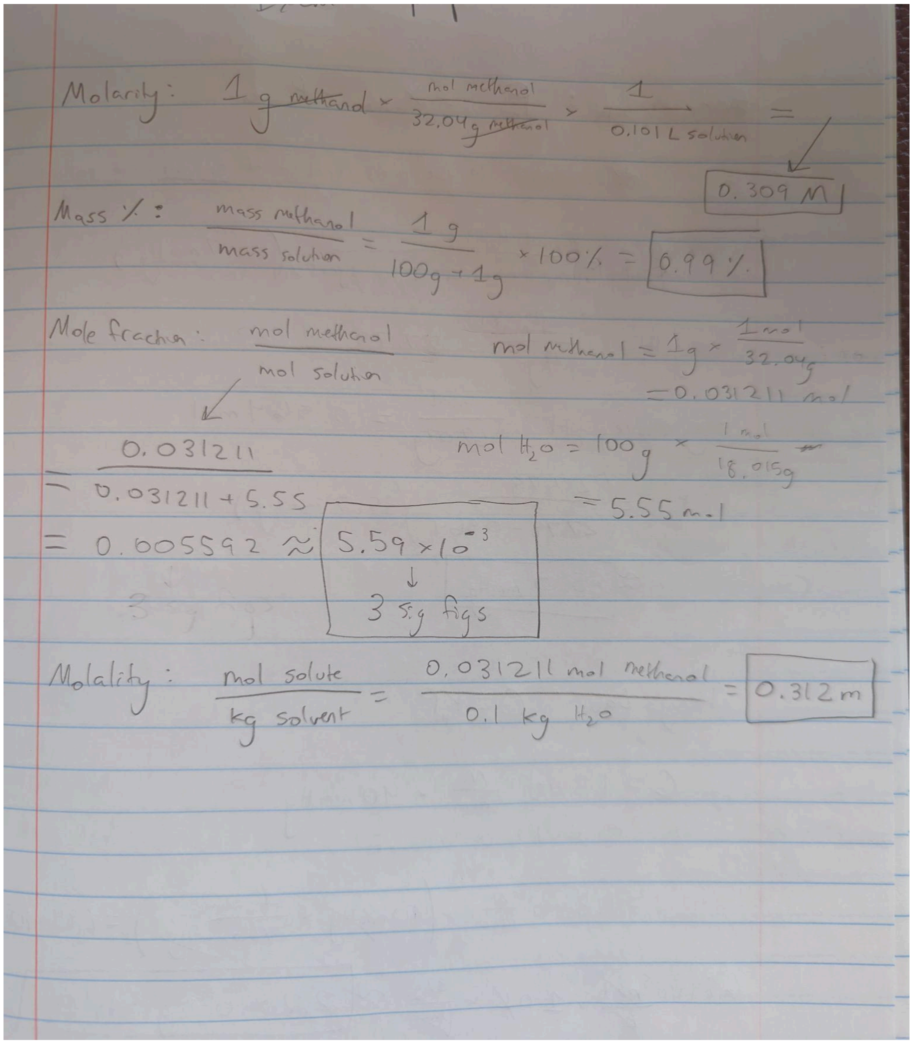
Lots of problems are available. Do whichever ones give you the most trouble.

Solutions & Colligative Properties 🧪

A solution is prepared by mixing 1.00 g methanol (CH_2OH) with 100.0 g of water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of methanol in this solution.



Molarity: $1\text{ g } \cancel{\text{methanol}} \times \frac{\text{mol methanol}}{32.04\text{ g } \cancel{\text{methanol}}} \times \frac{1}{0.101\text{ L solution}} = \boxed{0.309\text{ M}}$

Mass %: $\frac{\text{mass methanol}}{\text{mass solution}} = \frac{1\text{ g}}{100\text{ g} + 1\text{ g}} \times 100\% = \boxed{0.99\%}$

Mole fraction: $\frac{\text{mol methanol}}{\text{mol solution}}$

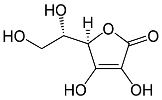
mol methanol $= 1\text{ g} \times \frac{1\text{ mol}}{32.04\text{ g}} = 0.031211\text{ mol}$

mol $H_2O = 100\text{ g} \times \frac{1\text{ mol}}{18.015\text{ g}} = 5.55\text{ mol}$

