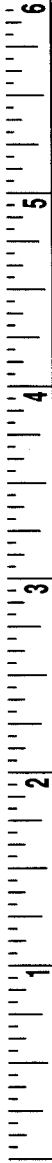


Inches



Periodic Table of the Elements

3	6.94	4	9.01
Li	Be	B	C
Lithium	Beryllium	Boron	Carbon
11	22.99	12	24.31
Na	Mg	Al	Si
Sodium	Magnesium	Aluminum	Silicon
19	39.10	20	40.08
K	Ca	Sc	Ti
Potassium	Calcium	Scandium	Titanium
37	85.47	38	87.62
Rb	Sr	Y	Zr
Rubidium	Strontium	Yttrium	Zirconium
55	132.91	56	137.33
Cs	Ba	La	Hf
Cesium	Barium	Lanthanum	Hafnium
87	(223)	88	226.03
Fr	Ra	Ac	
Francium	Radium	Actinium	
27	58.93	28	58.93
Co	Ni	Cu	Zn
Cobalt	Nickel	Copper	Zinc
25	54.94	26	55.85
Mn	Fe	Co	Ni
Manganese	Iron	Cobalt	Nickel
43	98	44	101.07
Tc	Ru	Rh	Pd
Technetium	Ruthenium	Rhodium	Palladium
75	186.21	76	190.20
Re	Os	Ir	Pt
Rhenium	Osmium	Iridium	Platinum
107	(262)	108	(265)
NS	HS	MT	
Niobium	Hassium	Mendelevium	
106	(266)	109	(266)
Sg	Hs	Mt	
Seaborgium	Hassium	Mendelevium	
72	178.49	73	180.95
Hf	Ta	W	Re
Hafnium	Tantalum	Tungsten	Rhenium
104	(261)	105	(262)
Rf	Ha	Hs	Mt
Rutherfordium	Hassium	Hassium	Mendelevium
89	227.03	90	232.04
Ac	Th	Pa	U
Actinium	Thorium	Protactinium	Uranium
91	231.04	92	238.03
Th	Pa	U	Np
Thorium	Protactinium	Uranium	Neptunium
93	237.05	94	(244)
Np	Pu	Am	Cm
Neptunium	Plutonium	Americium	Curium
95	(243)	96	(247)
Am	Cm	Bk	Cf
Americium	Curium	Berkelium	Californium
63	151.96	64	157.25
Eu	Gd	Tb	Dy
Europlum	Gadolinium	Terbium	Dysprosium
81	200.59	82	208.98
Tl	Pb	Bi	Po
Thallium	Lead	Bismuth	Polonium
83	208.98	84	(209)
Bi	Po	At	Rn
Bismuth	Polonium	Astatine	Radon
79	186.97	80	200.59
Au	Hg	Tl	Pb
Gold	Mercury	Thallium	Lead
78	195.08	79	186.97
Pt	Au	Hg	Tl
Platinum	Gold	Mercury	Thallium
110	(271)	111	(272)
Mt	Ds	Rg	Cn
Mendelevium	Darmstadtium	Roganium	Copernicium
68	167.26	69	168.93
Er	Tm	Yb	Lu
Erbium	Thulium	Ytterbium	Lutetium
101	(257)	102	(259)
Lr	103	104	105
Lawrencium	(262)	(263)	(264)
70	173.04	71	174.97
Yb	Lu	102	103
Ytterbium	Lutetium	(259)	(262)
67	164.93	68	167.26
Ho	Er	Tm	Yb
Holmium	Erbium	Thulium	Ytterbium
89	(252)	90	(260)
Fm	Md	No	Lr
Fermium	Mendelevium	Nobelium	Lawrencium
100	(260)	101	(262)
101	102	103	104
(262)	(263)	(264)	(265)

Note: Atomic masses shown here are the 1983 IUPAC values (maximum of six significant figures).

Physical Constants

Standard acceleration of terrestrial gravity	$g = 9.80665 \text{ m s}^{-2}$ (exactly)
Avogadro's number	$N_0 = 6.022137 \times 10^{23}$
Bohr radius	$a_0 = 0.52917725 \text{ \AA} = 5.2917725 \times 10^{-11} \text{ m}$
Boltzmann's constant	$k_B = 1.38066 \times 10^{-23} \text{ J K}^{-1}$
Electron charge	$e = 1.6021773 \times 10^{-19} \text{ C}$
Faraday constant	$\mathcal{F} = 96,485.31 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.109390 \times 10^{-31} \text{ kg}$
Proton	$m_p = 1.672623 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.674929 \times 10^{-27} \text{ kg}$
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15270$
Permittivity of vacuum	$\epsilon_0 = 8.8541878 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$
Planck's constant	$h = 6.626076 \times 10^{-34} \text{ J s}$
Speed of light in a vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$ (exactly)
Universal gas constant	$R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$

Values are taken from "Quantities, Units and Symbols in Physical Chemistry," International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, 1988.

