CHM 1311 - B **First Midterm** **Nov 25 – 2019**

(Prof. S. Gambarotta)

Your Name: ____________________ **Student #:** ______________
Readable please

Please do not un-staple the booklet

1. The solution key will be posted on the web on Wednesday.
2. You must respond to all exercises.
3. Periodic Table, Electronegativity Table and relevant values are at the end.
4. A few scratch sheets are at the very end. Report in the booklet the minimum amount of calculations to show your reasoning.

Read carefully:

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in your obtaining a **0** (zero) for the exam.

By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

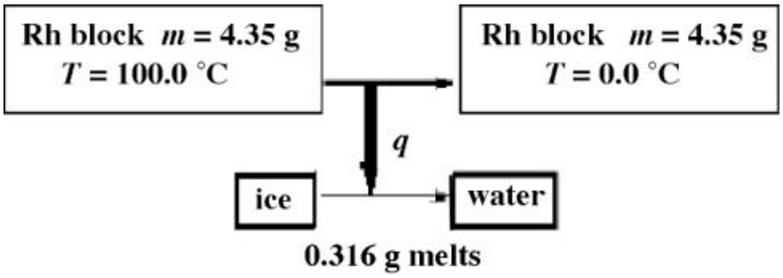
Signature: ________________________________

1	**/4**	**6**	**/3**
2	**/1**	**7**	**/3**
3	**/1**	**8**	**/3**
4	**/2**	**9**	**/5**
5	**/1**		

Total/23 =
Total/10 =

1. (4 points) A piece of rhodium metal whose mass is 4.35 g is heated to 100.0 °C and then dropped into an ice calorimeter. As the Rh metal cools to 0.0 °C, 0.316 g of ice melts (it takes 6.01 kJ of heat to melt exactly 1 mole of ice). What is the molar heat capacity of rhodium? ΔH_{fus} (ice) = 6.01 kJ/mol

To work a problem involving heat transfers, it is useful to set up a block diagram illustrating the process. In this problem, a rhodium block transfers energy to ice:



Thus, $q_{\text{ice}} = -q_{\text{Rh}}$ $\quad q_{\text{Rh}} = n_{\text{Rh}} C\Delta T$, and $q_{\text{ice}} = n_{\text{ice}}\Delta H_{\text{fus}}$

Substituting gives $\quad n_{\text{ice}}\Delta H_{\text{fus}} = -n_{\text{Rh}} C\Delta T$

Solve for C, the heat capacity of rhodium:

$$C = \frac{-n_{\text{ice}}\Delta H_{\text{fus}}}{n_{\text{Rh}}\Delta T}$$

Here are the data needed for the calculation:

$$n_{\text{Rh}} = \frac{m}{M} = \frac{4.35\text{ g}}{102.91\text{ g/mol}} = 0.04227\text{ mol} \quad n_{\text{ice}} = \frac{m}{M} = \frac{0.319\text{ g}}{18.01\text{ g/mol}} = 0.01771\text{ mol}$$

$$\Delta T = 0.0\ ^\circ\text{C} - 100.0\ ^\circ\text{C} = -100.0\ ^\circ\text{C}$$

$$\Delta H_{\text{fus}} = 6.01\text{ kJ/mol} = 6.01\times10^{3}\text{ J/mol}$$

Substitute and evaluate C:

$$C = \frac{-n_{\text{ice}}\Delta H_{\text{fus}}}{n_{\text{Rh}}\Delta T} = \frac{-(0.01771\text{ mol})(6.01\times10^{3}\text{ J/mol})}{(0.04227\text{ mol })(-100.0\ ^\circ\text{C })} = 25.2\text{ J mol}^{-1}\ ^\circ\text{C}^{-1}$$

2. (1 point) Phosgene ($Cl_2C{=}O$) is a highly toxic gas that was used for chemical warfare during World War I. Use the bond energies below to estimate the energy change that occurs when carbon monoxide and chlorine combine to make phosgene.

$$C{\equiv}O + Cl{-}Cl \rightarrow Cl_2C{=}O$$

Bond	No.	Energy (kJ/mol)	Bond	No.	Energy (kJ/mol)
C≡O	1	1070	C–Cl	2	330
Cl–Cl	1	240	C=O	1	750

To estimate the energy change in a reaction, determine Lewis structures to obtain types of bonds, list the number of bonds of each type in reactants and products, and subtract the sum of average bond energies for products from the sum of average bond energies for reactants, using values below.

