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.59	33 <b>As</b> 74.9216	34 <b>Se</b> 78.96	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80
5	37 <b>Rb</b> 85.4678	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.9059	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.9064	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.9055	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.8682	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.710	51 <b>Sb</b> 121.75	52 <b>Te</b> 127.60	53 <b>I</b> 126.9045	54 <b>Xe</b> 131.29
6	55 <b>Cs</b> 132.9054	56 <b>Ba</b> 137.34	57 <b>La*</b> 138.91	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.9479	74 <b>W</b> 183.85	75 <b>Re</b> 186.207	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.9665	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.383	82 <b>Pb</b> 207.2	83 <b>Bi</b> 208.9804	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)
7	87 <b>Fr</b> (223)	88 <b>Ra</b> 226.0254	89 <b>Ac**</b> 227.0278	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (264)	108 <b>Hs</b> (265)	109 <b>Mt</b> (266)	110 (270)	111 (272)	112 <b>***</b> (277)						

*Lanthanides	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.9077	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.96	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.925	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.930	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.9342	70 <b>Yb</b> 173.04	71 <b>Lu</b> 174.967
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**Actinides	90 <b>Th</b> 232.038	91 <b>Pa</b> 231.0659	92 <b>U</b> 238.0289	93 <b>Np</b> 237.0482	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (260)
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Mass numbers in parenthesis are the mass numbers of the most stable isotopes. As of 1997 elements 110-112 have not been named.

\*\*\*Peter Armbruster and Sigurd Hofman synthesized a single atom at the Heavy-Ion Research Center in Darmstadt, Germany in 1996. The atom survived for 280  $\mu$ s after which it decayed to element 110 by loss of an  $\alpha$ -particle

**Chapter 10 and 11**  
**Structure and Bonding**



## TABLE OF ELECTRONEGATIVITIES

H 2.1																	He --			
Li 1.0	Be 1.6															Ne --				
Na 0.9	Mg 1.3															Ar --				
		K 0.8		Ca 1.3	Sc 1.4	Ti 1.5	V 1.6	Cr 1.7	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 2.8	Kr --
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 2.1	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe 2.6			
Cs 0.8	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At 2.2	Rn --			
Fr 0.7	Ra 0.9	Ac 1.1																		

	0.5 - 0.9
	1.0 - 1.4
	1.5 - 1.9
	2.0 - 2.4

	2.5 - 2.9
	3.0 - 3.5
	3.6 - 3.9
	4.0

## TABLE OF AVERAGE BOND ENERGIES

BOND	BOND ENERGY, kJ/mol	BOND	BOND ENERGY, kJ/mol	BOND	BOND ENERGY, kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736	F—F	159
H—I	297	C—Cl	339	Cl—Cl	243
				Br—Br	193
				I—I	151

## TABLE OF AVERAGE BOND LENGTHS

BOND	BOND LENGTH, pm	BOND	BOND LENGTH, pm	BOND	BOND LENGTH, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—Cl	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266




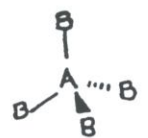
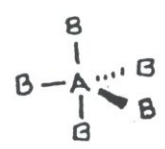

## Writing Lewis Structures

1. Count valence electrons for all atoms.  
add  $1 e^-$  for every negative charge if a polyatomic ion  
subtract  $1 e^-$  for every positive charge if an ion
2. Draw a skeletal structure (be reasonable, some rules apply)  
H is always a terminal atom  
Certain atoms do not normally complete the octet, namely;  
H, He, Li, Be, and B (Boron completes the octet with a formal charge of +1)  
In polyatomic ions the least electronegative atom is the central atom  
H 1 bond only  
B 3 bonds normally  
C 4 bonds  
N 3 bonds (uncharged species) 4 bonds (charged species)  
O 2 bonds (normally) 1 or 3 bonds if non-zero formal charges are present  
F 1 bond normally. The other halogens are 1 bond when terminal.  
When in doubt, try something.
3. Place a pair of electrons between every pair of atoms which are bonded.  
Subtract the number of electrons used for bonding from the total number of valence electrons available.
4. Complete the octet on the remaining atoms with lone-pairs.  
Remember, certain atoms do not fill their octet
5. If the octets cannot be filled on all appropriate atoms, make multiple bonds.  
Structures that exhibit resonance are usually stable  
Certain atoms can expand their octet as necessary, namely the period 3 and greater elements.

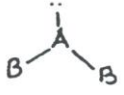






## GEOMETRY/SHAPE REVIEW VSEPR THEORY

Scheme      Bonding Picture      Geometry\*      Shape†

### Compounds without lone pairs on central atom

AB <sub>2</sub>	B—A—B	Linear	Linear
AB <sub>3</sub>		Trigonal Planar	Trigonal Planar
AB <sub>4</sub>		Tetrahedral	Tetrahedral
AB <sub>5</sub>		Trigonal bipyramidal	Trigonal bipyramidal
AB <sub>6</sub>		Octahedral	Octahedral

### Compounds with lone pairs on central atom

:AB <sub>2</sub>		Trigonal planar	Bent
:AB <sub>2</sub>		Tetrahedral	Bent
:AB <sub>3</sub>		Tetrahedral	Trigonal pyramidal
:AB <sub>4</sub>		Trigonal bipyramidal	Distorted tetrahedral
:AB <sub>2</sub>		Trigonal bipyramidal	Linear
:AB <sub>5</sub>		Octahedral	Square pyramidal
:AB <sub>4</sub>		Octahedral	Square planar

\*Geometry refers to the *electronic* geometry

†Shape refers to the *molecular* shape or *molecular* geometry



## VALENCE BOND THEORY AND HYBRIDIZATION

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**Hybridization:** Mixing of non-equivalent atomic orbitals (AO's) to generate a new set of degenerate hybrid orbitals.

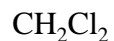
1. Does not occur on isolated atoms – only atoms used in bonding. Does not occur on terminal atoms.
2. Hybridization occurs to the extent that the electronic geometry predicted by VSEPR is produced.
3. Orbitals being hybridized must be in the same principle quantum shell.
4. Number of hybrids produced is equal to number of AO's used.
5. Requires energy: stabilization obtained by bond energy and repulsion stabilization.
6. Covalent bonds form as normal – *i.e.*, orbital overlap to share a pair of electrons.



