

# DAWSON COLLEGE

## DEPARTMENT OF CHEMISTRY & CHEMICAL TECHNOLOGY

### FINAL EXAMINATION CHEMISTRY 202-NYB-05

May 18, 2012

14:00 – 17:00

Print your Name: \_\_\_\_\_

Student Number: \_\_\_\_\_

#### MARK DISTRIBUTION

**INSTRUCTORS:**      *Please circle the name of your instructor:*

J. Ali	D. Baril	Y. Brouillette
I. Dionne	M. Di Stefano	M. Haniff
	S. Mutic	G. Rahil

#### **INSTRUCTIONS:**

This exam set consists of **16** questions. Please ensure that your copy of this examination is complete.

**Answer all questions in the space provided.**

1. Calculators may not be shared. Programmable calculators are not permitted.
2. No books or extra paper are permitted.
3. In order to obtain full credit, you must show the method used to solve all problems involving calculations and express your answers to the correct number of significant figures.
4. Your attention is drawn to the College policy on cheating.
5. A Periodic Table with constants is provided.
6. If a mathematical equation is used to solve a problem, the equation should be clearly written.

#### **USEFUL DATA:**

Avogadro's Number  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Gas Constant  $R = 0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $= 8.314 \text{ L}\cdot\text{kPa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $= 8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

1 atm = 101.3 kPa = 760 mmHg = 760 torr

1 J = 1 kg·m<sup>2</sup>·s<sup>-2</sup> = 1 kPa·L

101.3 J = 1 L·atm

1.	/	8
2.	/	5
3.	/	6
4.	/	5
5.	/	9
6.	/	6
7.	/	8
8.	/	3
9.	/	6
10.	/	6
11.	/	6
12.	/	9
13.	/	6
14.	/	7
15.	/	5
16.	/	4
Sig. fig.	/	1
<b>Total:</b>	<b>/</b>	<b>100</b>

### Question 1

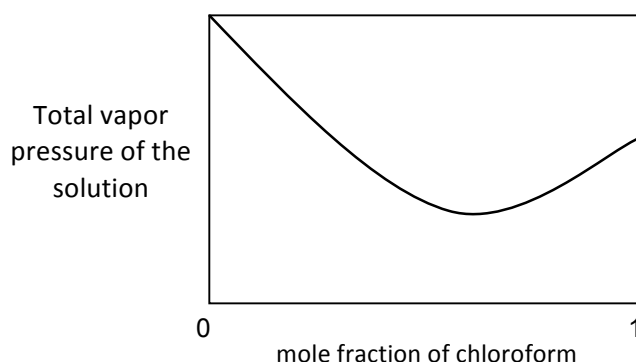
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- a. A 1.00 L concentrated KOH solution contains 655 g KOH. The solution density is 1.456 g/mL. Calculate the molality ( $m$ ) of this solution. (4 marks)

- 
- b. You are asked to prepare an aqueous solution of ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) with a mole fraction of 0.095. If you use 545 g of water, what mass of ethylene glycol should you use? (4 marks)

## Question 2

- a. The following plot shows the vapor pressure of various solutions of chloroform and acetone at some temperature.



Indicate whether the following statements are true or false:

(2.5 marks)

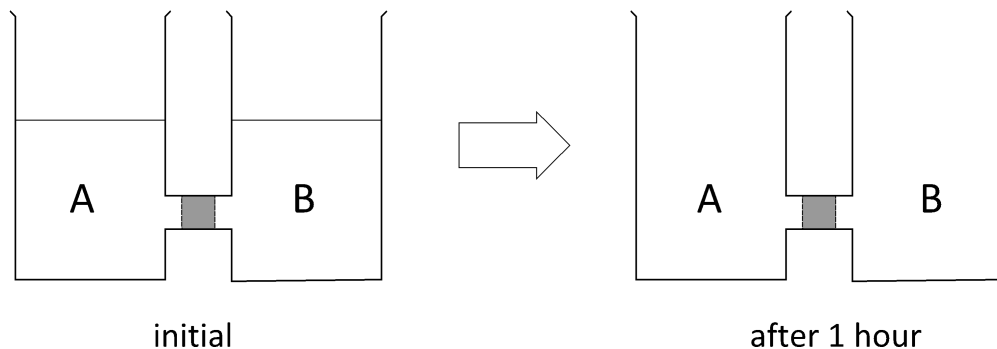
	True	False
i. The solution exhibits negative deviation from Raoult's law.	<input type="checkbox"/>	<input type="checkbox"/>
ii. $\Delta H$ for mixing this solution is endothermic.	<input type="checkbox"/>	<input type="checkbox"/>
iii. The intermolecular forces between chloroform and acetone are weaker in solution than in either pure chloroform or pure acetone.	<input type="checkbox"/>	<input type="checkbox"/>
iv. Pure chloroform has a higher vapor pressure than pure acetone.	<input type="checkbox"/>	<input type="checkbox"/>
v. The solution with a mole fraction of chloroform of 0.6 will have a lower boiling point than either pure chloroform or pure acetone.	<input type="checkbox"/>	<input type="checkbox"/>