$\Delta E_{\text{reaction}} \cong$ [1 mol(1070 kJ/mol) + 1 mol(240 kJ/mol)] – [2 mol(330 kJ/mol) + 1 mol(750 kJ/mol)] = 1310 kJ – 1410 kJ = –100 kJ

3. (1 point) A flask containing argon gas is connected to an open-ended mercury manometer. The open end is exposed to the atmosphere, where the prevailing pressure is 720 torr. The mercury level in the open arm is 50 mm/Hg below that in the arm connected to the flask of argon. What is the argon pressure, in torr?

$P_{int} = P_{ext} = P_{atm} = P_{Ar} + P_{Hg}$

$P_{atm} - P_{Hg} = P_{Ar}$ 720 - 50 = 670 torr

4. (2 points) Aluminum metal shavings (10.0 g) are placed in 100 mL of 6.00 *M* hydrochloric acid. What is the maximum volume of hydrogen, measured at STP (273K, 101.325 kPa), which can be produced?

$2Al(s) \quad + \quad 6HCl(aq) \quad \rightarrow \quad 2AlCl_3(aq) \quad + \quad 3H_2(g)$

Find the limiting reagent:

Based on Al: 10.0/26.98 x 3/2 = 0.557 moles of H_2

Based on HCl: 0.1 x 6.00 x 3/6 = 0.3 moles of H_2

Maximum moles of H_2 are 0.3 which at STP converts to 6.81 L

5. (1 point) For the following reaction, $K = 0.262$ at 1000°C:

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

At equilibrium, p_{H_2} is 1.22 bar. What is the equilibrium partial pressure of $CH_4(g)$?

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

$$K = \frac{p_{CH_4}}{p_{H_2}^2} = 0.262$$

$$p_{CH_4} = K \cdot p_{H_2}^2 = (0.262)(1.22)^2 = 0.38996 \text{ bar} = \mathbf{0.390\ bar}$$

6. (3 points) Compound A decomposes according to the following equation:

$$A(g) \rightleftharpoons 2B(g) + C(g)$$

A sealed 1.00-L container initially contains 1.75×10^{-3} mol of $A(g)$, 1.25×10^{-3} mol of $B(g)$, and 6.50×10^{-4} mol of $C(g)$ at 100°C. At equilibrium, [A] is 2.15×10^{-3} mol/L. Find [B] and [C].

Initial concentrations:

$[A] = (1.75\text{x}10^{-3}\text{ mol})/(1.00\text{ L}) = 1.75\text{x}10^{-3}\text{ mol/L}$
$[B] = (1.25\text{x}10^{-3}\text{ mol})/(1.00\text{ L}) = 1.25\text{x}10^{-3}\text{ mol/L}$
$[C] = (6.50\text{x}10^{-4}\text{ mol})/(1.00\text{ L}) = 6.50\text{x}10^{-4}\text{ mol/L}$

Concentration (mol/L)	A(g)	$\rightleftharpoons$	2B(g)	+	C(g)
Initial	$1.75\text{x}10^{-3}$		$1.25\text{x}10^{-3}$		$6.50\text{x}10^{-4}$
Change	$-\text{x}$		$+2\text{x}$		$+\text{x}$
Equilibrium	$1.75\text{x}10^{-3} - \text{x}$		$1.25\text{x}10^{-3} + 2\text{x}$		$6.50\text{x}10^{-4} + \text{x}$

