LAST NAME: ____

FIRST NAME: ____

Student Number: ____

CHM 1311 B
Midterm #2
Fall 2013

Please keep your work covered at all times and keep your eyes on your own paper! Cheating or any appearance of cheating will result in an F in the course and possible expulsion from the university.

There are 9 pages in this test. The last two pages include a periodic table, equations covered in the course, and data that may be useful for some questions. You may rip these pages off of the exam and use them to cover your work during the test.

You must show all work to receive partial credit.
Marks may be deducted if an unreasonable number of sig figs are shown in your final answer.

You have 75 minutes to complete this test.

**

Question	**Points Possible**	**Points Earned**
1	**12**	
2	**5**	
3	**5**	
4	**9**	
5	**10**	
6	**9**	
TOTAL	**50**	

#1. (12 points) Short Answer Questions (2 marks each)

a) Write the balanced chemical equation corresponding to the $\Delta_f H^o$ of NaH_2PO_4 (s). Be sure to include the phases.

$$Na\,(s) + H_2\,(g) + P\,(s) + 2\,O_2\,(g) \rightarrow NaH2PO_4\,(s)$$

b) What would be the value of K at 25°C for the reaction $4\,A + 2\,B \leftrightarrows 2\,C$, given the data below at 25°C:

$$2\,A + B \leftrightarrows X \qquad K = 100$$
$$2\,C \leftrightarrows 2\,X \qquad K = 10$$

K = __________1000__________________

c) The reaction 2A + B -> C has a rate constant that is equal to 45 s^{-1}. A plot of ln[A] versus time is linear. What is the rate law for this reaction?

$$\text{rate} = k \times [A] = 0.45\ s^{-1} \times [A]$$

d) Suppose 1 mol of NH_3, $HClO_4$, NaI, or HF is added to 1 L of water.

i. Which solution will have the lowest pH?

NH_3

ii. Which solution will have the highest pH?

$HClO_4$

e) What is the $[OH^-]$ concentration of a pH = 6.0 solution?

$$pH + pOH = pKw$$
$$pOH = pKw - pH = 14\,.0 - 6.0 = 8.0$$
$$[OH\text{-}] = 10^{-pOH} = 10^{-8}\ M$$

f) Which gas would you expect to have the greater heat of reaction per mole of combustion; methane (CH_4) or ethane (C_2H_6)? Explain your answer in ~one sentence.

C_2H_6 has more C-H bonds per mole than CH_4, therefore it will have a greater heat of reaction. A relatively small amount of energy is required to break a C-H bond, while a relatively large amount of energy is gained by the formation of C=O bonds, as shown by the corresponding BE values (423 kJ mol^{-1} for C-H, 745 kJ mol^{-1} for C=O). Therefore the compound with the larger number of C-H bonds per mole will yield the greater heat of reaction per mole of combustion.

#2. At 25^{o}C HI breaks down according to: rate =k [HI]^2 with a rate constant of 2.4 x10^{-21} L mol^{-1} s^{-1}. If 2.55 mol of HI is placed in a 10.0 L container, how many years will it take for 5.0% to react? (5 marks)

According to the rate equation given, this is a second order reaction, with the corresponding integrated rate law:

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

We have been given k, and have the information we need to calculate the initial concentration of reactant HI:

$$[\mathrm{HI}]_o = \frac{n}{V} = \frac{2.55\ \mathrm{mol}}{10\ \mathrm{L}} = 0.255\ \mathrm{mol\ L^{-1}}$$

To calculate the time it takes for 5% to react, we recognize that the concentration of HI at this time is 99% of the initial concentration; 0.95[HI]o. This can be substituted into the rate equation:

$$\frac{1}{0.95[\mathrm{HI}]_o} - \frac{1}{[\mathrm{HI}]_o} = kt$$

$$t = \frac{1}{k}\left(\frac{1}{0.95(0.255)} - \frac{1}{0.255}\right) = 8.60\times10^{19}\ \mathrm{s}$$

Convert into years: $\left(8.60\times10^{19}\ \mathrm{s}\right)\left(\frac{1\ \mathrm{min}}{60\ \mathrm{s}}\right)\left(\frac{1\ \mathrm{hour}}{60\ \mathrm{min}}\right)\left(\frac{1\ \mathrm{day}}{24\ \mathrm{hours}}\right)\left(\frac{1\ \mathrm{year}}{365\ \mathrm{days}}\right) = 2.7\times10^{12}\ \mathrm{years}$

