Name: ____________________________ Student Number: _________________________

Chemistry 2000 Practice Final A

INSTRUCTIONS

1) Read the exam carefully before beginning. There are 15 questions on pages 2 to 14 followed by 2 pages of data/formulas/periodic table as well as a blank page for rough work. **Please ensure that you have a complete exam. If not, let an invigilator know immediately**. All pages must be submitted at the end of the exam.
2) If your work is not legible, it will be given a mark of zero.
3) Marks will be deducted for incorrect information added to an otherwise correct answer.
4) Marks will be deducted for improper use of significant figures and/or missing units.
5) Show your work for all calculations. Numerical answers without supporting calculations will not be given full credit.
6) You may use a calculator but only for calculation. No text-capable calculators are allowed.
7) **DO NOT OPEN THE EXAM UNTIL YOU ARE TOLD TO BEGIN. Beginning prematurely will result in removal of your exam paper and a mark of 0.**
8) You have **3 hours** to complete this exam. Nobody may leave the exam room during the first hour or the last 15 minutes of the exam.

Q	Mark
1	/ 14
2	/ 3
3	/ 6
4	/ 6
5	/ 7
6	/ 13
7	/ 15
8	/ 6

Q	Mark
9	/ 8
10	/ 3
11	/ 5
12	/ 9
13	/ 6
14	/ 8
15	/ 1

Total	/ 110

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1. Fill in each blank with the word or short phrase that best completes the sentence. **[14 marks]**

(a) Conduction of electricity is possible when the energy required to excite an electron from the ________________________ band into the ________________________ band is small.

(b) A(n) ________________-type semiconductor has been doped to contain extra electrons.

(c) Vibrational energy spacings correspond to the __________________________ region of the electromagnetic spectrum.

(d) According to valence bond theory, the nitrogen atom in NH_3 is ______ hybridized.

(e) The conjugate acid of NH_3 is _____________.

(f) The conjugate base of NH_3 is _____________.

(g) When $\Delta_r G° > 0$, the reaction is ____.

(h) In the equation $S = k_B ln\Omega$, S represents ________________________________ and Ω represents ____.

(i) A substance which has the density of a liquid but whose particles have high enough energy that they do not feel intermolecular forces is a ______________________________________.

(j) The temperature and pressure at which a substance is in equilibrium between the solid, liquid and gas phases is known as the _________________________.

(k) Raoult's law demonstrates that dissolving a non-volatile solute in a liquid ___________________________ the vapour pressure above that liquid.

(l) Two molecules that are nonsuperimposable mirror images are best described as a pair of ____.

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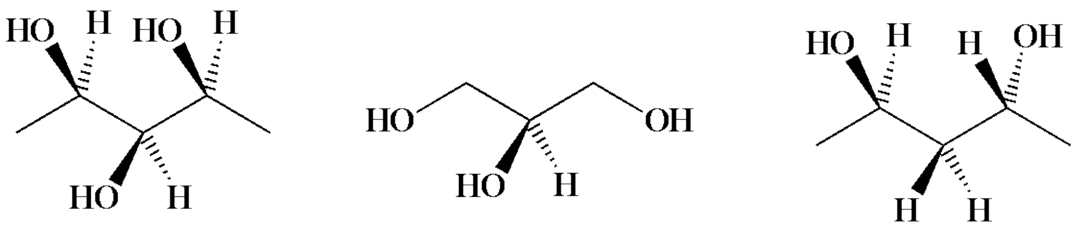
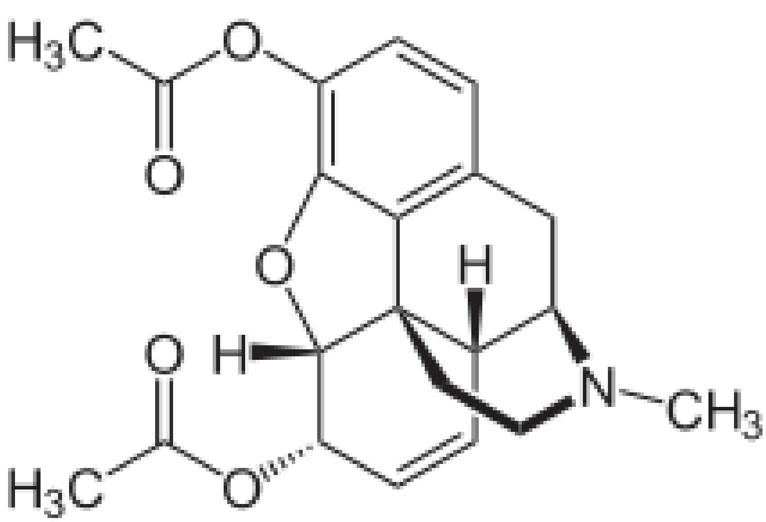
2. Consider the following three molecules. **[3 marks]**