- b. The vapor pressure of a solution containing 53.6 g glycerin ( $C_3H_8O_3$ , 92.10 g/mol nonvolatile, covalent compound) in 133.7 g ethanol ( $C_2H_5OH$ , 46.07 g/mol) is 113 torr at 40°C. Calculate the vapor pressure of pure ethanol at 40°C. Assume ideal behavior. (2.5 marks)

answer: \_\_\_\_\_

### Question 3

- a. A solution called A is prepared by dissolving 56.75 g glucose,  $C_6H_{12}O_6$ , (180.15 g/mol, a soluble non ionic solid) in enough distilled water to make 1.00 L solution at room temperature ( $25^\circ C$ ). This solution is isotonic with human blood (same osmotic pressure) and placed in part A of the container. A sodium chloride aqueous solution, called B, with an osmotic pressure of 6.0 atm is added to part B. Both parts are separated by a semi permeable membrane (only water molecule can pass). Draw on the container “after 1 hour” the level of the two liquids in both sides when the equilibrium will be reached. Assume NaCl is 100% dissociated. (3 marks)



- b. A red blood cell is actually a small “container” made up of a semipermeable membrane. What would happen to the volume of the red blood cell if it is submerged in: (1 mark)

	bigger	no change	smaller
i. solution A at $10^\circ C$ (assume red blood cell to be at $25^\circ C$ )	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
ii. solution B at $25^\circ C$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

- c. Consider the following aqueous solutions of salts completely ionized:

- i. 4 m potassium Iodite, KI
- ii. 3 m sodium sulfate,  $Na_2SO_4$
- iii. 3.5 m ammonium phosphate  $(NH_4)_3PO_4$

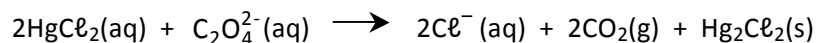
List the given solutions in increasing order of freezing point: (2 marks)

$\text{_____} < \text{_____} < \text{_____}$   
*lowest freezing point* *highest freezing point*

Question 4

a. For the following reaction,

(1 marks)

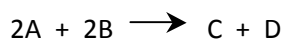


if the rate of disappearance (or consumption) of  $\text{C}_2\text{O}_4^{2-}$  is  $5.6 \times 10^{-5} \text{ M/min}$  what is the rate of formation of  $\text{Cl}^-$ ?

answer : \_\_\_\_\_

b. The initial rate for the reaction,

(4 marks)



was measured using initial concentrations of A and B. The results are summarized in the table:

Experiment	[A], M	[B], M	Initial rate, $\text{M} \cdot \text{s}^{-1}$
1	0.185	0.133	$3.35 \times 10^{-4}$
2	0.185	0.266	$1.35 \times 10^{-3}$
3	0.370	0.133	$6.75 \times 10^{-4}$

i. Write the rate law.

answer : \_\_\_\_\_

ii. What is the overall reaction order?

answer : \_\_\_\_\_

iii. What is the value of the rate constant, with units, for experiment 3?