Conversion Factors

Standard atmosphere	$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$ (exactly)
Atomic mass unit	$1 \text{ u} = 1.660540 \times 10^{-27} \text{ kg}$ $1 \text{ u} = 1.492419 \times 10^{-10} \text{ J} = 931.4943 \text{ MeV}$ (energy equivalent from $E = mc^2$)
Calorie	$1 \text{ cal} = 4.184 \text{ J}$ (exactly)
Electron volt	$1 \text{ eV} = 1.6021773 \times 10^{-19} \text{ J} = 96.48531 \text{ kJ mol}^{-1}$
Foot	$1 \text{ ft} = 12 \text{ in} = 0.3048 \text{ m}$ (exactly)
Gallon (U.S.)	$1 \text{ gallon} = 4 \text{ quarts} = 3.78541 \text{ L}$ (exactly)
Liter-atmosphere	$1 \text{ L atm} = 101.325 \text{ J}$ (exactly)
Metric ton	$1 \text{ metric ton} = 1000 \text{ kg}$ (exactly)
Pound	$1 \text{ lb} = 16 \text{ oz} = 0.45359237 \text{ kg}$ (exactly)

I. (4 points each)

- A) Professor Ahmed Zewail won the 1999 Nobel Prize in Chemistry. Briefly describe the work for which he was recognized.

using femtospectroscopy in observing transition states in chemical reactions using lasers one such rxn was the dissociation of NaI_2

- B) The chemical formula for the Strongest (measured) Acid in the World is
- $\text{HSO}_3\text{F} \cdot \text{SbF}_5$

but the strongest theoretically predicted acid is H^+

($\text{HF} \cdot \text{SbF}_5$ is currently being measured) supposed to be higher than

- C) The rigorous definition of pH is
- $-\log \left(\gamma_{\text{H}^+} \frac{[\text{H}^+]}{[\text{H}_3\text{O}^+]}\right)$
- , and the pH range of water is

0-14

- D) Define the Hammett acidity function.

$$\underbrace{-\log \left(a_{\text{H}^+} \frac{\gamma_{\text{B}}}{\gamma_{\text{BH}^+}} \right)}_{H_0} = -\log K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]}$$



- E) State the Principle of Detailed Balance (or microscopic reversibility).

At equilibrium of a reaction, the rate of formation of products equals the rate of formation of reactants (forward rate = reverse rate)

- II. (10 points) In class we measured the rate of the "iodine clock reaction" at several temperatures. Use the following data to calculate E_a for this reaction (t is the time required for blue color to appear).

$T(^{\circ}\text{C})$	$t(\text{sec})$
k_2 17.5	29
k_1 10.5	36

$$k = A e^{-E_a/RT}$$

$$\ln k_1 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_1} \right)$$

$$\ln k_2 = \ln A - \frac{E_a}{R} \left(\frac{1}{T_2} \right)$$

$$\ln \left(\frac{k_1}{k_2} \right) = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2}$$

$$\ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{290.5} - \frac{1}{289.5} \right)$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(2.50 \times 10^{-5} \right)$$

$$E_a = \ln \left(\frac{k_2}{k_1} \right) \div 1.02 \times 10^{-5}$$

$$= \ln \left(\frac{k_2}{k_1} \right) (9.7822)$$

$$= \ln \left(\frac{25.0}{20.1} \right) (9.7822)$$

$$= 21340 \frac{\text{J}}{\text{mol}} = 21.3 \frac{\text{kJ}}{\text{mol}}$$

-1 sp

9

III. (5 points each) Let's examine the collision theory result for the bimolecular reaction of H_2 with C_2H_4 at 273 K.

A) Calculate the reduced molar mass (in kg)

$$M = \left(\frac{M_x + M_y}{M_x M_y} \right)^{-1} = \left(\frac{M_x M_y}{M_x + M_y} \right)$$

$$= \frac{(0.02016 \text{ kg/mol} \cdot 0.02803 \text{ kg/mol})}{(0.02016 + 0.02803) \text{ kg/mol}}$$

$$= 0.0188 \frac{\text{kg}}{\text{mol}}$$

(5)