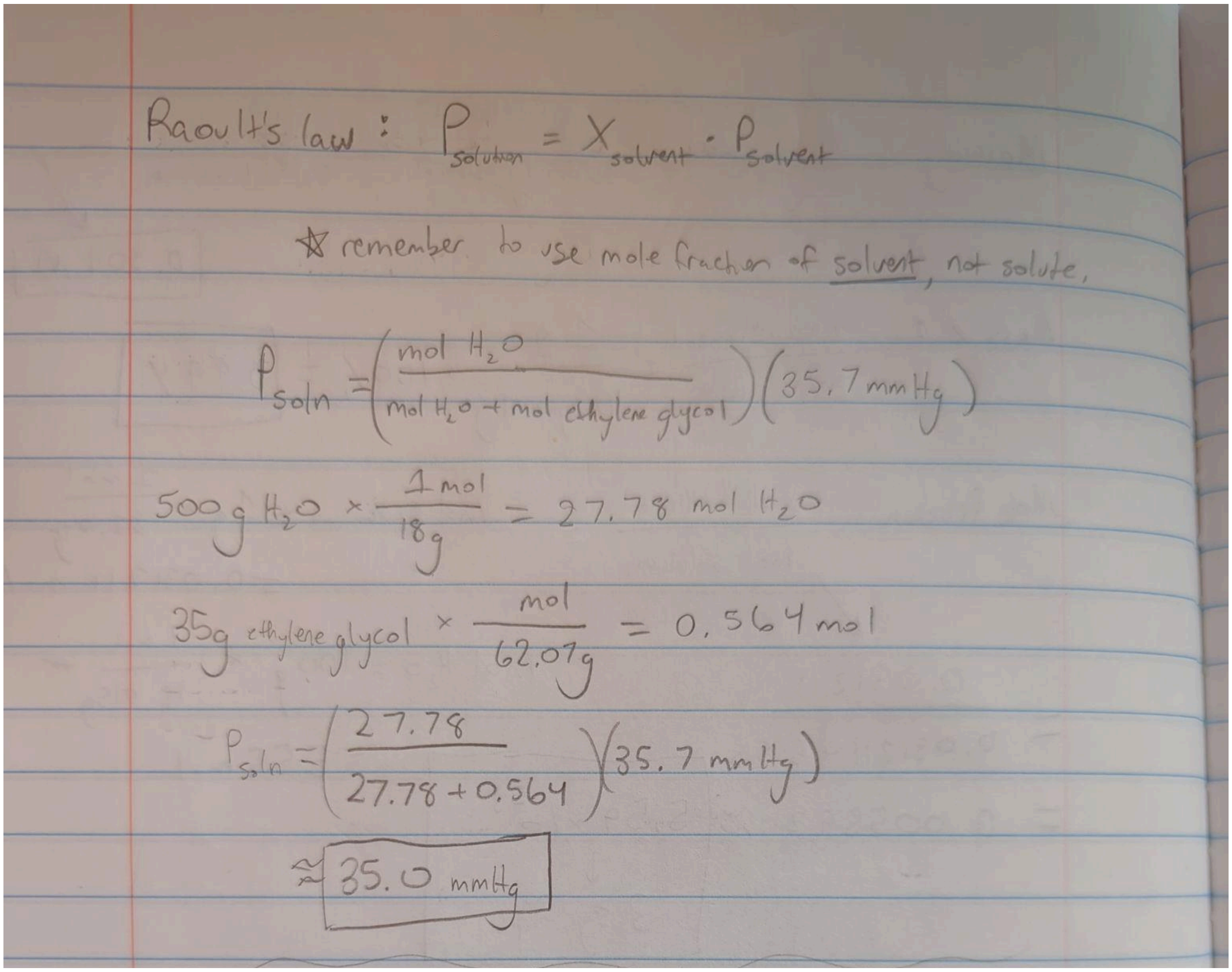
$= \frac{0.031211}{0.031211 + 5.55}$

$= 0.005592 \approx \boxed{5.59 \times 10^{-3}}$ ↓ 3 sig figs

Molality: $\frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.031211\text{ mol methanol}}{0.1\text{ kg } H_2O} = \boxed{0.312\text{ m}}$

Is vitamin C () miscible in water, hexane (C_6H_{12}), or both? Explain your choice.

A 35.0-g sample of ethylene glycol, $HOCH_2CH_2OH$, is dissolved in 500.0 g of water. The vapor pressure of water at 32 °C is 35.7 mm Hg. What is the vapor pressure of the water–ethylene glycol solution at 32 °C? (Ethylene glycol is nonvolatile.) *(Q13.25 from textbook)*



Raoult's law : $P_{solution} = X_{solvent} \cdot P_{solvent}$

☆ remember to use mole fraction of solvent, not solute,

$$P_{soln} = \left(\frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol ethylene glycol}}\right)(35.7 \text{ mmHg})$$

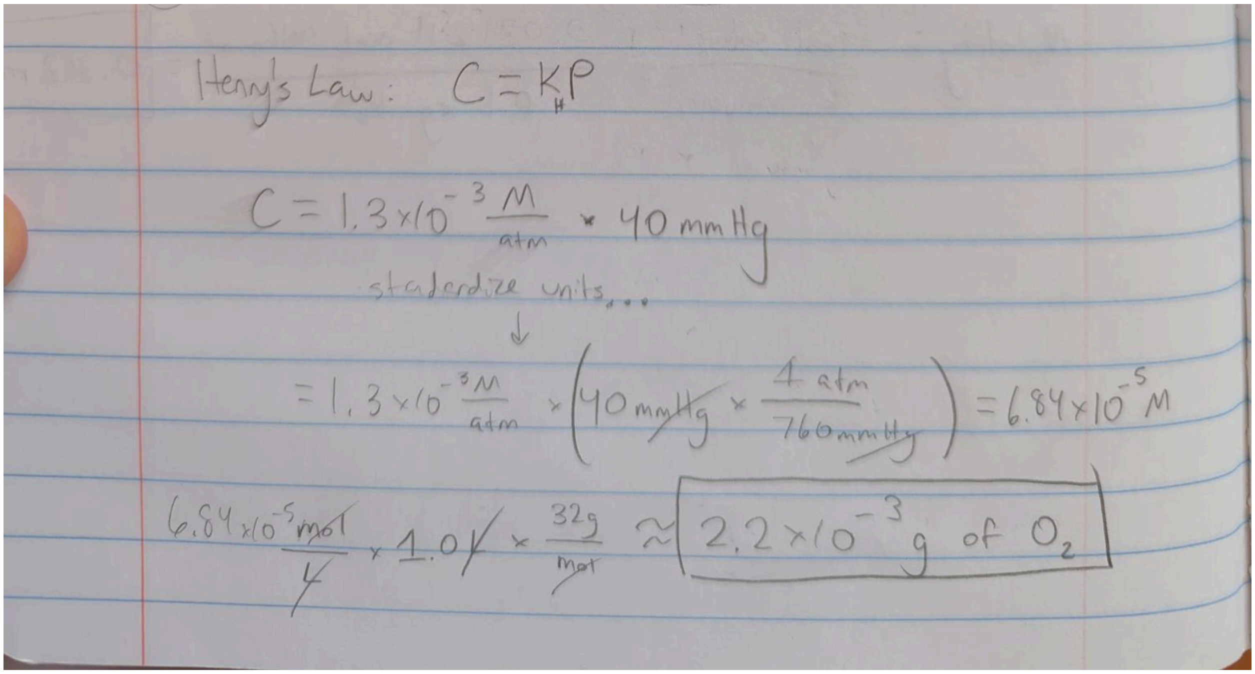
$$500 \text{ g } H_2O \times \frac{1 \text{ mol}}{18 \text{ g}} = 27.78 \text{ mol } H_2O$$

$$35 \text{ g ethylene glycol} \times \frac{\text{mol}}{62.07 \text{ g}} = 0.564 \text{ mol}$$

$$P_{soln} = \left(\frac{27.78}{27.78 + 0.564}\right)(35.7 \text{ mmHg})$$

$$\approx \boxed{35.0 \text{ mmHg}}$$

The partial pressure of O2 in your lungs varies from 25 mm Hg to 40 mm Hg. What mass of O2 can dissolve in 1.0 L of water at 25 °C if the partial pressure of O2 is 40 mm Hg? K_H for O_2 dissolved in H_2O at 25 °C is 1.3×10^{-3} mol/(L*atm). *(Q13.19 from textbook).*