$[A]_{eq} = 2.15\text{x}10^{-3} = 1.75\text{x}10^{-3} - \text{x}$

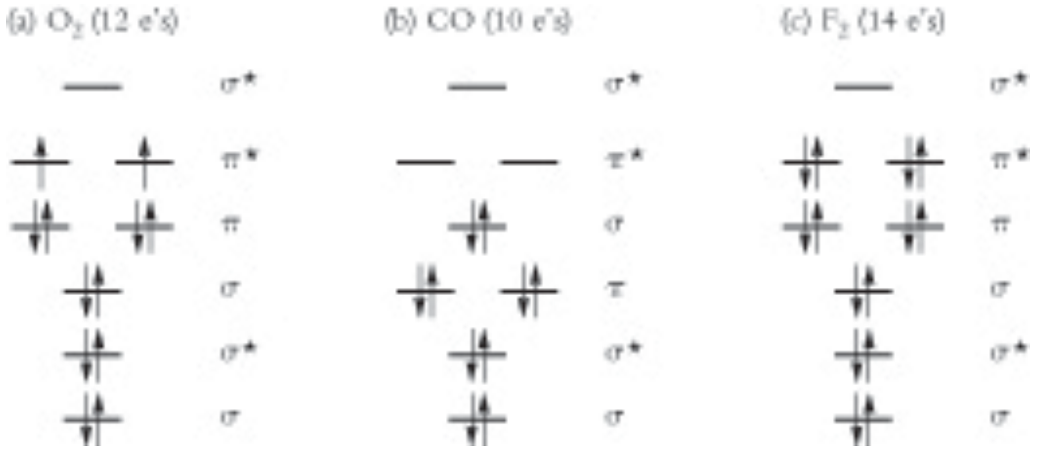
$\text{x} = -0.00040$

$[B]_{eq} = 1.25\text{x}10^{-3} + 2\text{x} = \mathbf{4.5x10^{-4}\ mol/L}$

$[C]_{eq} = 6.50\text{x}10^{-4} + \text{x} = \mathbf{2.5x10^{-4}\ mol/L}$

7. (3 points) In the following pairs, which has the strongest bond according to MO theory? Use orbital configurations to justify your selections: (a) O_2 or O_2^+; (b) CO or CO^-; and (c) F_2 or F_2^+.

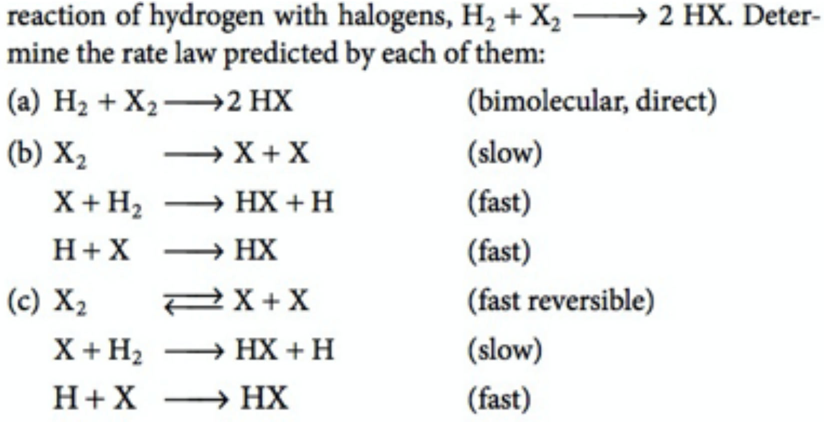
The stability of a diatomic molecule is determined by the number of bonding and antibonding electrons. To compare species, determine how many valence electrons each species possesses, and then place the electrons in the available orbitals, following the Pauli and aufbau principles. Here are the configurations for the three neutral species:



(a) To make O_2^+, an antibonding electron is removed from O_2, so O_2^+ has a stronger bond.
(b) An electron added to CO to produce CO^- occupies an antibonding orbital, so CO has a

stronger bond. (c) An antibonding electron is removed from F_2 to produce F_2^+, so F_2^+ has a stronger bond.

8. (3 points) At least three possible mechanisms exist for the



reaction of hydrogen with halogens, $H_2 + X_2 \longrightarrow 2\,HX$. Determine the rate law predicted by each of them:

(a) $H_2 + X_2 \longrightarrow 2\,HX$ (bimolecular, direct)

(b) $X_2 \longrightarrow X + X$ (slow)

$X + H_2 \longrightarrow HX + H$ (fast)

$H + X \longrightarrow HX$ (fast)

(c) $X_2 \rightleftarrows X + X$ (fast reversible)

$X + H_2 \longrightarrow HX + H$ (slow)

$H + X \longrightarrow HX$ (fast)

(a) The rate law is that for an elementary bimolecular reaction: Rate = $k[H_2][X_2]$.