## Lewis Symbolism, Molecular Structure (VSEPR), and Hybridization (VB Theory)

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1. Draw the Lewis structures for the following molecules or ions:



2. Draw the Lewis structure of benzene,  $\text{C}_6\text{H}_6$ . Benzene is a 6-carbon ring molecule. Show also the conventionally used abbreviated drawing of benzene.
3. Draw the Lewis structure of parahydroxybenzoic acid, (PABA,  $\text{C}_7\text{H}_6\text{O}_3$ ). PABA is an excellent UV-radiation absorber once used in sunscreens. As the name implies, PABA contains the benzene ring and the carboxylic acid group. The prefix “para” means “across the ring”.

5. Two kinds of covalent bonds exist; nonpolar covalent and polar covalent. Describe the carbon-hydrogen bond in  $\text{CH}_4$  as either polar or nonpolar.
6. Draw the Lewis structures of the following molecules or ions. For each, indicate the electronic geometry, molecular geometry, hybridization (if any) of central atoms, and whether the molecule or ion possesses a permanent dipole moment.



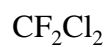
electronic geometry	_____	_____	_____
molecular geometry	_____	_____	_____
hybridization	_____	_____	_____
Dipole Moment	_____	_____	_____



electronic geometry	_____	_____	_____
molecular geometry	_____	_____	_____
hybridization	_____	_____	_____
Dipole Moment	_____	_____	_____



electronic geometry	_____	_____	_____
molecular geometry	_____	_____	_____
hybridization	_____	_____	_____
Dipole Moment	_____	_____	_____



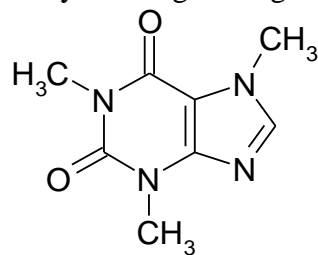
electronic geometry	_____	_____	_____
molecular geometry	_____	_____	_____
hybridization	_____	_____	_____
Dipole Moment	_____	_____	_____

NO

PBr<sub>5</sub>SF<sub>6</sub>

electronic geometry	_____	_____	_____
molecular geometry	_____	_____	_____
hybridization	_____	_____	_____
Dipole Moment	_____	_____	_____

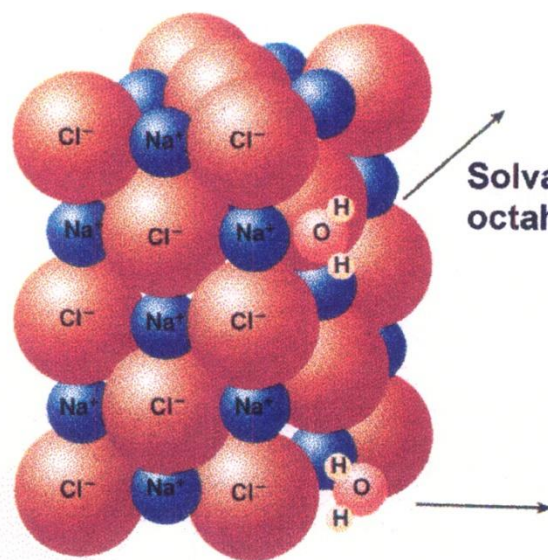
7. Shown below is the molecule caffeine. Describe the hybridization of every atom that uses hybridized atomic orbitals for bonding. Determine the approximate bond angles. Also indicate the type of bonds formed between atoms (*i.e.*,  $\sigma(sp^2-p)$ ,  $\pi(p-p)$ , etc.) Notice that lone-pairs are omitted but assumed present; this convention is typical of many drawings of organic molecules.



# **Chapter 12, 13**

## **Intermolecular Forces: Liquids and Solids and Solutions**

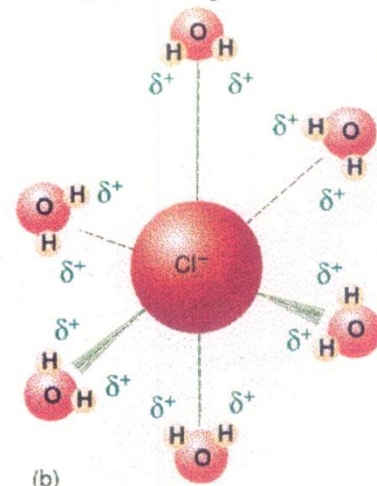
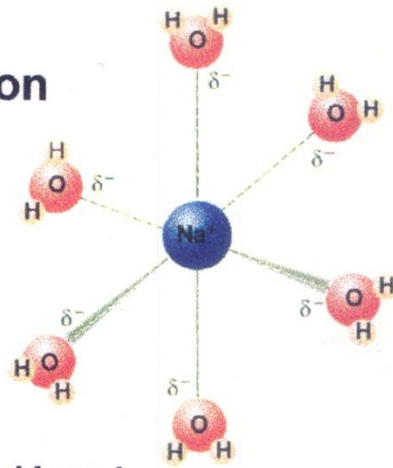
# Example of the ion-dipole interaction in the dissolution of NaCl in water



(a)