B) Calculate the average relative speed $(8RT/\pi\mu)^{1/2}$

$$\bar{u} = \sqrt{\frac{8RT}{\pi\mu}}$$

$$= \sqrt{\frac{8(8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}})(273 \text{ K})}{\pi(-0.0188 \frac{\text{kg}}{\text{mol}})}}$$

$$= 1750 \frac{\sqrt{\text{J}}}{\sqrt{\text{kg}}} = 1750 \text{ m/s}$$

(5)

C) Calculate A ($A = \sigma \bar{C}_{\text{rel}} N_0$) given that the collision cross section is $4.6 \times 10^{-19} \text{ m}^2$

$$\sigma = \pi d^2 = 4.6 \times 10^{-19} \text{ m}^2$$

$$A = (4.6 \times 10^{-19} \text{ m}^2) \left(1750 \frac{\text{m}}{\text{s}} \right) \left(6.022 \times 10^{23} \text{ mol}^{-1} \right)$$

$$4.86 \times 10^8 \frac{\text{m}^3}{\text{s} \cdot \text{mol}}$$

5

D) The measured value of A is 1.24×10^6 . Compute the steric factor for the reaction.

$$\frac{\text{m}^3}{\text{mol} \cdot \text{s}}$$

$$P \cdot A_0 = A$$

$$P \cdot 4.86 \times 10^8 \frac{\text{m}^3}{\text{mol} \cdot \text{s}} = 1.24 \times 10^6 \frac{\text{m}^3}{\text{mol} \cdot \text{s}}$$

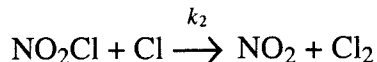
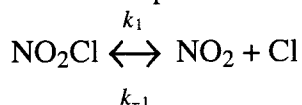
$$P = .00255$$

5

E) Describe the effects that the steric factor corrects for.

The steric factor corrects for the necessity for two colliding particles to be oriented correctly in order to react (which means fewer molecules react than collide)

IV. (10 points) The mechanism for the decomposition of NO_2Cl is



By making a steady-state approximation for $[\text{Cl}]$, express the rate of appearance of Cl_2 in terms of the concentrations of NO_2Cl and NO_2 .

$$\frac{d[\text{Cl}]}{dt} = k_1 [\text{NO}_2\text{Cl}] - k_{-1} [\text{NO}_2][\text{Cl}] - k_2 [\text{NO}_2\text{Cl}][\text{Cl}]$$

= 0 (after time)

$$k_{-1} [\text{NO}_2][\text{Cl}] + k_2 [\text{NO}_2\text{Cl}][\text{Cl}] = k_1 [\text{NO}_2\text{Cl}]$$

$$[\text{Cl}] = \frac{k_1 [\text{NO}_2\text{Cl}]}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2\text{Cl}]}$$

$$k_1 [\text{NO}_2\text{Cl}]$$

$$\frac{d[\text{Cl}_2]}{dt} \text{ Rate} = k_2 [\text{NO}_2\text{Cl}][\text{Cl}]$$

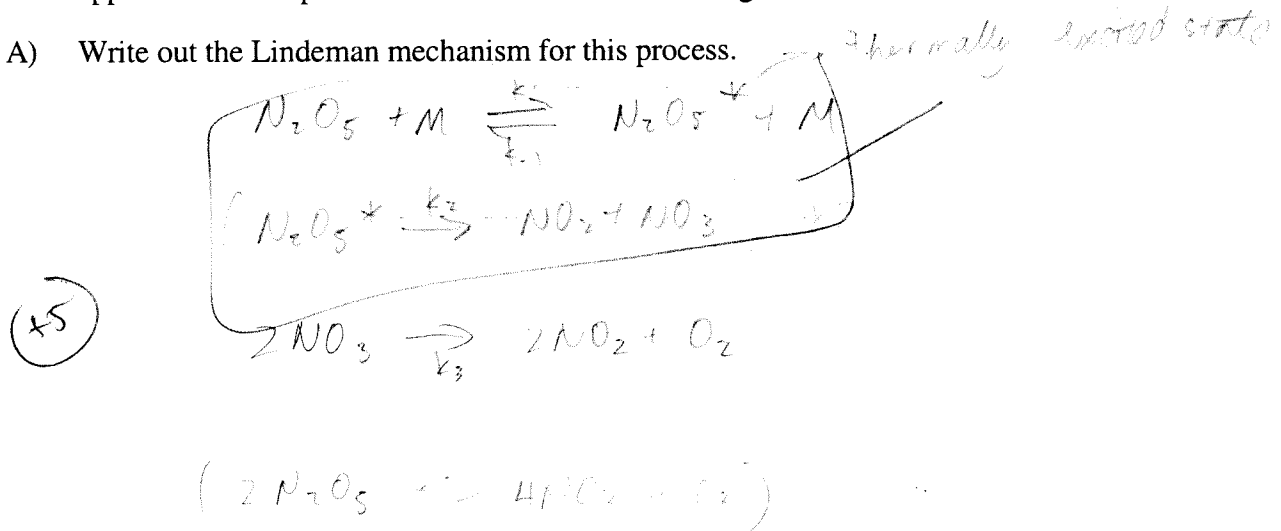
$$= k_2 [\text{NO}_2\text{Cl}] \left(\frac{k_1 [\text{NO}_2\text{Cl}]}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2\text{Cl}]} \right)$$