(b) When a first step is rate-determining, it determines the rate law: Rate = $k[X_2]$.

(c) The rate law is determined by the rate-determining step: Rate = $k_2[X][H_2]$.

Set the rates equal for the forward and reverse first step: $k_1[X_2] = k_{-1}[X]^2$

Solve this equality for $[X]$: $[X] = \left(\dfrac{k_1}{k_{-1}}\right)^{1/2} [X_2]^{1/2}$

Substitute into the rate expression: Rate = $k_2\left(\dfrac{k_1}{k_{-1}}\right)^{1/2} [H_2][X_2]^{1/2}$

9. **(5 points)** Acetaldehyde decomposes to methane and carbon monoxide

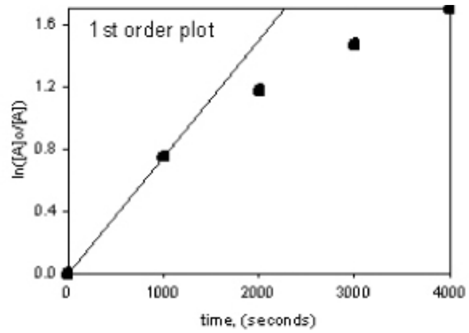
Kinetic data for the decomposition of acetaldehyde follow:

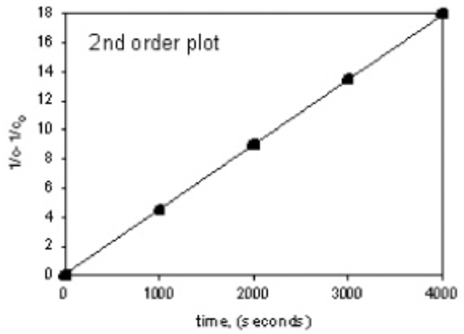
t (10^3 s)	0	1.000	2.000	3.000	4.000
[CH_3CHO] (mol/L)	0.250	0.118	0.0770	0.0572	0.0455

(a) Determine the rate law for the decomposition of acetaldehyde. (b) What is the value of the rate constant? (c) How long does it take for 75% of the acetaldehyde to decompose?

(a) Prepare first-order and second-order plots and look for linear behaviour:

t	s	0	1000	2000	3000	4000
c	M	0.250	0.118	0.0770	0.0572	0.0455
$\ln\left(\frac{[A]_0}{[A]}\right)$		0.000	0.751	1.18	1.47	1.70
$\frac{1}{[A]}-\frac{1}{[A]_0}$	M^{-1}	0.00	4.47	8.99	13.5	18.0





The second-order plot is linear, so rate = $k[CH_3CHO]^2$

(b) Determine the rate constant from the slope of the second-order plot:

$$k = \text{slope} = \frac{18.0\ \text{M}^{-1} - 0.00\ \text{M}^{-1}}{4000\ \text{s} - 0\ \text{s}} = 4.5 \times 10^{-3}\ \text{M}^{-1}\ \text{s}^{-1}$$

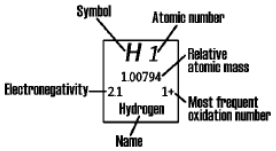
(c) Use Equation 13-5, suitably rearranged:

$$kt = \frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}$$

$$[\mathrm{A}]_0 = 0.250\ \mathrm{M} \text{ and } [\mathrm{A}] = 0.250\ \mathrm{M}\left(\frac{100\% - 75\%}{100\%}\right) = 0.0625\ \mathrm{M}$$

$$t = \frac{16.0\ \mathrm{M}^{-1} - 4.00\ \mathrm{M}^{-1}}{4.5 \times 10^{-3}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}} = 2.7 \times 10^{3}\ \mathrm{s}$$