By D Green, mod from Kroschwitz

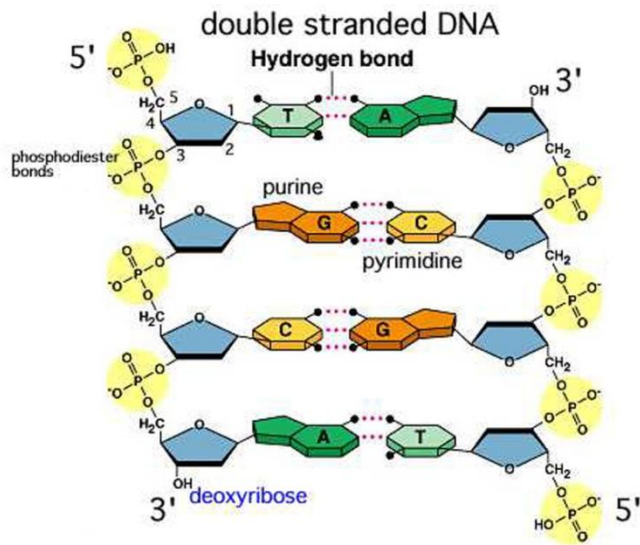
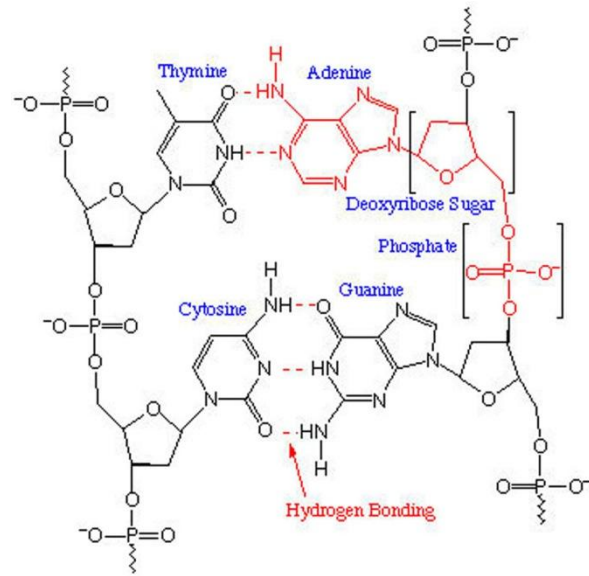
Solvated ions in octahedral symmetry



(b)



# Hydrogen Bonding in the Double-Helix



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Dipole Moments of Selected Molecules. Unspecified temperatures are assumed to be 25°C

<b>Compound</b>	<b>Dipole Moment (D)</b>	
Cyclohexane	0	(20°C)
Cyclopentane	0	
Heptane	0	
Iso-octane	0	(20°C)
Pentane	0	
Hexane	0.08	
Toluene	0.31	(20°C)
1,4-Dioxane	0.45	
<i>o</i> -Xylene	0.45	
Dichloromethane	1.14	
Chloroform	1.15	
Ethyl Ether (diethyl ether)	1.15	(20°C)
2-Chlorophenol	1.24	
Dimethyl ether	1.30	
Methyl <i>t</i> -Butyl Ether	1.32	
<i>o</i> -Cresol	1.35	
Phenol	1.49	
Chlorobenzene	1.56	
Bromobenzene	1.56	
<i>p</i> -Cresol	1.58	
<i>m</i> -Cresol	1.61	
Ethyl Alcohol (ethanol)	1.66	(20°C)
2-Propanol	1.66	(30°C)
Methanol	1.69	(20°C)
Glyme	1.71	
1-Butanol	1.75	
Tetrahydrofuran	1.75	
Isobutyl Alcohol	1.79	
Ethylene Dichloride	1.83	
<i>n</i> -Butyl Acetate	1.84	(22°C)
Water	1.87	(20°C)
Ethyl Acetate	1.88	
1,3-Dioxane	1.90	
1-Chlorobutane	1.90	
2-Methoxyethanol	2.04	
3-Chlorophenol	2.08	
<i>o</i> -Dichlorobenzene	2.14	(20°C)
4-Chlorophenol	2.24	
Pyridine	2.37	
Acetone	2.69	(20°C)
Methyl <i>n</i> -Propyl Ketone	2.70	(20°C)
Methyl Ethyl Ketone	2.76	
1-Propanol	3.09	(20°C)
2-Nitrophenol	3.12	
Acetonitrile	3.44	(20°C)
Dimethyl Acetamide	3.72	
3-Nitrophenol	3.76	
<i>N,N</i> -Dimethylformamide	3.86	
<i>N</i> -Methylpyrrolidone	4.09	(30°C)
Dimethyl Sulfoxide	4.1	
4-Nitrophenol	4.72	
Propylene Carbonate	4.94	(20°C)

## Intermolecular Forces

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1. From *Lange's Handbook of Chemistry*, 13<sup>th</sup> Ed. (McGraw Hill), we find  $\Delta H_{\text{vap}}$  for H<sub>2</sub>O to be 40.7 kJ/mol. We also know the vapor pressure of water at 100°C. Calculate the vapor pressure of water at 25.0°C in a closed container.

2. The vapor pressure and associated temperatures for ethanol were found in the *CRC Handbook of Chemistry and Physics*. Determine  $\Delta H_{\text{vap}}$  for ethanol from these data. Is it different from water? Why?

v.p. (mm Hg)	Temp (°C)
40.0	19.0
400.0	63.5
760.0	78.4

3. The vapor pressures measured at several temperatures for benzene are shown in the table. Calculate the normal boiling point (1 atm) for benzene. (The literature value is 80.1°C)

Temp (°C)	v.p. (kPa)
0.0	4.11
10.0	6.77
20.0	10.78
40.0	25.00

4. How much energy is needed to melt an ice cube (at constant temperature) that has a mass of 28.0 g?  
( $\Delta H_{\text{fusion}} = 6.02 \text{ kJ mol}^{-1}$ )
5. How much energy is required to convert 28.0 g of ice at  $-12.0^\circ\text{C}$  to steam at  $100^\circ\text{C}$  in a closed vessel?  
(Hint: What information not listed will be needed?)



4. What is the molal concentration of the solution prepared by dissolving 60.0 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ , 180.2 g/mol) in 100.0 mL of water?
5. What quantity of methanol ( $\text{CH}_3\text{OH}$ ) must be added to 250.0 g of water to make a 0.25 *m* solution?

## A Short Interlude: Vapor Pressure Lowering

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The colligative property of vapor pressure lowering is best explained from the perspective of *entropy*. Entropy is an important “driving force” (certainly a misnomer phrase, but let’s keep going) in physical and chemical processes. Entropy is a measure of the number of different microstates (“microscopic states”) a system can be in. “Disorder” is only one possible microstate: entropy is really more complicated than that and includes all of the possible microscopic configurations the system can have.