Henry's Law: $C = K_H P$

$$C = 1.3\times10^{-3}\,\frac{M}{atm} \times 40\ mmHg$$

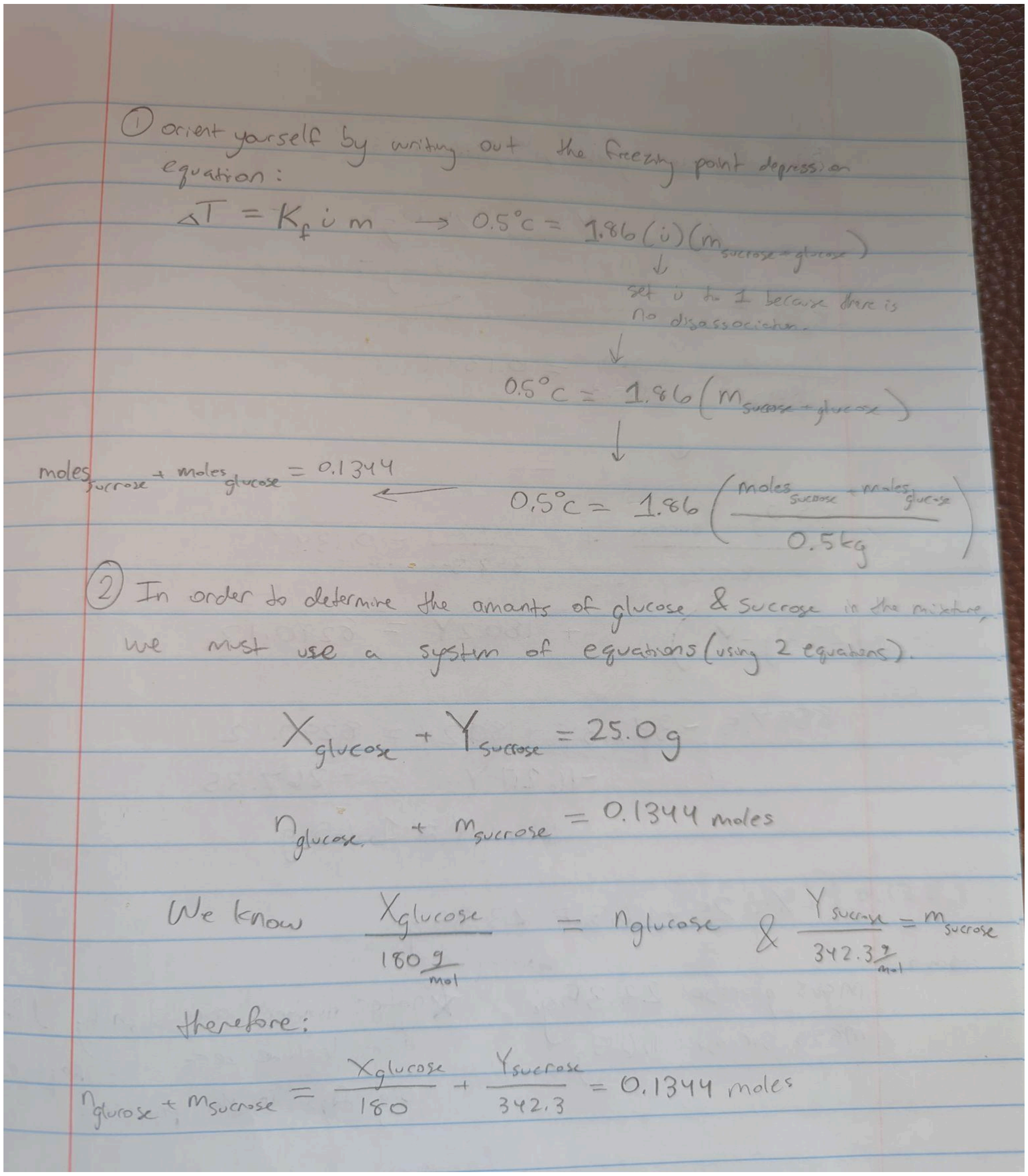
staderdize units...

↓

$$= 1.3\times10^{-3}\,\frac{M}{atm} \times \left(40\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}}\right) = 6.84\times10^{-5}\ M$$

$$6.84\times10^{-5}\,\frac{\cancel{mol}}{\cancel{L}} \times 1.0\,\cancel{L} \times \frac{32g}{\cancel{mol}} \approx \boxed{2.2\times10^{-3}\ g\ of\ O_2}$$

Challenge (*review from lecture*): A 25.0 gram mixture of sucrose, $C_{12}H_{22}O_{11}$, and glucose, $C_6H_{12}O_6$, both non-volatile, non-electrolytes are dissolved in 500.0 g of water. The change in freezing point is 0.500 °C, and the K_f is 1.86 °C/m. What is the mass of glucose in the mixture? The mass of sucrose? (Molar mass of glucose is 180.2 g/mol. Molar mass of sucrose is 342.3 g/mol.)



① orient yourself by writing out the freezing point depression equation:

$$\Delta T = K_f i m \rightarrow 0.5°c = 1.86(i)(m_{sucrose+glucose})$$

$\downarrow$ set i to 1 because there is no disassociation.

$$0.5°c = 1.86(m_{sucrose+glucose})$$

$$\downarrow$$

$$moles_{sucrose} + moles_{glucose} = 0.1344 \longleftarrow 0.5°c = 1.86\left(\frac{moles_{sucrose} + moles_{glucose}}{0.5kg}\right)$$

② In order to determine the amants of glucose & sucrose in the mixture, we must use a system of equations (using 2 equations).

$$X_{glucose} + Y_{sucrose} = 25.0g$$

$$n_{glucose} + m_{sucrose} = 0.1344 \text{ moles}$$

We know $\frac{X_{glucose}}{180\frac{g}{mol}} = n_{glucose}$ & $\frac{Y_{sucrose}}{342.3\frac{g}{mol}} = m_{sucrose}$

therefore:

$$n_{glurose} + m_{sucrose} = \frac{X_{glucose}}{180} + \frac{Y_{sucrose}}{342.3} = 0.1344 \text{ moles}$$