Mokeur's Periodic table of the elements



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	*H 1* 1.00794 2.1 1+ Hydrogen																	*He 2* 4.002602 - - Helium
2	**Li 3** 6.941 1.0 1+ Lithium	**Be 4** 9.012182 1.5 2+ Beryllium											**B 5** 10.811 2.0 3+ Boron	**C 6** 12.011 2.5 4+,4- Carbon	*N 7* 14.00674 3.0 3+,3- Nitrogen	*O 8* 15.9994 3.5 2- Oxygen	*F 9* 18.9984032 4.0 1- Fluorine	*Ne 10* 20.1797 - - Neon
3	**Na 11** 22.989768 0.9 1+ Sodium	**Mg 12** 24.3050 1.2 2+ Magnesium											**Al 13** 26.981539 1.5 3+ Aluminum	**Si 14** 28.0855 1.8 4+ Silicon	**P 15** 30.973762 2.1 5+ Phosphorus	**S 16** 32.066 1.8 4+ Sulfur	*Cl 17* 35.4527 3.0 1- Chlorine	*Ar 18* 39.948 - - Argon
4	**K 19** 39.0983 0.8 1+ Potassium	**Ca 20** 40.078 1.0 2+ Calcium	**Sc 21** 44.955910 1.3 3+ Scandium	**Ti 22** 47.88 1.5 4+ Titanium	**V 23** 50.9415 1.6 5+ Vanadium	**Cr 24** 51.9961 1.6 3+ Chromium	**Mn 25** 54.93805 1.5 2+ Manganese	**Fe 26** 55.847 1.8 3+ Iron	**Co 27** 58.9332 1.8 2+ Cobalt	**Ni 28** 58.6934 1.8 2+ Nickel	**Cu 29** 63.546 1.9 2+ Copper	**Zn 30** 65.39 1.6 2+ Zinc	***Ga 31*** 69.723 1.6 3+ Gallium	**Ge 32** 72.61 1.6 4+ Germanium	**As 33** 74.92159 2.0 3+,3- Arsenic	**Se 34** 78.96 2.4 4+ Selenium	***Br 35*** 79.904 2.8 1- Bromine	*Kr 36* 83.80 - - Krypton
5	**Rb 37** 85.4678 0.8 1+ Rubidium	**Sr 38** 87.62 1.0 2+ Strontium	**Y 39** 88.90585 1.3 3+ Yttrium	**Zr 40** 91.224 1.4 4+ Zirconium	**Nb 41** 92.90638 1.6 5+ Niobium	**Mo 42** 95.94 1.8 6+ Molybdenum	Tc 43 98.9063 1.9 7+ Technetium	**Ru 44** 101.57 2.2 3+,4+ Ruthenium	**Rh 45** 102.9055 2.2 3+ Rhodium	**Pd 46** 106.42 2.2 2+ Palladium	**Ag 47** 107.8682 1.9 1+ Silver	**Cd 48** 112.411 1.7 2+ Cadmium	**In 49** 114.82 1.7 3+ Indium	**Sn 50** 118.71 1.8 4+ Tin	**Sb 51** 121.757 1.9 3+,3- Antimony	**Te 52** 127.60 2.1 4+ Tellurium	**I 53** 126.90447 2.5 1- Iodine	*Xe 54* 131.29 - - Xenon
6	***Cs 55*** 132.90543 0.7 1+ Cesium	**Ba 56** 137.327 0.9 2+ Barium	**La 57** 138.9055 1.1 3+ Lanthanum	**Hf 72** 178.49 1.3 4+ Hafnium	**Ta 73** 180.9479 1.5 5+ Tantalum	**W 74** 183.85 1.7 6+ Tungsten	**Re 75** 186.207 1.9 7+ Rhenium	**Os 76** 190.2 2.2 4+ Osmium	**Ir 77** 192.22 2.2 4+ Iridium	**Pt 78** 195.08 2.2 4+ Platinum	**Au 79** 196.96654 2.4 3+ Gold	***Hg 80*** 200.59 1.9 2+ Mercury	**Tl 81** 204.3833 1.8 1+ Thallium	**Pb 82** 207.2 1.8 2+ Lead	**Bi 83** 208.98037 1.9 3+ Bismuth	**Po 84** 208.9824 2.0 2+ Polonium	**At 85** 209.9871 2.2 1- Astatine	*Rn 86* 222.0176 - - Radon
7	***Fr 87*** 223.0197 0.7 1+ Francium	**Ra 88** 226.0254 0.9 2+ Radium	**Ac 89** 227.0278 1.1 3+ Actinium	Rf 104 261.11 - - Rutherfordium	Db 105 262.11 - - Dubnium	Sg 106 263.12 - - Seaborgium	Bh 107 262.12 - - Bohrium	Hs 108 264 - - Hassium	Mt 109 266.1378 - - Meitnerium	Uun 110 269 - - Ununnilium	Uuu 111 272 - - Unununium	Uu 112 277 - - Ununbium		Uuq 114 289 - - Ununquadium		Uuh 116 289 - - Ununhexium		Uuo 118 293 - - Ununoctium