Molecules at the surface of a liquid enter the gas phase, in part, because they have sufficient kinetic energy to escape the intermolecular forces holding them to the liquid. Accompanying this phase transition is a concomitant increase in entropy; *i.e.*, the entropy of the liquid is lower than the entropy of the gas.

Now, make a solution of a non-volatile solute in the liquid. The  $\Delta H_{\text{vap}}$  for a dilute solution changes very little but the entropy of the solution starts higher than the pure liquid. There are more possible microstates that the solution can be in with the added solute. However, the vapor above the solution has the same entropy as the vapor above the pure solvent. Having the same  $\Delta H_{\text{vap}}$ , the energy required to release a solvent molecule from the liquid remains unchanged.

This means that the entropy gain for the solvent going from solution to vapor is comparatively less than that for pure solvent going to the vapor phase. There is less “driving force” to go into the vapor phase and, thus, a lower vapor pressure.

Some texts, and even some teachers, explain this phenomenon as resulting from the solute particles somehow “blocking” the escape of solvent molecules. This is just wrong. Think about it: how many solute particles would you need at the surface to prevent the solvent from escaping? What if the intermolecular forces between solute and solvent were stronger than solvent and solvent? I suspect this “blocking” explanation is given as a simplified rationalization for vapor pressure lowering but it succeeds only in introducing a misconception and avoidance of thermodynamics.

### Problem

The vapor pressure of water at 25°C is 23.8 mmHg. What is the vapor pressure of a solution of 10.0 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ , 180.16 g/mol) in 100.0 g of water?

## Solutions II: Colligative Properties

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1. What is the boiling point of the solution prepared to be 10.0 g of  $\text{C}_2\text{H}_6\text{O}_2$  ( $62.07 \text{ g mol}^{-1}$ ) dissolved in 100.0 g of water?
2. What is the predicted freezing point of the solution from (1)?
3. How many gallons of antifreeze (ethylene glycol) must be added to 4.0 gallons of water to lower the freezing point of the solution to  $-10.0^\circ\text{F}$  (a fairly bad winter day on the east coast)? (Hint: You will probably need to use the *CRC Handbook of Chemistry and Physics*, *Merck Index*, or other resource to get some of the information you need.)



4. A solution of the male hormone, testosterone, containing 0.363 g of the hormone in 5.00 g of benzene has a freezing point of  $4.27^{\circ}\text{C}$ . What is the molar mass of testosterone? The freezing point of pure benzene is  $5.50^{\circ}\text{C}$ . Additional data: A solution of 1.13 g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 10.00 g of benzene had a freezing point of  $0.99^{\circ}\text{C}$ .)

5. Testosterone contains only carbon, hydrogen, and oxygen. The percentage composition of the molecule is 79.12% C and 9.79% H. What is the molecular formula and accurate molar mass?

## Colligative Properties: Freezing Point Depression, Vapor Pressure Lowering, Boiling Point Elevation Additional Problems

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1. Adding a nonvolatile ionic solute to water has what effect on the boiling point of the solvent?  
...  Does not affect the b.p.  
...  Lower the b.p.  
...  Raises the b.p.  
...  Cannot tell without more information, such as concentration
  
2. What is the van't Hoff factor?
  
  
  
  
  
  
  
  
  
  
3. What is a *colligative property* (a definition; not "it's freezing point depression", etc.)
  
  
  
  
  
  
  
  
  
  
4. Give an example of a colligative property other than freezing point depression.
  
  
  
  
  
  
  
  
  
  
5. What is the equation that relates the freezing point depression and concentration? Define each variable.
  
  
  
  
  
  
  
  
  
  
6. Calculate the molal concentration of a sucrose ( $C_{12}H_{22}O_{11}$ ) solution that is prepared by dissolving 10.0 g of the solid in 150.0 g of water.

7. What is the freezing point of the solution prepared in question 6? The molal freezing point depression constant for water is  $1.86\text{ }^{\circ}\text{C}/\text{m}$ .
8. A certain pheromone from the gypsy moth has a percentage composition of 79.12% C, 9.79% H and 11.09% O. A solution containing 0.363 g of the compound in 5.00 g of benzene freezes at  $4.27^{\circ}\text{C}$ . What is the molar mass of the pheromone and what is its molecular formula?  $K_{f,\text{benzene}} = 5.12^{\circ}\text{C}/\text{m}$ .
9. Assuming complete dissociation of the solid, what is the predicted melting point of a  $1.5\text{ m}$  solution of sodium chloride?

10. Draw a typical cooling curve for a pure solvent. Draw the cooling curve for a 1-m solution of the same solvent which has a molal freezing point depression constant of  $2.0\text{ }^{\circ}\text{C}/\text{m}$ . Identify each region of the curve.

11. The vapor pressure of water at  $25.0^{\circ}\text{C}$  is 23.8 torr. What is the vapor pressure of a solution of 10.0 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ,  $180.2\text{ g mol}^{-1}$ ) dissolved in 100.0 g of water?

12. Assume no deviation from ideal behavior, what is the vapor pressure at  $25^{\circ}\text{C}$  of the solution prepared by mixing 50.0 mL of benzene with 50.0 mL of hexane? Some important information is given in the table. Not all information may be necessary.

<b>Property</b>	<b>Hexane</b>	<b>Benzene</b>
Formula	$\text{C}_6\text{H}_{14}$	$\text{C}_6\text{H}_6$
Vapor Pressure at $25^{\circ}\text{C}$ (mm Hg)	151.6	95.1
Density (g/mL)	0.659	0.874
Normal boiling point ( $^{\circ}\text{C}$ )	68.7	80.1

13. Starting with a 454 g block of ice at 0.0°C, how much energy is needed to melt the ice and heat the liquid water produced to 100°C but not evaporate the water? (some possibly useful information:  $\Delta H_{\text{fusion}} = 6.02 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{vap}} = 40.7 \text{ kJ mol}^{-1}$ , specific heat, water = 4.18 J/mol K)

14. The enthalpy of combustion of methane, CH<sub>4</sub>, is -890 kJ/mol. What mass of methane will be consumed in the above process? Assume 100% energy transfer to the system.