③ solve the system of equations:

$$X_{glucose} + Y_{sucrose} = 25.0g$$

$$X_{glucose} = 25.0g - Y_{sucrose}$$

substitute

$$\frac{X_{glucose}}{180.2} + \frac{Y_{sucrose}}{342.3} = 0.1344$$

$$\downarrow$$

$$\frac{25.0g - Y_{sucrose}}{180.2} + \frac{Y_{sucrose}}{342.3} = 0.1344$$

$$342.3(25.0g - Y) + 180.2Y = 8290.12$$

$$8557.5 - 342.3Y + 180.2Y = 8290.12$$

$$-162.1Y = -267.35$$

$$Y \approx 1.65g$$

$$X = 25 - 1.65 = 23.35g$$

mass glucose: 23.35g
mass sucrose: 1.65g

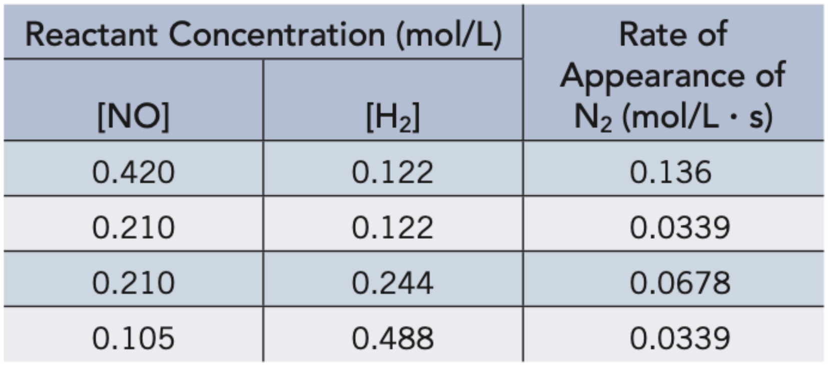
☆ note: numbers are slightly different from lecture because I kept more sig figs in the problem.

Kinetics ⏰

The reaction

2 NO(g) + 2 H2(g) n N2(g) + 2 H2O(g)

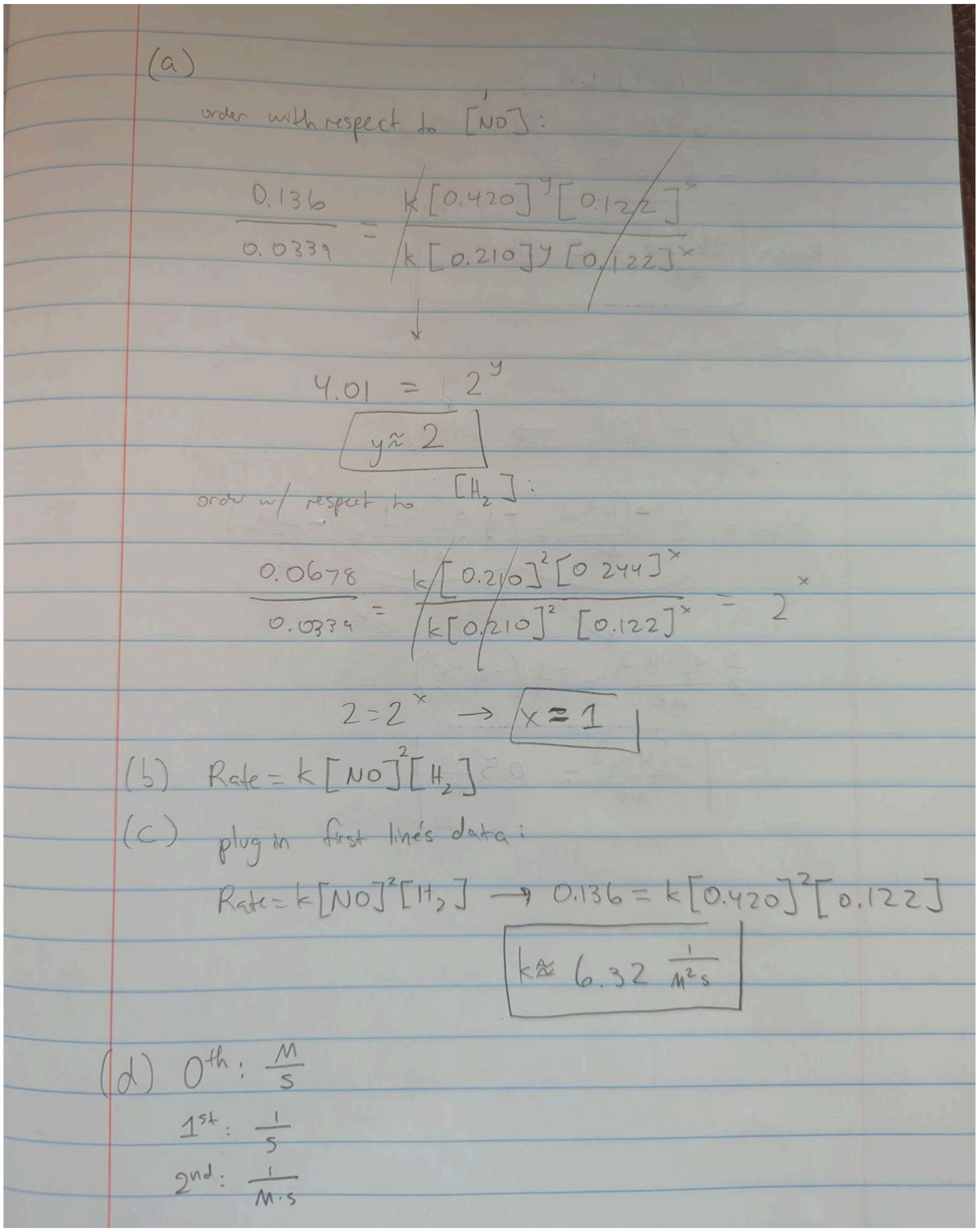
was studied at 904 °C, and the data in the table were collected:



Reactant Concentration (mol/L)		Rate of Appearance of N_2 (mol/L · s)
[NO]	[H_2]	
0.420	0.122	0.136
0.210	0.122	0.0339
0.210	0.244	0.0678
0.105	0.488	0.0339

(a) Determine the order of the reaction for each reactant.

(b) Write the rate equation for the reaction.
(c) Calculate the rate constant for the reaction
(d) As an aside, what are the units of k for 0th, 1st, and 2nd order reactions?
(e) Find the rate of appearance of N_2 at the instant when [NO] = 0.350 mol/L and [H_2] = 0.205 mol/L.