Answer: ________2.7x10^{12}_________________ years

#3. 2.55 g of a hydrocarbon was placed in the bomb of a calorimeter. The bomb was immersed in 5.220 L of water and the sample was burned. The water temperature rose from 25.2 ^{o}C to 26.6 ^{o}C. If the calorimeter (excluding the water) had a heat capacity of 1065 J/K, what was the heat released per gram of hydrocarbon? (5 marks)

$$q_{\mathrm{HC}} = -\left(q_{calorimeter} + q_{\mathrm{H2O}}\right)$$

$$\begin{aligned} q_{\mathrm{HC}} &= -\left(c_{\mathrm{Calorimeter}} \times \Delta T_{\mathrm{Calorimeter}} + m_{\mathrm{H_2O}} \times c_{\mathrm{H_2O}} \times \Delta T_{\mathrm{H_2O}}\right) \\ &= -\left(c_{\mathrm{Calorimeter}} \times \Delta T_{\mathrm{Calorimeter}} + d_{\mathrm{H_2O}} V_{\mathrm{H_2O}} \times c_{\mathrm{H_2O}} \times \Delta T_{\mathrm{H_2O}}\right) \\ &= -\left(1065\ \mathrm{J/K} \times (26.6-25.2)\mathrm{K} + (1.00\ \mathrm{g/mL})(10^3\ \mathrm{mL/L})(5.220\ \mathrm{L}) \times (4.184\ \mathrm{J/g/K}) \times (26.6-25.2)\mathrm{K}\right) \\ &= -32.1\ \mathrm{kJ} \end{aligned}$$

This is the total energy produced in the combustion reaction. To find the heat released per gram of hydrocarbon, we just divide this heat by the mass of hydrocarbon burned.

$$\frac{q_{\mathrm{HC}}}{g} = \frac{-32.07\ \mathrm{kJ}}{2.55\ \mathrm{g}} = -12.6\ \mathrm{kJ/g}$$

Answer: __12.6 kJ per gram of hydrocarbon of heat is produced

#4. The following reaction was started by the addition of a catalyst to a 1.000 L flask containing 0.7000 bar of nitric oxide gas at 298 K, where K = 4.35 x 10^{-31} at this temperature:

$$N_2 (g) + O_2 (g) \leftrightarrows 2NO (g)$$

a) What is the partial pressure of N_2 at equilibrium? (5 marks)

	N_2	O_2	2 NO
Initial	0	0	0.700 bar
Change	x	x	-2x
Equilibrium	x	x	0.700 – 2x

$$K = \frac{p_{NO}^2}{p_{N_2}p_{O_2}} = \frac{(0.700-2x)^2}{x^2}$$

$$\sqrt{K} = \frac{(0.700-2x)}{x}$$

$$x = \frac{0.700}{2+\sqrt{K}} = 0.350 = p_{N_2}$$

Answer: **0.350 bar**

b) What is Kc for this reaction? (1 mark)

$$K = K_c(RT)^{\Delta n(\text{gas})}$$

Since the number of moles of gas in the reactants is the same as the number of moles of gas in the products, *K* = *Kc*.

c) Given that $\Delta_f H^o$ for NO is 91.3 kJ/mol, at what temperature should the reaction be run to increase the equilibrium constant by a factor of 1000 (*i.e.* increase the equilibrium constant 1000-fold)? (3 marks)

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = -\frac{2(\Delta_f H^o)}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\frac{1}{T_2} = -\frac{R}{2(\Delta_f H^o)}\ln\left(\frac{K_2}{K_1}\right)+\frac{1}{T_1}$$

$$= -\frac{8.314 \text{ J/K/mol}}{2(91.3 \text{ kJ/mol})(10^3 \text{ J/kJ})}\ln\left(\frac{1000K_1}{K_1}\right)+\frac{1}{298 \text{ K}} = 0.003041 \text{ K}^{-1}$$

$$T_2 = 329 \text{ K}$$

#5. For the oxidation of nitric oxide into nitrogen dioxide, the following mechanism has been proposed:

$$2NO\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2\,(g) \qquad \textbf{Rapid equilibrium}$$

$$N_2O_2\,(g) + O_2\,(g) \xrightarrow{k_2} 2\,NO_2\,(g)$$

With the following values for the rate constants: $k_1 = 4.8 \times 10^3$, $k_{-1} = 3.6 \times 10^3$ and $k_2 = 1.3 \times 10^{-2}$.