15. If the gas flowrate of the methane to the burner of a stove is 5 L/min at 25°C and assuming complete heat transfer from combustion to the container containing the ice, quantitatively predict how long it would take for the ice to be converted to water at 100°C?

## An Application of the van't Hoff Factor in Acid/Base Equilibrium

---

The freezing point of 0.10 *m* acetic acid is  $-0.19^{\circ}\text{C}$ . What is the van't Hoff factor for acetic acid at this concentration and what fraction (in percentage) of the acetic acid molecules are ionized?

Hints:

$$i = \frac{\Delta T_{\text{measured}}}{\Delta T_{\text{theoretical}}}$$

$$\text{percentage ionization} = \frac{[\text{H}^+]}{C_{\text{total acetic acid}}} \times 100 = \frac{[\text{CH}_3\text{CO}_2^-]}{C_{\text{total acetic acid}}} \times 100$$

# **Chapter 14**

## **Chemical Kinetics**

# CHEMICAL KINETICS

## CHAPTER 15

---

### INTRODUCTION

A properly written chemical equation tells that a reaction may occur to yield certain products. The rate of the reaction or how fast the reaction proceeds is, however, only experimentally determined. The field of chemistry dedicated to the study of reaction rates and the mechanism by which products are formed is known as chemical kinetics and mechanisms. The focus of lecture for this chapter is on chemical kinetics.

### GOALS

1. You should be able to describe the rate of reaction as a change in concentration per change in time for any species in the reaction.
2. You should be able to take graphical data and deduce average and instantaneous rates.
3. From experimental data, it is possible to derive the rate law and from the rate law calculate rates of reactions for experimental conditions.
4. Three reaction orders have been explicitly covered: zeroth-, first-, and second-order. An understanding of the how a rate plot would look and how to analyze for each of these is important.
5. You should be comfortable with using the integrated rate law for 1st- and 2nd-order reactions and understand how to calculate and use half-life.

### DEFINITIONS

You should have a working knowledge of at least these terms and any others used in lecture.

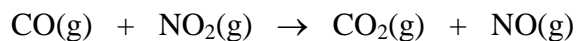
First-order reaction	Overall reaction order	Instantaneous rate
Second-order reaction	Integrated rate law	Average rate
Zeroth-order reaction	Half-life	Initial rate
Rate law	Rate constant	Mechanism



## Chemical Kinetics, Reaction Rates, and the Rate Law

---

1. Consider the following reaction



The kinetic data of initial reaction rate were collected for the initial concentration conditions. The rates are average initial rates, obtained graphically from the original kinetic data. Use the method of initial rates to determine the rate law and rate constant.

	[CO] <sub>0</sub> (M)	[NO <sub>2</sub> ] <sub>0</sub> (M)	Initial Rate (M/h)
1	$5.1 \times 10^{-4}$	$0.35 \times 10^{-4}$	$3.4 \times 10^{-8}$
2	$5.1 \times 10^{-4}$	$0.70 \times 10^{-4}$	$6.8 \times 10^{-8}$
3	$5.1 \times 10^{-4}$	$0.18 \times 10^{-4}$	$1.7 \times 10^{-8}$
4	$1.0 \times 10^{-3}$	$0.35 \times 10^{-4}$	$6.8 \times 10^{-8}$
5	$1.5 \times 10^{-3}$	$0.35 \times 10^{-4}$	$10.2 \times 10^{-8}$

- 
2. A first-order reaction proceeds with a rate constant of  $0.020/\text{s}$ . If the initial concentration of the reactant is  $0.012 \text{ M}$ , what will be the concentration after  $30 \text{ s}$ ?
3. Referring to the previous question, what fraction of starting material remains after  $15 \text{ s}$ ?
4. What is the half-life of this reaction?

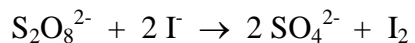
5. Radioactive isotopes decay obeying a first-order kinetic rate law. Tritium, a radioactive isotope of hydrogen, has a half-life of 12.3 y. It has a natural abundance of  $10^{-18}$  percent (by mol). What mass of tritium (atomic weight 3.016 u) is present in 1000 kg of water? After 100 years, what mass of tritium will remain?

## Temperature Dependence on the Rate Constant

---

### 1. Experiment

Determine the activation energy for the reaction



The rate law for the reaction is

$$\text{Rate} = k[\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

Experimental Setup:

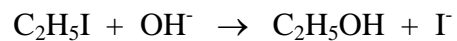
	Volumes of Reagents (mL)						Reaction Time (s)
	Temp (°C)	0.20 M NaI	0.010 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	2% Starch Indicator	Water	0.20 M K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	
1							
2							
3							
4							
5							

For reasons we won't go into here:

$$\text{Rate} = \frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{t_{\text{rxn}}} = \frac{1}{2} \frac{\Delta[\text{S}_2\text{O}_3^{2-}]_0}{t_{\text{rxn}}}$$

	Rate (M/s)	Rate Constant
1		
2		
3		
4		
5		

2. The reaction to produce ethyl alcohol from ethyl iodide

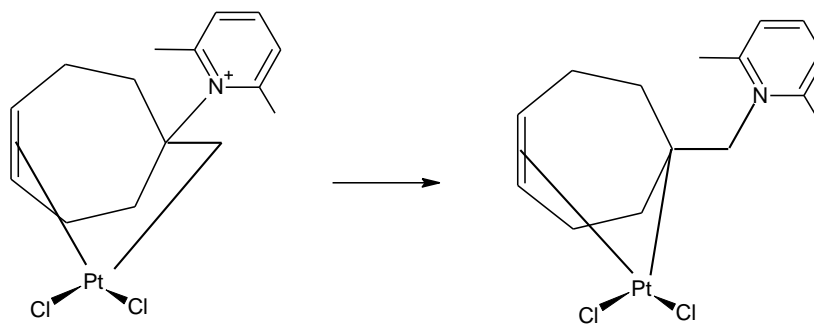


was studied at several temperatures. The following rate constants for the reaction were determined:

Temperature (°C)	Rate Constant (M <sup>-1</sup> s <sup>-1</sup> )
15.83	5.03 × 10 <sup>-5</sup>
32.02	3.68 × 10 <sup>-4</sup>
59.75	6.71 × 10 <sup>-3</sup>
90.61	0.119

Determine the activation energy of the reaction graphically and by using the Arrhenius equation.