6	**Ce 58** 140.115 1.1 3+ Cerium	**Pr 59** 140.90765 1.1 3+ Praseodymium	**Nd 60** 144.24 1.1 3+ Neodymium	Pm 61 144.9127 1.1 3+ Promethium	**Sm 62** 150.36 1.2 3+ Samarium	**Eu 63** 151.965 1.2 3+ Europium	**Gd 64** 157.25 1.2 3+ Gadolinium	**Tb 65** 168.92534 1.2 3+ Terbium	**Dy 66** 162.50 1.2 3+ Dysposium	**Ho 67** 164.93032 1.2 3+ Holmium	**Er 68** 167.26 1.2 3+ Erbium	**Tm 69** 168.93421 1.2 3+ Thulium	**Yb 70** 173.04 1.1 3+ Ytterbium	**Lu 71** 174.967 1.2 3+ Lutetium
7	**Th 90** 232.0381 1.3 4+ Thorium	**Pa 91** 231.03588 1.5 5+ Protactinium	**U 92** 238.0289 1.4 6+ Uranium	Np 93 237.082 1.3 5+ Neptunium	Pu 94 244.0642 1.3 4+ Plutonium	Am 95 243.0614 1.3 3+ Americium	Cm 96 247 1.3 3+ Curium	Bk 97 247.0703 1.3 3+ Berkelium	Cf 98 251.0796 1.3 3+ Californium	Es 99 252.03 1.3 - Einsteinium	Fm 100 257.0951 1.3 - Fermium	Md 101 258.01 1.3 - Mendelevium	No 102 259.1009 1.3 - Nobelium	Lr 103 260.1053 - - Lawrencium

Under normal conditions, bold symbols correspond to solid state, bold italic correspond to liquid state, italic correspond to gaseous state and normal correspond to synthetic elements.

Data For Water

Density = 1.00 g/mL (at 25°C)
s = 2.13 J g^{-1} K^{-1} (solid)
s = 4.184 J g^{-1} K^{-1} (liquid) ΔH°_{fus} = 6.02 kJ mol^{-1}
s = 2.01 J g^{-1} K^{-1} (gas) ΔH°_{vap} = 40.7 kJ mol^{-1}

Constants and Conversion Factors

1 mmHg = 1 torr 760 mmHg = 1 atm 1 atm = 101.325 kPa 1 atm = 1.013125 bar
1 cm^3 = 1 mL 1000 mL = 1 L 1000 L = 1 m^3

Avogadro's Number	*N*	$6.022\text{x}10^{23}$ mol^{-1}	
Boltzmann's constant	*k*	$1.30866\text{x}10^{-23}$ $J{\cdot}K^{-1}$	
Faraday's constant	*F*	96,485 $C{\cdot}mol^{-1}$	
Gas constant	*R*	8.31451 $J{\cdot}K^{-1}{\cdot}mol^{-1}$	
	R	0.08206 $atm{\cdot}L{\cdot}K^{-1}{\cdot}mol^{-1}$	
	R	8.31451 $m^3Pa{\cdot}K^{-1}{\cdot}mol^{-1}$	
	R	0.0831451 bar $L{\cdot}K^{-1}{\cdot}mol^{-1}$	
Planck's constant	*h*	$6.62608\text{x}10^{-34}$	J·s
Speed of Light	*c*	$2.99792458\text{x}10^{8}$	$m{\cdot}s^{-1}$