a) **What is the molecularity of the slowest step in this mechanism? (1 mark)**

The second step has the smallest rate constant – its molecularity is 2.

b) **Derive the rate law for the overall reaction in terms of the concentration of reactants. (4 marks)**

$$\text{rate} = k_2[N_2O_2][O_2]$$

Since the first step is in rapid equilibrium, rate of the forward reaction = rate of reverse reaction:

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

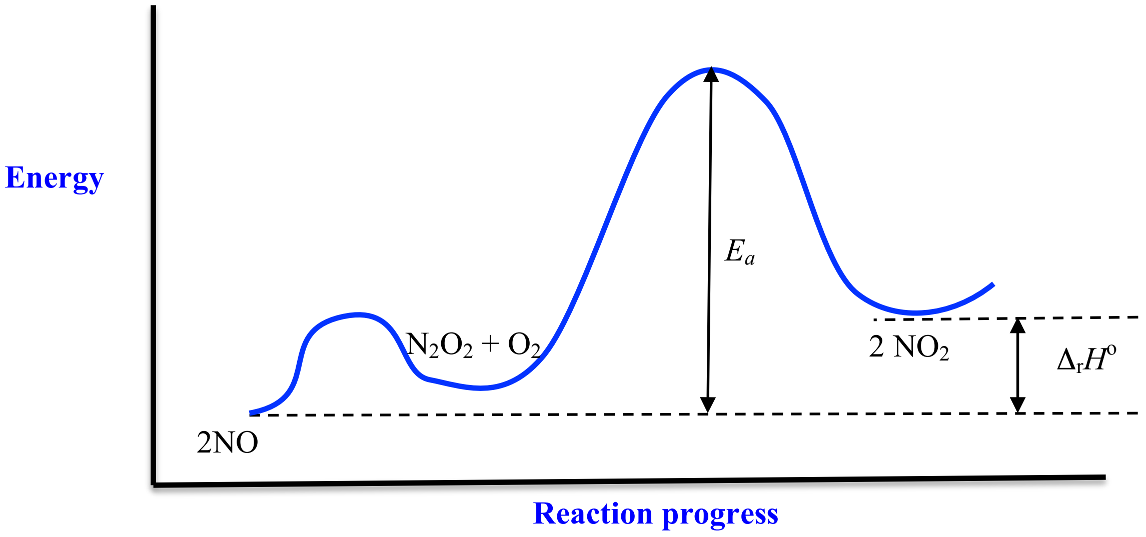
$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

Substitute this into first rate equation:

$$\text{rate} = \frac{k_2 k_1}{k_{-1}}[NO]^2[O_2] = \frac{(1.3\times10^{-2})(4.8\times10^{3})}{(3.6\times10^{3})}[NO]^2[O_2] = 0.017[NO]^2[O_2]$$

Rate Law: ________________ **Rate = $0.017[NO]^2[O^2]$** ________________

c) **Draw the reaction energy profile for this reaction (Δ_rH^o is 51.8 kJ/mol for the overall reaction). Be sure to label your axes, and indicate where in the graph each species in the reaction occurs. Also label the graph with Δ_rH^o and E_a. (5 marks)**



#6. a) Some species of ant will spray concentrated solutions of formic acid (HCOOH) from the abdomen as a defense mechanism. What is the pH of a 17.8 mol/L solution of formic acid? Ka = 1.70 x 10^{-4}. (5 marks)

$$\textbf{HCOOH (aq) + H}_2\textbf{O} \rightleftharpoons \textbf{HCOO- (aq) + H}_3\textbf{O}^+\textbf{ (aq)}$$

	HCOOH	HCOO-	$H3O^+$
Initial	17.8 M	0	$10^{-7} \approx 0$
Change	-x	x	x
Equilibrium	17.8 - x	x	x

$$Ka = \frac{[\text{HCOO-}][\text{H}_3\text{O}^+]}{[\text{HCOOH}]} = \frac{x^2}{17.8 - x}$$

$$\text{Since } \frac{[\text{HCOOH}]_o}{Ka} = \frac{17.8}{1.7 \times 10^{-4}} > 400 \quad 17.8 - \text{x} \approx 17.4$$

$$Ka = \frac{x^2}{17.8} \qquad x = \sqrt{17.8Ka} = 0.0550 \text{ M} = [\text{H}_3\text{O}^+]$$

pH = -log[H3O+] = 1.26

pH = 1.26

b) Write the net balanced chemical reaction that would be expected if NaCN is added to a solution of formic acid. (2 marks)

$$\textbf{CN- (aq) + HCOOH (aq)} \rightleftharpoons \textbf{HCN (aq) + HCOO- (aq)}$$

c) Given that the pKa of the conjugate acid of NaCN is 9.2, what will be the preferred direction for the reaction in b)? Provide a brief explanation justifying your answer. (2 marks)