3. The following reaction is possibly important in the catalytic hydrogenation of alkene hydrocarbons. Determine the activation energy for the reaction.



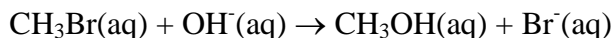
What is the rate constant for the reaction at 25°C?

Data	
Temp (°C)	Rate Constant (s <sup>-1</sup> )
-60.0	$1.3 \times 10^{-3}$
-70.0	$2.4 \times 10^{-4}$
-80.0	$5.8 \times 10^{-5}$

## Chemical Kinetics: Additional Problems

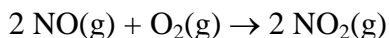
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1. In the reaction



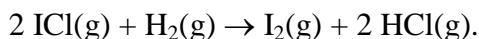
when the  $\text{OH}^-$  concentration alone was doubled, the rate doubled; when the  $\text{CH}_3\text{Br}$  concentration alone was increased by a factor of 1.2, the rate increased by a factor of 1.2. Write the rate law for the reaction.

2. In the reaction



when the  $\text{NO}$  concentration alone was doubled, the rate increased by a factor of 4; when both the  $\text{NO}$  and the  $\text{O}_2$  concentrations were increased by a factor of 2, the rate increased by a factor of 8. What is the rate law for the reaction?

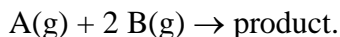
3. The following kinetic data were obtained for the reaction



Experiment	Initial Concentration (mmol L <sup>-1</sup> )		Initial Rate (mmol·L <sup>-1</sup> ·s <sup>-1</sup> )
	[ICl] <sub>o</sub>	[H <sub>2</sub> ] <sub>o</sub>	
1	1.5	1.5	$3.7 \times 10^{-7}$
2	3.0	1.5	$7.4 \times 10^{-7}$
3	3.0	4.5	$2.2 \times 10^{-6}$
4	4.7	2.7	?

- (a) Write the rate law for the reaction.  
(b) From the data, determine the value of the rate constant.  
(c) Use the data to predict the reaction rate for Experiment 4.

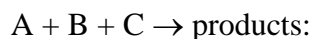
4. The following kinetic data were obtained for the reaction



Experiment	Initial Concentration (mmol·L <sup>-1</sup> )		Initial Rate (mmol·L <sup>-1</sup> ·s <sup>-1</sup> )
	[A] <sub>o</sub>	[B] <sub>o</sub>	
1	0.60	0.30	1.6
2	0.20	0.30	1.4
3	0.60	0.10	4.2
4	0.17	0.25	?

- What is the order with respect to each reactant and the overall order of the reaction?
- Write the rate law for the reaction.
- From the data, determine the value of the rate constant.
- Use the data to predict the reaction rate for Experiment 4.

5. The following data were obtained for the reaction



Experiment	Initial Concentration (mmol L <sup>-1</sup> )			Initial Rate (mmol A · L <sup>-1</sup> s <sup>-1</sup> )
	[A] <sub>o</sub>	[B] <sub>o</sub>	[C] <sub>o</sub>	
1	1.25	1.25	1.25	8.7
2	2.50	1.25	1.25	17.4
3	1.25	3.02	1.25	50.8
4	1.25	3.02	3.75	457
5	3.01	1.00	1.15	?

- Write the rate law for the reaction.
  - What is the order of the reaction?
  - Determine the value of the rate constant.
  - Use the data to predict the reaction rate for Experiment 5.
6. Determine the rate constant for each of the following first- order reactions, in each case expressed for the rate of loss of A:
- A → B, given that the concentration of A decreases to one-half its initial value in 1000 s
  - A → B, given that the concentration of A decreases from 0.67 mol L<sup>-1</sup> to 0.53 mol L<sup>-1</sup> in 25 s
  - 2 A → B + C, given that [A]<sub>o</sub> = 0.153 mol L<sup>-1</sup> and that after 115 s the concentration of B rises to 0.034 mol L<sup>-1</sup>.
7. Determine the rate constant for each of the following first- order reactions:
- 2 A → B + C, given that the concentration of A decreases to one-fourth its initial value in 38 min
  - 2 A → B + C, given that [A]<sub>o</sub> = 0.039 mol L<sup>-1</sup> and that after 75 s the concentration of B increases to 0.0095 mol L<sup>-1</sup>
  - 2 A → 3 B + C, given that [A]<sub>o</sub> = 0.040 mol L and that after 8.8 min the concentration of B rises to 0.030 mol L<sup>-1</sup>.
- In each case, write the rate law for the rate of loss of A.
8. Dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>, decomposes by first-order kinetics with a rate constant of 3.7 × 10<sup>-5</sup> s<sup>-1</sup> at 298 K.
- What is the half-life (in hours) for the decomposition of N<sub>2</sub>O<sub>5</sub> at 298 K?
  - If [N<sub>2</sub>O<sub>5</sub>]<sub>o</sub> = 0.0567 mol L<sup>-1</sup>, what will be the concentration of N<sub>2</sub>O<sub>5</sub> after 3.5 h?
  - How much time (in minutes) will elapse before the N<sub>2</sub>O<sub>5</sub> concentration decreases from 0.0567 mol L<sup>-1</sup> to 0.0135 mol L<sup>-1</sup>?



9. The half-life for the first-order decomposition of A is 355 s. How much time must elapse for the concentration of A to decrease to (a) one-fourth; (b) 15% of its original value; (c) one-ninth of its initial concentration?