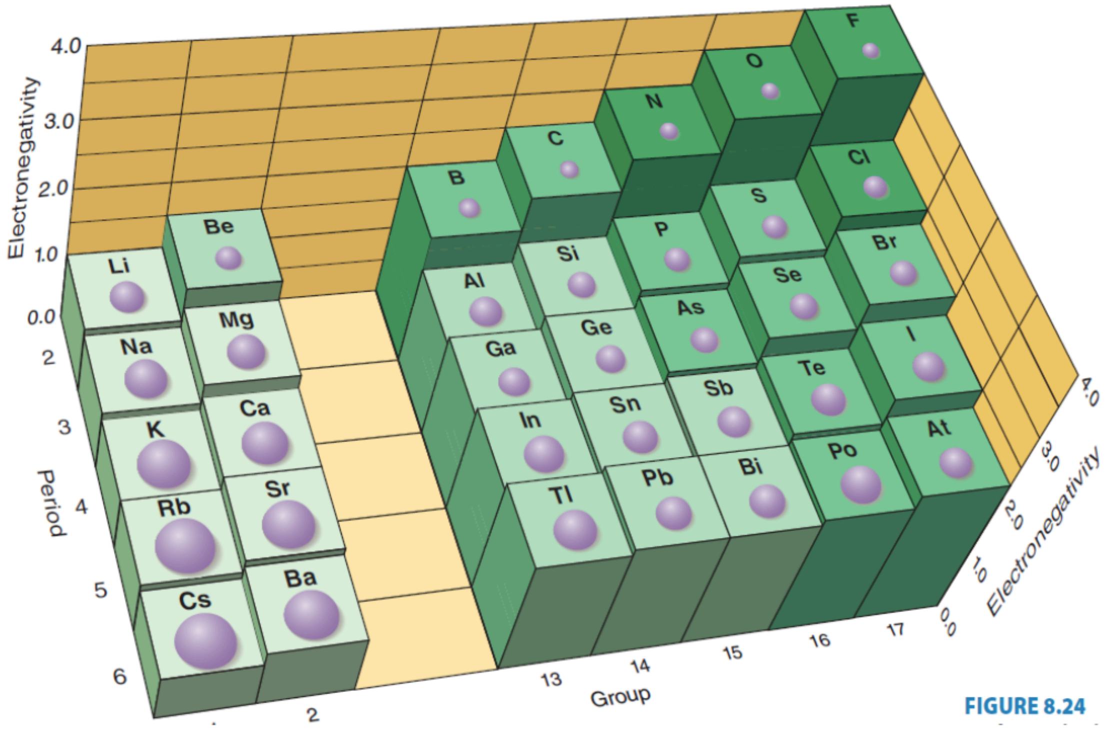


FIGURE 8.24

Gas Laws

$PV = nRT$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P_T = P_1 + P_2 + P_3 + \ldots$

$$d = \frac{m}{V} = \frac{P \cdot MM}{RT}$$

$$E_K = \frac{1}{2}mv^2$$

$$u_{rms} = \sqrt{\frac{3RT}{MM}}$$

$$\frac{Rate\ A}{Rate\ B} = \sqrt{\frac{MM_B}{MM_A}}$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Equilibrium

$K_P = K_C(RT^{)\Delta n}$

Acid/Base

$pOH = -\log[OH^{-]}$

$pH = -\log[H^+]$

$pH + pOH = 14$

$K_a \times K_b = K_W$

$pH = pK_a + \log [A^-]/[HA]$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

Thermochemistry

$\Delta U = q + W$

$W_{system} = -P\Delta V = -\Delta nRT$

$\Delta H = \Delta U + P\Delta V$

$q_P = \Delta U + P\Delta V$

$q = ms\Delta T$

$\Delta H_{rxn}° = \sum n\Delta H_f°(\text{pdts}) - \sum n\Delta H_f°(\text{rxts})$

The atom

$E = h\nu$

$c = \nu\lambda$

$E = -B/n^2$

Kinetics

$[A]_t = [A]_o - kt$

$\ln[A]_t = \ln[A]_o - kt$

$1/[A]_t = 1/[A]_o + kt$

$k = Ae^{(-Ea/RT)}$

$\ln(k_2/k_1) = (-Ea/R)(1/T_2 - 1/T_1)$