Ka (HCOOH) = 1.7 x 10^{-4} Ka (HCN) = $10^{-9.2}$ = 6.3 x 10^{-10}

Since HCOOH is the stronger acid the preferred direction will be forward.

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 $1\ dm^3 =$ 1000 mL = 1 L $1\ m^3 = 1000$ L
1 cal = 4.184 J

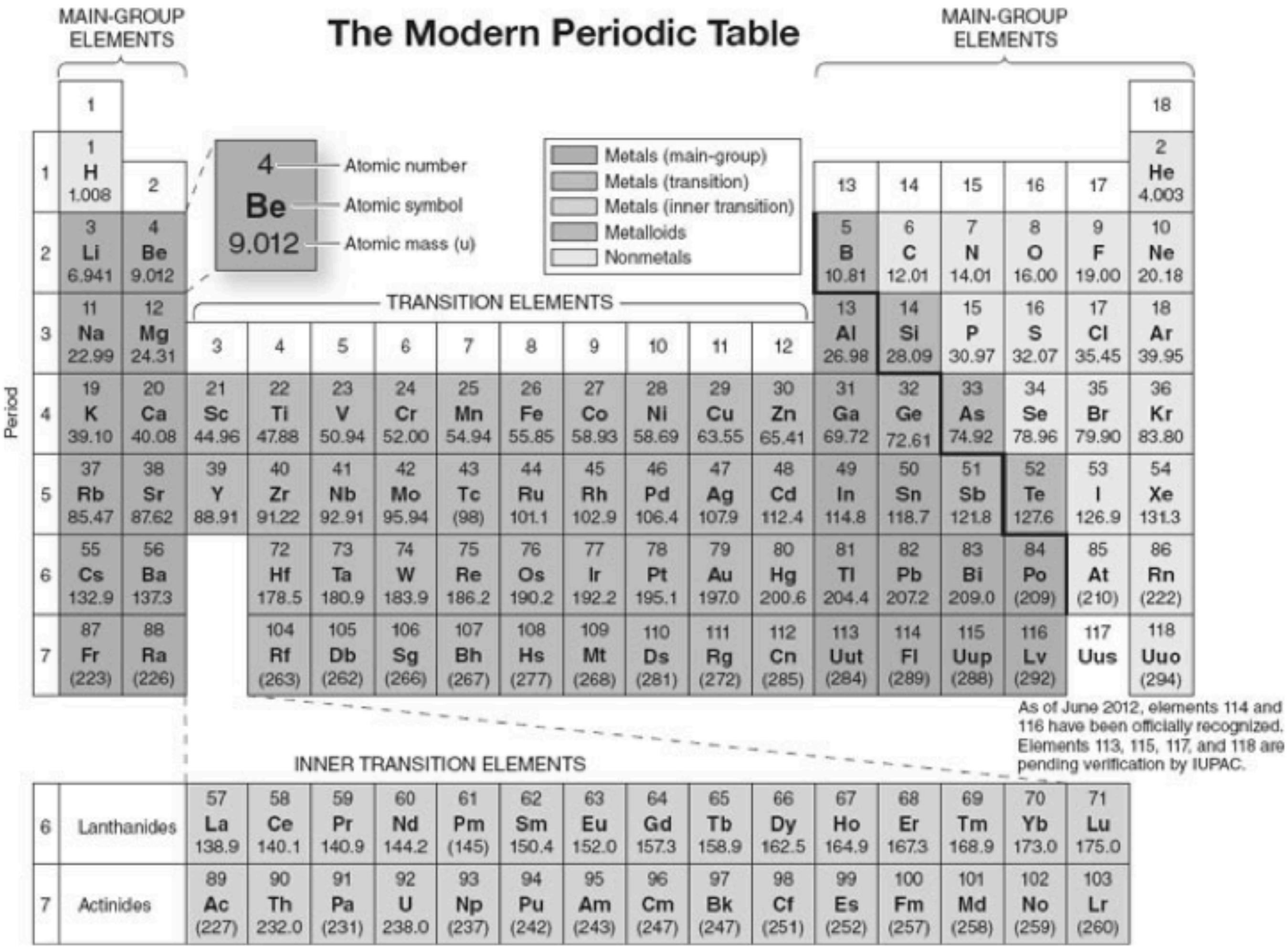
Avogadro's Number	N	$6.022\times10^{23}\ mol^{-1}$
Atomic mass unit	u	1.66054×10^{-27} kg
Gas constant	R	$8.31451\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
	R	$0.08206\ atm{\cdot}L{\cdot}K^{-1}{\cdot}mol^{-1}$
	R	$8.31451\ m^3\ Pa{\cdot}K^{-1}{\cdot}mol^{-1}$
	R	$0.0831451\ bar\ L{\cdot}K^{-1}{\cdot}mol^{-1}$