answer : \_\_\_\_\_

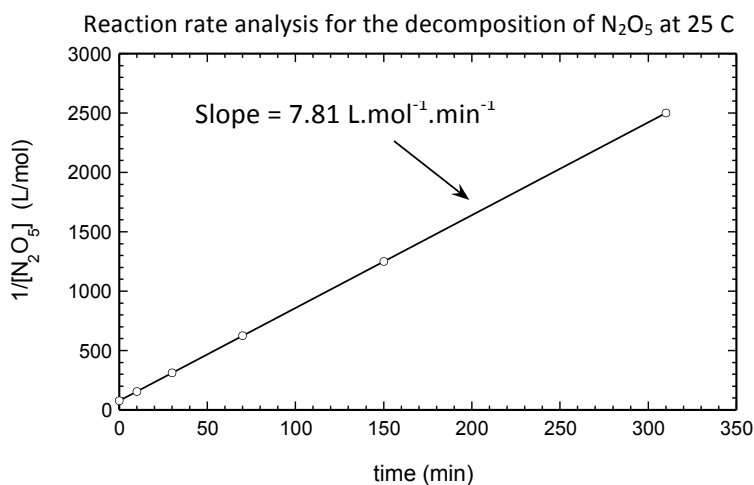
### Question 5

a. For the reaction:



(5 marks)

the following graph was made:



i. What order is the rate law for this reaction?

answer : \_\_\_\_\_

ii. What is the half-life of this reaction if the initial concentration is  $1.28 \times 10^{-2} \text{ M}$ ?

answer : \_\_\_\_\_

b. For the same reaction:  $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ , a catalyst was introduced. Measurements showed the rate of reaction was directly proportional to the concentration of  $\text{N}_2\text{O}_5$  with a rate constant of  $0.055 \text{ min}^{-1}$  at  $25^\circ\text{C}$ . (4 marks)

i. What order is the rate law for this catalyzed reaction?

answer : \_\_\_\_\_

ii. Calculate the time that it will take for the  $[\text{N}_2\text{O}_5]$  to fall from  $1.28 \times 10^{-2} \text{ M}$  to  $0.32 \times 10^{-2} \text{ M}$  with the catalyst at  $25^\circ\text{C}$ .

answer i. order: \_\_\_\_\_

answer ii. time with catalyst: \_\_\_\_\_

# Question 6

a. Consider this two-step mechanism for a reaction

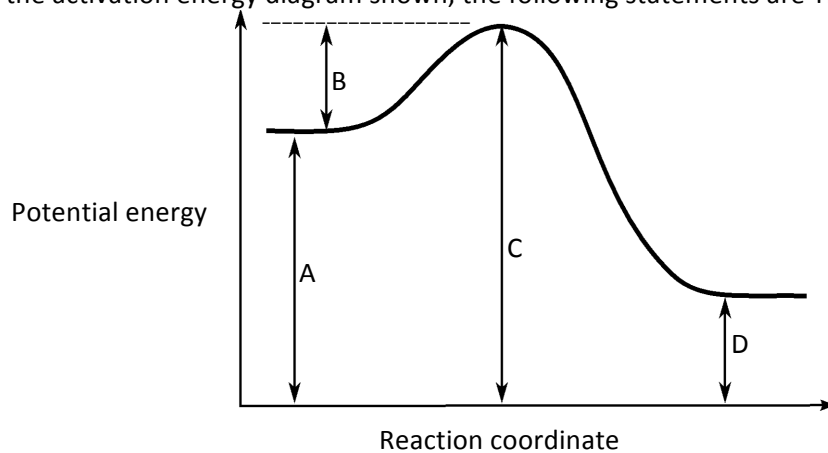
(3 marks)



- What is the overall reaction?
- Identify the intermediates in the mechanism (if any)
- What is the predicted rate law?

b. For the activation energy diagram shown, the following statements are True or False?

(3 marks)



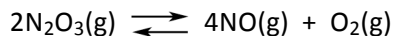
	True	False
i. $\Delta E_{\text{reaction}} = A - D$	<input type="checkbox"/>	<input type="checkbox"/>
ii. The reaction is exothermic	<input type="checkbox"/>	<input type="checkbox"/>
iii. D represents the energy of the products	<input type="checkbox"/>	<input type="checkbox"/>
iv. $E_a(\text{forward}) = C - A$	<input type="checkbox"/>	<input type="checkbox"/>
v. $E_a(\text{forward}) > E_a(\text{reverse})$	<input type="checkbox"/>	<input type="checkbox"/>
vi. B represents the energy of the transition state.	<input type="checkbox"/>	<input type="checkbox"/>