**Chapter 15 – 17**

**Chemical Equilibrium**

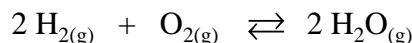


## Equilibrium I: Basic Principles and Calculations

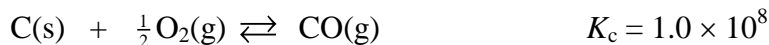
**Remember the important associations about mass actions and equilibrium constant expressions:**

- ✓ Reverse the direction the equation is written → invert  $K$
- ✓ Add chemical equations → multiply the  $K$ 's for the reactions
- ✓ Increase stoichiometric coefficients by a factor → raise  $K$  to the power of factor

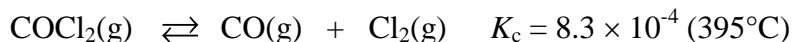
1. What is the calculated  $K_c$  for



given the the following reactions:

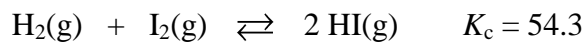


2. For the reaction:

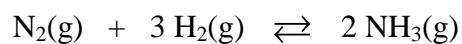


- a. What direction will the reaction proceed if 0.100 mol of  $\text{COCl}_2$  is placed in a 2.0 L container and heated to  $395^\circ\text{C}$ ?
  
  
  
  
  
  
  
  
  
  
- b. What direction will the reaction proceed if 0.030 mol of each gas are placed in a 2.0 L vessel and heated?
  
  
  
  
  
  
  
  
  
  
- c. For question a, what is the final concentration of each gas?
  
  
  
  
  
  
  
  
  
  
- d. For question b, what is the final concentration of each gas?

3. A quantity of 0.10 mol of I<sub>2</sub> and 0.10 mol H<sub>2</sub> are placed in a 1.00-L reaction vessel at 430°C. Calculate the equilibrium concentration of all species after equilibrium has been established.



4. The  $K_c$  for the reaction



At 300°C is 0.45. Predict whether the reaction will proceed to the right, left, or is already at equilibrium when 0.10 mol N<sub>2</sub>, 0.30 mol H<sub>2</sub>, and 0.2 mol NH<sub>3</sub> are placed in a 2.00-L container and heated to 300°C. If a reaction occurs, what is the final concentration of each species?

5. The following quantities of reagents are introduced into a 1.00-L reaction vessel: 0.15 mol  $\text{H}_2$ , 0.23 mol  $\text{I}_2$ , and 0.015 mol  $\text{HI}$ . The reaction vessel is then thermostatted at  $430^\circ\text{C}$ . Convince yourself that the system is not at equilibrium and will shift right (to produce more product). What are the equilibrium concentrations of all species? (See problem 3 for additional information.)
6. For question 5, what will be the effect on the equilibrium concentrations if the volume of the container is reduced to 500.0 mL with no loss of reagents.

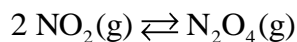
7. Consider the system at equilibrium in problem 4: what will be the new equilibrium concentrations if the volume of the container is reduced to 1.00 L with no loss of reactants or products?
8. Consider the system at equilibrium in problem 4: what will be the new equilibrium concentrations if the total pressure in the container is increased by adding 1.0 atm of helium gas?



## Equilibrium Problems Using $K_p$

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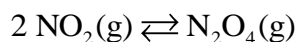
1. Nitrogen dioxide is a component of the brown smog seen over some industrialized cities. The brown nitrogen dioxide participates in an equilibrium with colorless dinitrogen tetraoxide according to the equation



The  $K_{p,\text{atm}}$  for the reaction is 7.5 at 298K (25°C). What is the partial pressure of each gas (in atm) if 0.10 mol of  $\text{N}_2\text{O}_4$  is placed in a 1.0 L container, sealed, and allowed to come to equilibrium at 298 K?

Unimportant information pertaining to the problem: The  $\text{N}_2\text{O}_4$  is transferred as a solid at -100°C then the reaction vessel is sealed and the  $\text{N}_2\text{O}_4$  allowed to vaporize at the experimental temperature.

2. Nitrogen dioxide is a component of the brown smog seen over some industrialized cities. The brown nitrogen dioxide participates in an equilibrium with colorless dinitrogen tetraoxide according to the equation



The  $K_{p,\text{atm}}$  for the reaction is 7.5 at 298K. What is the partial pressure of each gas (in atm) if a  $\text{NO}_2/\text{N}_2\text{O}_4$  mixture, already at equilibrium, is introduced into a container to a total pressure of 150 mmHg?

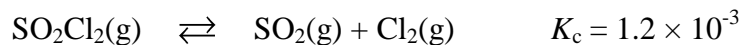
## Equilibrium II: A Couple More Equilibrium Problems

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1. A solution of 0.1 M acetic acid is about 1.4% ionized in water as measured by solution's electrical conductivity. What is  $K_c$  for



2. A quantity of 0.050 mol of  $\text{SO}_2$  gas and 0.025 mol of  $\text{Cl}_2$  gas are introduced into an evacuated 1.75 L flask and the following equilibrium is established at 303 K:



What are the final concentrations of each gas?

## Some Relative Acid-Conjugate Base Strengths

---

<b>Strong Acids</b>		$K_a$	<b>Conjugate Bases</b>	
perchloric acid	HClO <sub>4</sub>	large	perchlorate	ClO <sub>4</sub> <sup>-</sup>
hydroiodic acid	HI	large	iodide	I <sup>-</sup>
hydrobromic acid	HBr	large	bromide	Br <sup>-</sup>
hydrochloric acid	HCl	large	chloride	Cl <sup>-</sup>
sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	large	hydrogen sulfate	HSO <sub>4</sub> <sup>-</sup>
nitric acid	HNO <sub>3</sub>	large	nitrate	NO <sub>3</sub> <sup>-</sup>