$$= \frac{k_1 k_2 [\text{NO}_2\text{Cl}]^2}{k_{-1} [\text{NO}_2] + k_2 [\text{NO}_2\text{Cl}]}$$

10

V. (5+5+5 points) The Lindeman mechanism accounts for the decomposition of N_2O_5 with apparent first order kinetics at high pressure. One can construct a mechanism and apply the steady state approximation to produce a differential rate law that gives this behavior.

A) Write out the Lindeman mechanism for this process.



B) Apply the steady-state approximation to obtain the differential rate law in terms of stable reactants.

$$\begin{aligned}
 d[N_2O_5^*] &= k_1[N_2O_5][M] - k_{-1}[N_2O_5^*][M] - k_2[N_2O_5^*] \\
 &= 0 \\
 [N_2O_5^*] &= \frac{k_1[N_2O_5][M]}{k_{-1}[M] + k_2}
 \end{aligned}$$

(x5)

$$\text{Rate} = k_2[N_2O_5^*] = \frac{k_1 k_2 [N_2O_5][M]}{k_{-1}[M] + k_2}$$

C) Obtain the appropriate limit of the above result.

as pressure \uparrow , $k_1[M] \gg k_2$

(x5)

$$\text{so } \frac{d[N_2O_5]}{dt} = \frac{k_1 k_2 [N_2O_5][M]}{k_{-1}[M]} = \frac{k_1 k_2 [N_2O_5]}{k_{-1}}$$

1st order kinetics

$$K_1 = \frac{k_1}{k_{-1}}$$

$$K_1 k_2 [N_2O_5]$$

VI. (10 points) The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is first order, with a rate constant of $2.2 \times 10^{-5} \text{ s}^{-1}$ at 320°C . The partial pressure of $\text{SO}_2\text{Cl}_2(\text{g})$ in a sealed vessel at 320°C is 1.0 atm. How long will it take for the partial pressure of $\text{SO}_2\text{Cl}_2(\text{g})$ to fall to 0.50 atm?

$$\ln\left(\frac{P_0}{P}\right) = kt$$

$$\int_{c_0}^c \frac{dc}{c} = \int_0^t kt \, dt$$

$$\ln\left(\frac{2P_0}{P_0}\right) = kt$$

$$\ln\left(\frac{c}{c_0}\right) = -kt$$

$$\ln 2 = (2.2 \times 10^{-5} \text{ s}^{-1}) t$$

$$t = \frac{\ln 2}{2.2 \times 10^{-5} \text{ s}^{-1}} = 3.15 \times 10^4 \text{ s}$$

SF

9

$$-\frac{dc}{dt} = kc$$

$$\int_{c_0}^c \frac{dc}{c} = \int_0^t k dt \quad \ln \frac{c}{c_0} = -kt$$

VII. (10 points) The dimerization of tetrafluoroethylene (C_2F_4) to octafluorocyclobutane (C_4F_8) is second order in the reactant C_2F_4 , and at 450 K its rate constant is $k = 0.0448 \text{ L mol}^{-1} \text{ s}^{-1}$. If the initial concentration of C_2F_4 is 0.100 mol L^{-1} , what will its concentration be after 205 s ?



$$\ln\left(\frac{c_0}{c}\right) = kt$$

Not 1st order

$\ln \frac{c_0}{c} = \ln c_0 - \ln c$

$$\ln\left(\frac{0.100 \text{ mol}}{c}\right) = \frac{0.0448 \text{ L}}{\text{mol} \cdot \text{s}} (205 \text{ s})$$

$$\ln(0.100) - \ln c = \dots$$

$$c = [\text{C}_2\text{F}_4] = 0.0399 \frac{\text{mol}}{\text{L}}$$

10

$$-\frac{1}{2} \frac{dc}{dt} = kc^2$$

$$\int_{c_0}^c \frac{dc}{c^2} = \int_0^t -2k dt \quad \left[-\frac{1}{c}\right]_{c_0}^c = -2kt \quad \frac{1}{c} - \frac{1}{c_0} = 2kt$$