### Question 7

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- a. Dinitrogen trioxide decomposes to nitrogen monoxide and oxygen gas in a rigid container at 300°C by the reaction written below. At equilibrium, the concentrations are  $[\text{N}_2\text{O}_3] = 4.36 \text{ M}$ ,  $[\text{NO}] = 7.27 \text{ M}$  and  $[\text{O}_2] = 1.82 \text{ M}$ . (5 marks)



- i. For this reaction, calculate  $K_c$

answer  $K_c$  : \_\_\_\_\_

- ii. Calculate  $K_p$

answer  $K_p$  : \_\_\_\_\_

- iii. If only  $\text{N}_2\text{O}_3(\text{g})$  was initially present, what was its starting concentration?

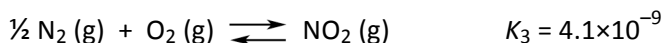
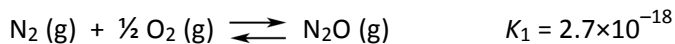
[Hint: the equilibrium concentrations are given in part a.]

answer  $[\text{N}_2\text{O}_3(\text{g})]_0$  : \_\_\_\_\_

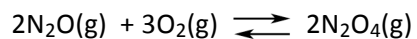
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- b. Given the equilibrium constants for the following reactions:

(3 marks)



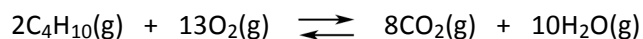
Calculate the value of  $K$  for the following reaction.



answer : \_\_\_\_\_

### Question 8

Consider the following exothermic reaction at equilibrium:



Predict the effect of each of the following on the equilibrium position of this system:

(3 marks)

		shift of the equilibrium		
		to the left	no change	to the right
a.	The mixture is cooled and water vapour condenses	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
b.	More $\text{C}_4\text{H}_{10}(\text{g})$ is added	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
c.	The volume of the container is increased	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
d.	He gas is added to increase the total pressure	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
e.	The temperature is increased	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
f.	A catalyst is added	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Question 9

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- a. A solution is made by diluting 25.0 mL of concentrated HCl (stock solution) to exactly 500. mL. If this diluted solution has a pH of 0.222, calculate the molarity of HCl in the stock solution. (3 marks)

answer : \_\_\_\_\_

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- b. If a 0.0100 M solution of caproic acid, a monoprotic acid thought to be at least partially responsible for the unique (and generally considered foul) smell of goats, has a pH of 3.43, calculate  $K_a$  and  $pK_a$  for caproic acid. (3 marks)

answers :  $K_a$  \_\_\_\_\_  $pK_a$  \_\_\_\_\_

Question 10

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a. Are the aqueous solutions of the following salts acidic, basic or neutral?

(3 marks)

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		basic	neutral	acid
i.	$\text{NaNO}_2$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
ii.	$\text{CsCl}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
iii.	$\text{NaClO}_3$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
iv.	$\text{NH}_4\text{I}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
v.	$\text{KF}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
vi.	$\text{Li}_2\text{SO}_4$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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b. At  $25^\circ\text{C}$ , a 250.0 mL solution has 0.814 g KCN. Calculate the pH of this solution.

(3 marks)

answer : \_\_\_\_\_

Question 11

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a. Which of the following combinations can be used to prepare a buffer? (2.5 marks)

	buffer	not buffer
i. HF/KF	<input type="checkbox"/>	<input type="checkbox"/>
ii. HBr/LiBr	<input type="checkbox"/>	<input type="checkbox"/>
iii. HCN/NaCN	<input type="checkbox"/>	<input type="checkbox"/>
iv. $\text{Ca(OH)}_2/\text{CaBr}_2$	<input type="checkbox"/>	<input type="checkbox"/>
v. $\text{H}_2\text{O}/\text{oil}$	<input type="checkbox"/>	<input type="checkbox"/>

---

b. Calculate the pH of a solution that is 0.50 M HF and 1.00 M NaF. (2 marks)

answer : \_\_\_\_\_

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c. Calculate the ratio  $[\text{NH}_3]/[\text{NH}_4^+]$  in ammonia/ammonium chloride buffered solution with a pH of 9.50. (1.5 marks)

answer : \_\_\_\_\_

Question 12

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A 50.0 mL aliquot of 0.300 M nitrous acid ( $\text{HNO}_2$ ) is titrated with 0.500 M  $\text{Ba}(\text{OH})_2$

- a. Calculate the pH of the solution after the addition of 5.00 mL of  $\text{Ba}(\text{OH})_2$

(4 marks)

answer : \_\_\_\_\_

Question 12 (Cont.)