Data For Water

Density = 1.00 g/mL (at 25°C) $\Delta H°_{vap} = 40.7\ kJ\ mol^{-1}$
$c = 4.184\ J\ g^{-1}\ K^{-1}$ (liquid) $\Delta H°_{fus} = 6.02\ kJ\ mol^{-1}$

Average Bond Energies

O – H 467 $kJ\ mol^{-1}$	C – H 413 $kJ\ mol^{-1}$	C – C 347 $kJ\ mol^{-1}$
C – O 358 $kJ\ mol^{-1}$	C = O 745 $kJ\ mol^{-1}$	O = O 498 $kJ\ mol^{-1}$



The Modern Periodic Table

MAIN-GROUP ELEMENTS   TRANSITION ELEMENTS   MAIN-GROUP ELEMENTS

4 – Atomic number
Be – Atomic symbol
9.012 – Atomic mass (u)

Metals (main-group)
Metals (transition)
Metals (inner transition)
Metalloids
Nonmetals

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3		72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)		104 Rf (263)	105 Db (262)	106 Sg (266)	107 Bh (267)	108 Hs (277)	109 Mt (268)	110 Ds (281)	111 Rg (272)	112 Cn (285)	113 Uut (284)	114 Fl (289)	115 Uup (288)	116 Lv (292)	117 Uus	118 Uuo (294)

As of June 2012, elements 114 and 116 have been officially recognized. Elements 113, 115, 117, and 118 are pending verification by IUPAC.

INNER TRANSITION ELEMENTS

6	Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
7	Actinides	89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Equations Covered Since Midterm 1

$\Delta_r H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reactants})$

$\Delta_r H^o = \sum m\text{BE}(\text{reactants}) - \sum n\text{BE}(\text{products})$

$q = c \times m \times \Delta T$

$\text{Rate} = \frac{1}{v_\text{X}}\frac{\Delta[\text{X}]}{\Delta t}$

$\text{Rate} = k[\text{A}]^m[\text{B}]^n\ldots$

$k = Ae^{-\frac{E_a}{RT}}$

$[\text{A}]_t - [\text{A}]_o = -kt$

$\ln\frac{[\text{A}]_o}{[\text{A}]_t} = kt$

$\frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_o} = kt$

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

$K = K_c(RT)^{\Delta n(\text{gas})}$

$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$ax^2 + bx + c = 0$

$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\text{pH} = -\log[\text{H}_3\text{O}^+]$

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

$\text{pH} + \text{pOH} = 14$

$K_a \times K_b = K_w$

$pK_a = -\log K_a$

$pK_b = -\log K_b$

Midterm 1 Equations

$T(\text{in K}) = T(\text{in }^\circ\text{C}) + 273.15\text{ K}$

$n = \frac{m}{M}$

$\%\text{ Yield} = \frac{\text{actual yield}}{\text{theoretical yield}}$

$c(\text{mol/L}) = \frac{n}{V}$

$m(\text{mol}/kg) = \frac{n_{solute}}{m_{solvent}}$

$c_1V_1 = c_2V_2$

$pV = nRT$

$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$p_T = p_1 + p_2 + p_3 + \ldots$

$p_A = X_A \times p_T$

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

$E_K = \frac{1}{2}m\text{v}^2$

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

$\frac{Rate\ A}{Rate\ B} = \sqrt{\frac{M_B}{M_A}}$

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

$w = -p\Delta V$

$\Delta U = U_{final} - U_{initial} = q + w$

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