(a)

order with respect to [NO]:

$$\frac{0.136}{0.0339} = \frac{\cancel{k}[0.420]^y\cancel{[0.122]^x}}{\cancel{k}[0.210]^y\cancel{[0.122]^x}}$$

$$\downarrow$$

$$4.01 = 2^y$$

$$\boxed{y \approx 2}$$

order w/ respect to $[H_2]$:

$$\frac{0.0678}{0.0339} = \frac{\cancel{k}\cancel{[0.210]^2}[0.244]^x}{\cancel{k}\cancel{[0.210]^2}[0.122]^x} = 2^x$$

$$2 = 2^x \rightarrow \boxed{x \approx 1}$$

(b) $\text{Rate} = k[NO]^2[H_2]$

(c) plug in first line's data:

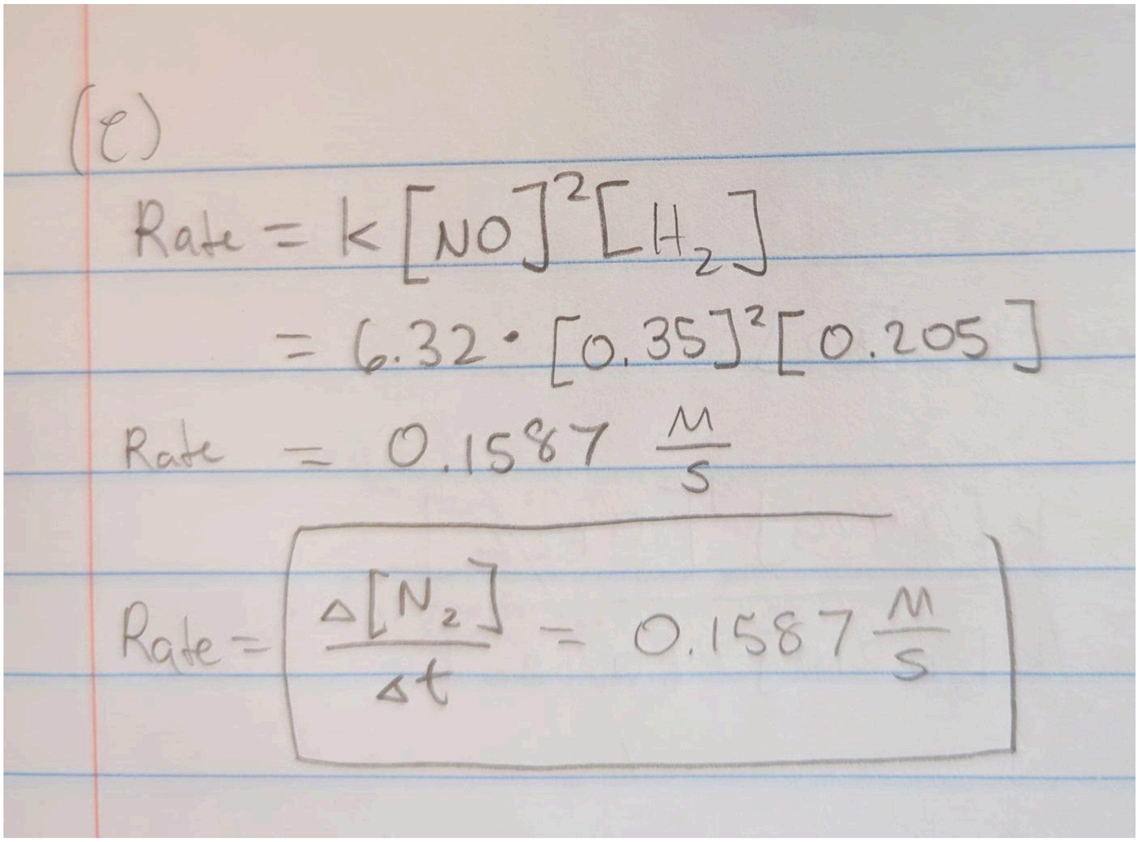
$\text{Rate} = k[NO]^2[H_2] \rightarrow 0.136 = k[0.420]^2[0.122]$

$$\boxed{k \approx 6.32\ \frac{1}{M^2 s}}$$

(d) 0^{th}: $\frac{M}{s}$

1^{st}: $\frac{1}{s}$

2^{nd}: $\frac{1}{M \cdot s}$



(e)

$$Rate = k[NO]^2[H_2]$$

$$= 6.32 \cdot [0.35]^2[0.205]$$

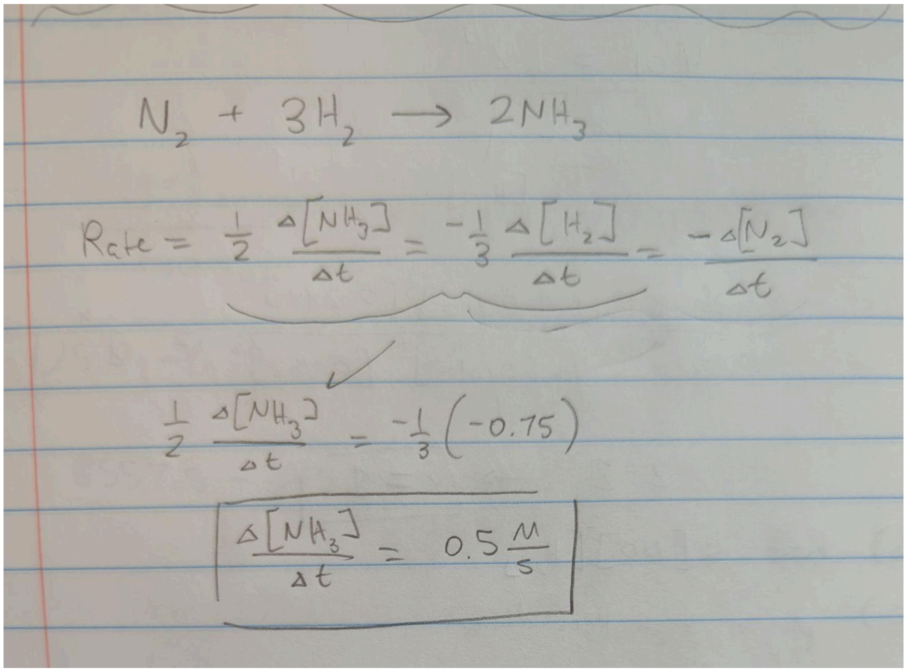
$$Rate = 0.1587 \frac{M}{s}$$

$$Rate = \boxed{\frac{\Delta[N_2]}{\Delta t} = 0.1587 \frac{M}{s}}$$

Consider the following unbalanced chemical reaction:

N_2 + H_2 -> NH_3

If the H_2 is consumed at a rate of -0.75 M/s in this reaction, what is the rate at which NH_3 is produced (i.e. $\Delta[NH_3]/\Delta s$)?