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b. Calculate the volume of  $\text{Ba}(\text{OH})_2$  needed to reach the equivalence point

(2 marks)

answer : \_\_\_\_\_

---

c. What is the pH of the solution at equivalence point?

(3 marks)

answer : \_\_\_\_\_

Question 13

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- a. A 10.00 mL aliquot of a saturated solution of barium hydroxide,  $\text{Ba(OH)}_2$ , requires 25.9 mL of 0.0833 M  $\text{HCl}$  to titrate it to the equivalence point. Calculate  $K_{\text{sp}}$  for  $\text{Ba(OH)}_2$ . (3 marks)

answer : \_\_\_\_\_

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- b. Calculate the solubility of  $\text{Ca(OH)}_2$  in a 0.200 M  $\text{NaOH}$  solution.  $K_{\text{sp}} \text{ Ca(OH)}_2 : 5.0 \times 10^{-6}$ . (3 marks)

answer : \_\_\_\_\_



#### Question 14

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- a. For a particular reaction,  $\Delta H = -32 \text{ kJ}$  and  $\Delta S = -98 \text{ J/K}$ . Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature. (3 marks)

i. At what temperature will the reaction occur spontaneously?

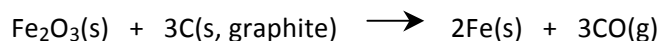
answer : \_\_\_\_\_

ii. If the temperature is increased from that in part (i), will the reaction be spontaneous or nonspontaneous?

answer : \_\_\_\_\_

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- c. Using the data in the table below determine whether iron(III) oxide can be reduced by carbon at  $25^\circ\text{C}$ . (4 marks)



Compounds	$\Delta H_f^\circ (\text{kJ}\cdot\text{mol}^{-1})$	$S^\circ (\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
$\text{Fe}_2\text{O}_3(\text{s})$	-824	87.4
$\text{C}(\text{s, graphite})$	0	5.8
$\text{Fe}(\text{s})$	0	27.3
$\text{CO}(\text{g})$	-110.5	198

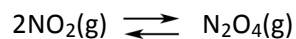
answer : \_\_\_\_\_

### Question 15

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The standard molar free energies of formation of  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$  at  $25^\circ\text{C}$  are  $51.840 \text{ kJ/mol}$  and  $98.085 \text{ kJ/mol}$ , respectively.

- a. What is the value of the standard molar free energy of formation ( $\Delta G^\circ$ ) in Joules for the reaction written as follows at  $25^\circ\text{C}$ ? (2 marks)



answer : \_\_\_\_\_

- b. What is the value of  $K_p$  (in atm) for the same reaction at  $25^\circ\text{C}$ ? (3 marks)

answer : \_\_\_\_\_

**Laboratory: Colligative properties***(4 marks)*

Objective: to find the molar mass of phenanthrene.

In this experiment, the freezing point of two substances will be measured:

Part 1. Pure cyclohexane,  $\text{C}_6\text{H}_{12}$  (solvent)  $K_f = 20.2 \text{ kg} \cdot ^\circ\text{C} \cdot \text{mol}^{-1}$ .

Part 2. A solution of phenanthrene, a non volatile covalent compound, dissolved in cyclohexane.

The molar mass of phenanthrene will be obtained from the freezing point depression

Data sheet.