<b>Weak Acids</b>			<b>Conjugate Bases</b>	
hydrogen sulfate	HSO <sub>4</sub> <sup>-</sup>	$1.1 \times 10^{-2}$	sulfate	SO <sub>4</sub> <sup>-</sup>
nitrous acid	HNO <sub>2</sub>	$7.2 \times 10^{-4}$	nitrite	NO <sub>2</sub> <sup>-</sup>
formic acid	HCO <sub>2</sub> H	$1.8 \times 10^{-4}$	formate	HCO <sub>2</sub> <sup>-</sup>
acetic acid	CH <sub>3</sub> COOH	$1.8 \times 10^{-5}$	acetate	CH <sub>3</sub> COO <sup>-</sup>
carbonic acid	H <sub>2</sub> CO <sub>3</sub>	$4.4 \times 10^{-7}$	hydrogen carbonate	HCO <sub>3</sub> <sup>-</sup>
ammonium ion	NH <sub>4</sub> <sup>+</sup>	$5.6 \times 10^{-10}$	ammonia	NH <sub>3</sub>
hydrogen carbonate	HCO <sub>3</sub> <sup>-</sup>	$4.8 \times 10^{-11}$	carbonate	CO <sub>3</sub> <sup>2-</sup>
ammonia	NH <sub>3</sub>	very small	amide ion	NH <sub>2</sub> <sup>-</sup>



4. What is the  $K_a$  of nitrous acid if a 0.050 M solution has a pH of 2.34?
5. What is the pH of 0.010 M ammonia?  $K_b = 1.8 \times 10^{-5}$
6. Assuming that  $K_a = 1.75 \times 10^{-5}$  for acetic acid, what is  $K_b$  for acetate ion? What is the pH of 0.010 M sodium acetate?

## Equilibrium IV: Polyprotic Acid-Base Equilibrium

---

1. Calculate the approximate pH of a solution prepared to be 0.0010 M malonic acid ( $\text{H}_2\text{C}_3\text{H}_2\text{O}_4$ ,  $K_1 = 1.5 \times 10^{-3}$ ,  $K_2 = 2.0 \times 10^{-6}$ ).

2. Calculate the concentration of all species in 0.10 M  $\text{H}_3\text{PO}_4$ .

$$K_1 = 7.5 \times 10^{-3} \quad K_2 = 6.2 \times 10^{-8} \quad K_3 = 4.8 \times 10^{-13}$$

3. Calculate the pH of the solution prepared to be 0.015 M sodium malonate ( $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4$ )





3. A 10.0 mL quantity of 0.1 M HCl is mixed with 95 mL of 0.15 M sodium nitrite. What is the pH of the new solution?

4. What is the calculated pH of the solution formed by mixing 10.0 mL of 0.15 M NaOH with 85 mL of 0.10 M benzoic acid?

## Titration Problems

---

1. In 1 or 2 sentences, explain back-titration.
  
  
  
  
  
  
  
  
  
  
2. Name and give the formulas for any 2 different substances used in common antacids.
  
  
  
  
  
  
  
  
  
  
3. Write the reaction of HCl with one of the two substances listed in question 2. If you cannot answer question 2, write the reaction of HCl with barium hydroxide.
  
  
  
  
  
  
  
  
  
  
4. To a 0.100 g sample of an antacid was added 50.00 mL of 0.100 M HCl. The antacid tablet dissolved and CO<sub>2</sub> gas was produced. The solution was boiled and cooled to remove the last of the CO<sub>2</sub>. Phenolphthalein was added to the solution and the excess HCl titrated with standard 0.100 M NaOH to the phenolphthalein endpoint. It required 3.00 mL of the NaOH.
  - a. What color is the phenolphthalein endpoint?
  
  
  
  
  
  
  
  
  
  
  - b. What is the number of moles of HCl neutralized per gram of antacid?
  
  
  
  
  
  
  
  
  
  
  - c. What is the percentage CaCO<sub>3</sub> in the antacid?

5. 25 mL of 0.1 M acetic acid is titrated with 0.1 M NaOH. Calculate the pH of the solution after the addition of the following amounts of base. What acid-base indicator would be best to indicate endpoint?

0 mL of NaOH

1 mL

5 mL

15 mL

25 mL

30 mL

For personal extra credit, calculate more points and plot the curve of pH vs Volume of base added. Then compare this curve to that obtained by titrating 25 mL of 0.1 M HCl with 0.1 M NaOH.

# **Chapter 19**

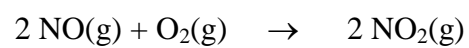
## **Thermodynamics**



## Thermodynamics I: Basic Problems

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Consider the reaction



1. Calculate  $\Delta G^\circ$  from  $\Delta H^\circ$  and  $\Delta S^\circ$  at  $25^\circ\text{C}$
2. Calculate  $\Delta G^\circ$  from standard free energies of formation.
3. Calculate the thermodynamic equilibrium constant,  $K_p$ .

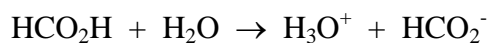
4. Determine the direction the reaction would proceed and the free energy when starting pressure of each gas is 0.33 atm.

5. What will be the total pressure in the container at equilibrium?

6. Estimate the  $K_p$  at 100.0°C assuming  $\Delta H_f^\circ$  and  $\Delta S_f^\circ$  remain constant at this temperature.



7. The standard free energy,  $\Delta G^\circ$ , for the acid dissociation of formic acid



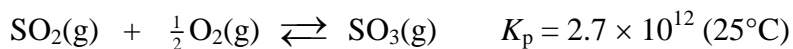
is 21.4 kJ/mol. Determine the direction that the reaction will proceed and free energy of the reaction, in kJ/mol, when a mixture of formic acid and sodium formate are prepared with an initial concentration of 0.20 M formic acid and 0.10 M sodium formate in neutral pH water.

8. What is the pH of the final solution from problem 7? (Hint: don't get so hung up in thermodynamics calculations that you forget this is an equilibrium problem.)

## Thermodynamics II: The Equilibrium Constant as a Function of Temperature

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1. The Ostwald process is used to make sulfuric acid from sulfur trioxide, which is itself made from the combustion of sulfur. The first product in the combustion of sulfur is sulfur dioxide which then reacts with excess oxygen to form sulfur trioxide.



The sulfur trioxide produced is then passed through a fine mist of water. The sulfur trioxide reacts with the water to produce sulfuric acid.



Calculate the  $\Delta H^\circ$  for the reaction of sulfur trioxide with water.

Calculate the equilibrium constant for the reaction at the boiling point of sulfuric acid (340°C).