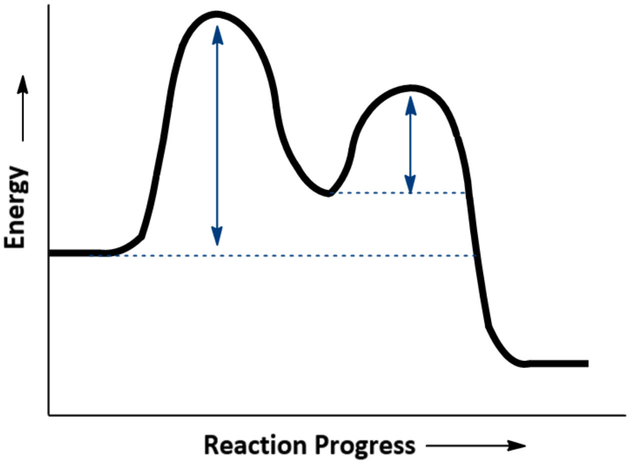
$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$\text{Rate} = \underbrace{\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t}} = -\frac{\Delta[N_2]}{\Delta t}$$

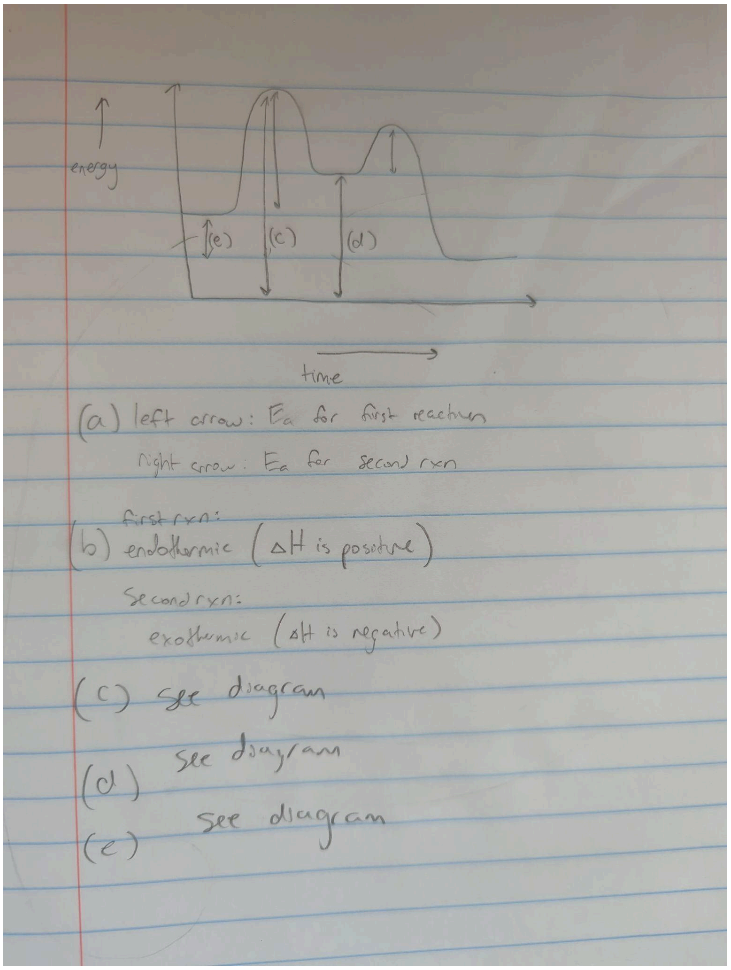
$$\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{3}(-0.75)$$

$$\boxed{\frac{\Delta[NH_3]}{\Delta t} = 0.5\,\frac{M}{s}}$$

Consider the following energy diagram showing a two step reaction:



(a) What does the left arrow represent? What about the right?
(b) Is the first reaction exothermic or endothermic? What about the second reaction?
(c) Draw an double pointed arrow (like the ones on the diagram) representing the total energy of the first transition state.
(d) Draw another double pointed arrow representing the total energy of the intermediate.
(e) Draw another double pointed arrow representing the total ΔH of the reaction.



(a) left arrow: E_a for first reaction

right arrow: E_a for second rxn

first rxn:

(b) endothermic (ΔH is positive)

Second rxn:

exothermic (ΔH is negative)

(c) see diagram

(d) see diagram

(e) see diagram

97) The oxidation of iodide ion by the hypochlorite ion in the presence of hydroxide ions $I^-(aq) + ClO^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$ was studied at 25 °C, and the following initial rates data (Y. Chia and R. E. Connick, Journal of Physical Chemistry, 1959, 63, 1518–1519) were collected:

	Initial Concentrations (mol/L)			Initial Rate
Experiment	$[ClO^-]$	$[I^-]$	$[OH^-]$	(mol IO^-/L · s)
1	4.0×10^{-3}	2.0×10^{-3}	1.0	4.8×10^{-4}
2	2.0×10^{-3}	4.0×10^{-3}	1.0	5.0×10^{-4}
3	2.0×10^{-3}	2.0×10^{-3}	1.0	2.4×10^{-4}
4	2.0×10^{-3}	2.0×10^{-3}	0.50	4.6×10^{-4}

(a) Determine the rate law for this reaction

The reaction is first order in $[ClO^-]$ (experiments 1 and 3), first order in $[I^-]$ (experiments 2 and 3), and −1 order in [OH−] (experiments 3 and 4).

Therefore, Rate = k[ClO−][I−]/[OH−].

(b) One mechanism that has been proposed for this reaction is the following:

Step 1: $ClO^- + H_2O \rightleftharpoons HOCl + OH^-$ fast, reversible

Step 2: $I^- + HOCl \rightarrow HOI + Cl^-$ slow

Step 3: $HOI + OH^- \rightarrow IO^- + H_2O$ fast

Show that the rate law predicted by this mechanism matches the experimentally determined rate law in part a.

Step 2 is the rate determining step. For this step, rate = $k[I^-][HOCl]$.