**PART 1**

- |  |            |
|--|------------|
| a. Mass of the empty test tube with stopper:                   | 131.7552 g |
| b. Mass of the test tube with stopper and 25.0 mL cyclohexane: | 150.6133 g |
| c. Freezing point of pure cyclohexane:                         | 6.348°C    |

**PART 2**

The same solution from part 1 is used for part 2

- |  |            |
|--|------------|
| d. Mass of the test tube with stopper, cyclohexane and phenanthrene: | 151.3124 g |
| e. Freezing point of the cyclohexane + phenanthrene solution:        | 2.141°C    |

Calculations:

Molar mass of phenanthrene: \_\_\_\_\_

Periodic Table of the Elements																		8A
1A	1 <b>H</b> 1.008	2A											3A	4A	5A	6A	7A	2 <b>He</b> 4.003
2	3 <b>Li</b> 6.941	4 <b>Be</b> 9.012											5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
3	11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	3B	4B	5B	6B	7B	8B	9B	10B	1B	2B	13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95
4	19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.87	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80
5	37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> 98.00	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3
6	55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57 <b>La*</b> 138.9	72 <b>Hf</b> 178.5	73 <b>Ta</b> 181.0	74 <b>W</b> 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> 209.0	85 <b>At</b> 210.0	86 <b>Rn</b> 222.0
7	87 <b>Fr</b> 223.0	88 <b>Ra</b> 226.0	89 <b>Ac<sup>a</sup></b> 227.0	104 <b>Rf</b> 261.0	105 <b>Db</b> 262.0	106 <b>Sg</b> 263.0	107 <b>Bh</b> 262.0	108 <b>Hs</b> 265.0	109 <b>Mt</b> 266.0	110 <b>Uun</b> 269.0	111 <b>Uuu</b> 272.0	112 <b>Uub</b> 277.0						
																		<div></div> = metalloid

6

C

12.01

atomic number

symbol

atomic mass

\*Lanthanides

58 <b>Ce</b> 140	59 <b>Pr</b> 141	60 <b>Nd</b> 144	61 <b>Pm</b> 145	62 <b>Sm</b> 150	63 <b>Eu</b> 152	64 <b>Gd</b> 157	65 <b>Tb</b> 159	66 <b>Dy</b> 163	67 <b>Ho</b> 165	68 <b>Er</b> 167	69 <b>Tm</b> 169	70 <b>Yb</b> 173	71 <b>Lu</b> 175
90 <b>Th</b> 232	91 <b>Pa</b> 231	92 <b>U</b> 238	93 <b>Np</b> 237.1	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

#### Dissociation constants (all values are at 25°C)

compound	formula	$K_a$	compound	formula	$K_b$
hydrogen sulfate ion	$\text{HSO}_4^-$	$1.2 \times 10^{-2} (K_{a2})$	ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	$5.6 \times 10^{-4}$
hydrofluoric acid	$\text{HF}$	$7.2 \times 10^{-4}$	methylamine	$\text{CH}_3\text{NH}_2$	$4.4 \times 10^{-4}$
nitrous acid	$\text{HNO}_2$	$4.0 \times 10^{-4}$	trimethylamine	$(\text{CH}_3)_3\text{N}$	$6.4 \times 10^{-5}$
formic acid	$\text{HCOOH}$	$1.8 \times 10^{-4}$	ammonia	$\text{NH}_3$	$1.77 \times 10^{-5}$
benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	$6.5 \times 10^{-5}$	pyridine	$\text{C}_5\text{H}_5\text{N}$	$1.7 \times 10^{-9}$
acetic acid	$\text{CH}_3\text{COOH}$	$1.8 \times 10^{-5}$	aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$3.8 \times 10^{-10}$
propanoic acid	$\text{C}_2\text{H}_5\text{COOH}$	$1.3 \times 10^{-5}$			
hypochlorous acid	$\text{HClO}$	$2.9 \times 10^{-8}$			
hydrocyanic acid	$\text{HCN}$	$4.9 \times 10^{-10}$			
phenol	$\text{HOC}_6\text{H}_5$	$1.6 \times 10^{-10}$			
			compound	formula	$K_w$
			water	$\text{H}_2\text{O}$	$1.0 \times 10^{-14}$

**Conversions:**  $R = 8.314 \text{ L.kPa.K}^{-1}.\text{mol}^{-1} = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1} = 0.08206 \text{ L.atm.K}^{-1}.\text{mol}^{-1}$   
 $1 \text{ atm} = 101.3 \text{ kPa} = 760.0 \text{ mmHg or torr.}$   
 $K = 273.15 + ^\circ\text{C}$