From the first step, $K_{eq} = [HOCl][OH^-]/[ClO^-]$, so $[HOCl] = K_{eq}\,[ClO^-]/[OH^-]$; substituting for [HOCl] in the rate equation for the second step gives the observed rate law

92) Many biochemical reactions are catalyzed by acids. A typical mechanism consistent with the experimental results (in which HA is the acid and X is the reactant) is:

Step 1: Fast, reversible: $HA \rightleftharpoons H^+ + A^-$

Step 2: Fast, reversible: $X + H^+ \rightleftharpoons XH^+$

Step 3: Slow $XH^+ \rightarrow \text{products}$

a) What rate law is derived from this mechanism?

$R_3 = k'[XH^+]$ $[XH^+] = K_2[X][H^+]$

$R_3 = k''[X][H^+]$ $[H^+] = \dfrac{K_1[HA]}{[A^-]}$

$$R_3 = \frac{k[X][HA]}{[A^-]}$$

b) What is the order of the reaction with respect to HA?

First Order

c) How would doubling the concentration of HA affect the reaction?

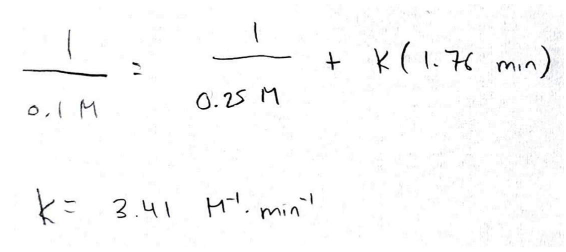
Double the reaction rate

85) The decomposition of nitrogen dioxide at a high temperature:

$$NO_2(g) \rightarrow NO(g) + 1/2\ O_2(g)$$

is second-order in this reactant.

(a) Determine the rate constant for this reaction if it takes 1.76 min for the concentration of NO_2 to fall from 0.250 mol/L to 0.100 mol/L.



$$\frac{1}{0.1\ M} = \frac{1}{0.25\ M} + k(1.76\ min)$$

$$k = 3.41\ M^{-1} \cdot min^{-1}$$

(b) If the chemical equation is written as:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

what is the value of the rate constant?

The rate constant (k') for the rewritten equation is 1/2 the value of the rate constant, k, for the original equation.

The rate equation for the original equation is $-\Delta[NO_2]/\Delta t = k[NO_2]$.

For the rewritten equation the rate equation is $-(1/2)\Delta[NO_2]/\Delta t = k'[NO_2]$ or $-\Delta[NO_2]/\Delta t = 2k'[NO2]$. Therefore, $k = 2k'$ or $k' = (1/2)k$.

84) The decomposition of SO_2Cl_2 to SO2 and Cl_2 is first-order in SO_2Cl_2.

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

$$\text{Rate} = k[SO_2Cl_2] \text{ where } k = 0.17/\text{h}$$

a) What is the rate of decomposition when $[SO_2Cl_2] = 0.010$ M?
b) What is the half-life of the reaction?
c) If the initial pressure of SO_2Cl_2 in a flask is 0.050 atm, what is the pressure of all gases (i.e., the total pressure) in the flask after the reaction has proceeded for one half-life?

84) a) $\text{Rate} = (0.17 / h)(0.01\ M) = 0.0017\ M/h$

b) $t_{1/2} = \dfrac{\ln(2)}{0.17\ h^{-1}} = 4.08\ h$

c) $P_{Total} = 1/2(0.05\ atm) + 2(0.025\ atm) = 0.075\ atm$

45) Calculate the activation energy, E_a, for the reaction $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$ from the observed rate constants: k at 25 °C = $3.46 \times 10^{-5}\ s^{-1}$ and k at 55 °C = $1.5 \times 10^{-3}\ s^{-1}$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{3.46 \times 10^{-5}\ s^{-1}}{1.5 \times 10^{-3}\ s^{-1}}\right) = \frac{E_a}{R}\left(\frac{1}{328\ K} - \frac{1}{298\ K}\right)$$

$$12281.1\ K = \frac{E_a}{R}$$

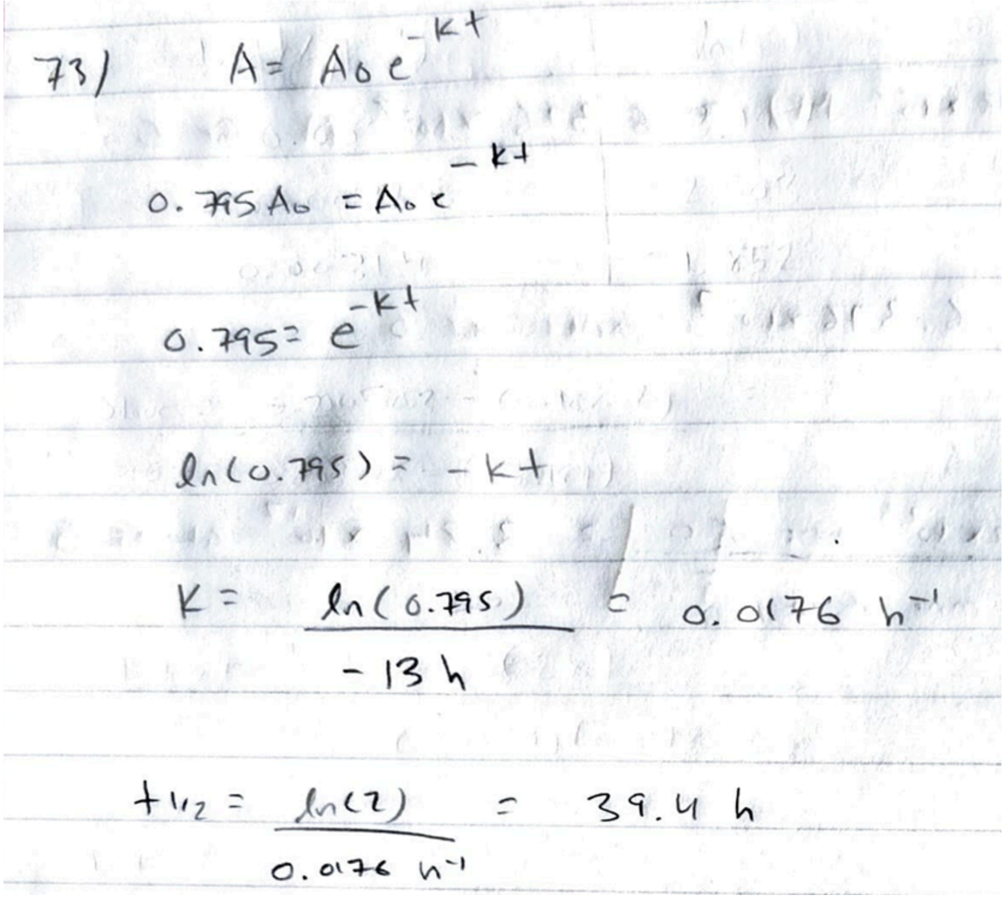
$$E_a = (12281.1\ K)(8.314\ J/mol \cdot K)$$

$$E_a = 102105\ J/mol \times \frac{1\ kJ}{1000\ J} = 102\ kJ/mol$$

73) The decomposition of dinitrogen pentaoxide

$$N_2O_5(g) \rightarrow 2\ NO_2(g) + 1/2\ O_2(g)$$

has the following rate equation: Rate = $k[N_2O_5]$. It has been found experimentally that the decomposition is 20.5% complete in 13.0 hours at 298 K. Calculate the rate constant and the half-life at 298 K.



73) $A = A_0 e^{-kt}$

$0.795 A_0 = A_0 e^{-kt}$

$0.795 = e^{-kt}$

$\ln(0.795) = -kt$

$$K = \frac{\ln(0.795)}{-13\ h} = 0.0176\ h^{-1}$$

$$t_{1/2} = \frac{\ln(2)}{0.0176\ h^{-1}} = 39.4\ h$$

Equilibrium

63) At 1800 K, oxygen dissociates very slightly into its atoms.

$$O_2(g) \rightleftharpoons 2\,O(g)$$

$$K_p = 1.2 \times 10^{-10}$$

If you place 0.050 mol of O_2 in a 10.-L vessel and heat it to 1800 K, how many O atoms are present in the flask?

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.2 \times 10^{-10}}{(0.082 \times 1800)^1} = 8.13 \times 10^{-13}$$

$$[O_2] = \frac{0.05\ \text{mol}}{10\ \text{L}} = 0.005\ \text{M}$$

	O_2	$\rightleftharpoons$	$2O$
I	0.005		0
C	$-x$		$+2x$
E	$0.005-x$		$2x$

$$8.13 \times 10^{-13} = \frac{[2x]^2}{0.005-x} \Rightarrow 4x^2 + 8.13 * 10^{-13}\,x - 4.065 * 10^{-15} = 0$$

$$x = 3.188 \times 10^{-8}\ \text{M}$$

$$[O]_E = 2(3.188 \times 10^{-8}\ \text{M}) = 6.376 \times 10^{-8}\ \text{M}$$

$$6.376 \times 10^{-8}\ \frac{\text{mol}}{\text{L}} \times 10\ \text{L} \times \frac{6.02 \times 10^{23}\ \text{atoms of O}}{1\ \text{mole of O}} = 3.84 \times 10^{17}\ \text{atoms of O}$$

31) Dinitrogen trioxide decomposes to NO and NO_2 in an endothermic process ($\Delta_rH°$ = 40.5 kJ/mol-rxn).

$$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$$

Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made.

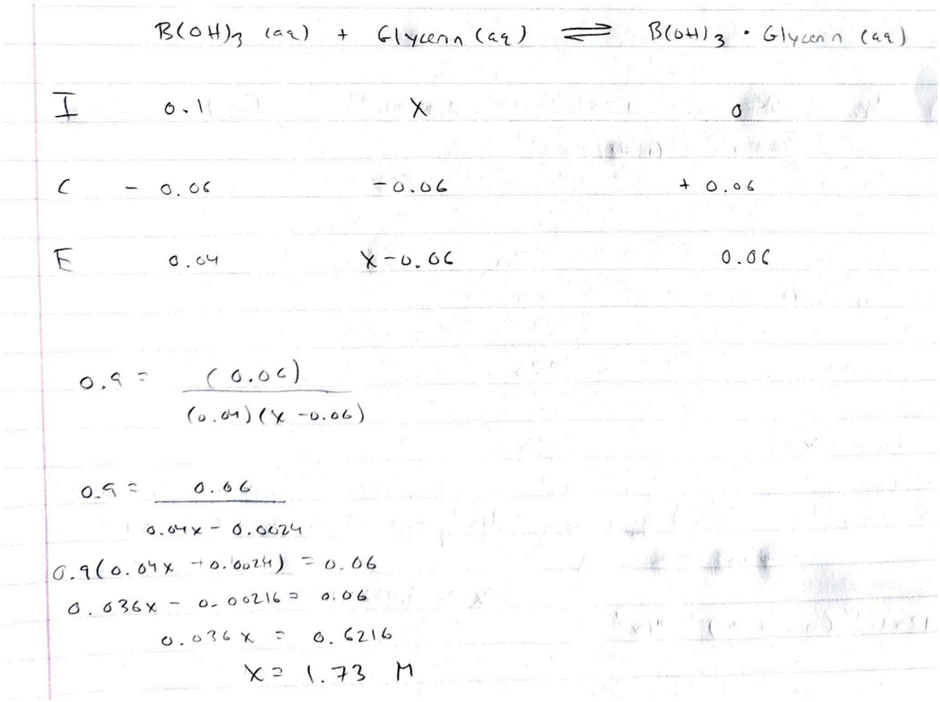
a) adding more $N_2O_3(g)$
b) adding more $NO_2(g)$
c) increasing the volume of the reaction flask
d) lowering the temperature

a) Equilibrium shifts to the right
b) Equilibrium shifts to the left
c) Equilibrium shifts to the right
d) Equilibrium shifts to the left

65) Boric acid and glycerin form a complex

$$B(OH)_3(aq) + glycerin(aq) \rightleftharpoons B(OH)_3 \cdot glycerin(aq)$$

with an equilibrium constant of 0.90. If the concentration of boric acid is 0.10 M, how much glycerin should be added, per liter, so that 60.% of the boric acid is in the form of the complex?



	$B(OH)_3$ (aq)	+ Glycerin (aq)	$\rightleftharpoons$ $B(OH)_3 \cdot$ Glycerin (aq)
I	0.1	x	0
C	− 0.06	−0.06	+ 0.06
E	0.04	x − 0.06	0.06

$$0.9 = \frac{(0.06)}{(0.04)(x - 0.06)}$$

$$0.9 = \frac{0.06}{0.04x - 0.0024}$$

$$0.9(0.04x + 0.0024) = 0.06$$

$$0.036x - 0.00216 = 0.06$$

$$0.036x = 0.6216$$

$$x = 1.73 \text{ M}$$