(a) Circle any of these molecules which are chiral. *[1 mark]*

(b) Mark all chirality centers on all the molecules above with a *. *[2 marks]*

3. Circle and label the functional groups in heroin (shown below): **[6 marks]**
It must be clear which functional group name goes with each circle.



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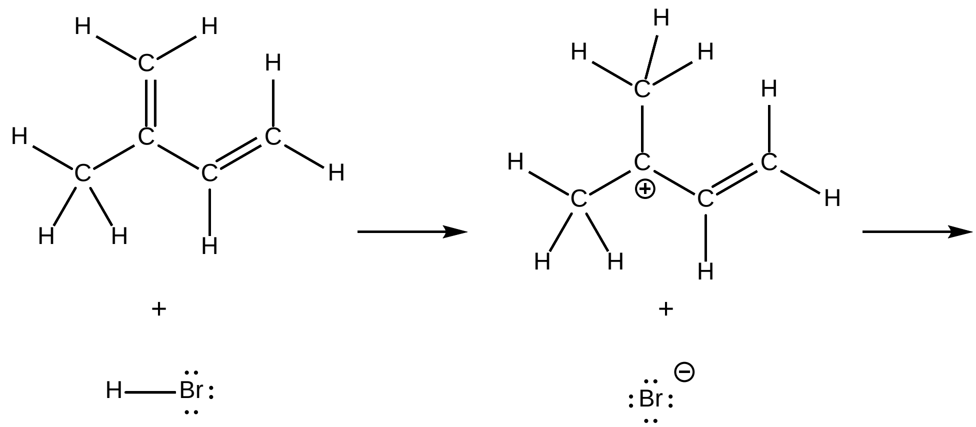
4. The chemical structure of isoprene is shown at the left below. When isoprene is reacted with HBr, a carbocation is formed, as shown, in the first step of a two-step reaction. **[6 marks]**



(a) Add curly arrows to the diagram above to show how the carbocation is formed. *[2 marks]*

(b) Add curly arrows to the diagram above to show what happens in the second step. *[1 mark]*

(c) On the diagram above, draw the product(s) of the second step. *[1 mark]*

(d) In theory, four different carbocations could have been produced by reacting isoprene with HBr. Briefly, explain why the one shown is the best. There are **two** important factors to address. *You may find it helpful to include a diagram in your answer.* *[2 marks]*

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5. **[7 marks]**

(a) Draw all isomers of C_3H_5Cl. *[5 marks]*

You may either draw expanded structures or use line-bond notation.
Marks will be deducted for incorrect or duplicate answers.

(b) Consider the set of molecules you just drew as your answer to part (a).
In the space below, redraw any pairs of stereoisomers and clearly indicate what makes them stereoisomers. *[2 marks]*

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6. Boron monofluoride (BF) is an unstable gas in isolation but has been found to exist as a stable ligand when combined with transition metals. **[13 marks]**

Orbital energies (Ry)			
	1s	2s	2p
B	-14.5	-1.03	-0.42
F	-51.2	-2.95	-1.37

(a) Draw a Lewis diagram for boron monofluoride. *[1 mark]*
Include any nonzero formal charges.

(b) What bond order does your Lewis diagram predict? *[1 mark]*

(c) Draw a valence molecular orbital energy level diagram for BF. *[9 marks]*

- Label all of the atomic and molecular orbitals. To the best of your ability, clearly indicate whether each molecular orbital is bonding, nonbonding or antibonding.
- Include the lines to show the linear combinations that form each MO.
- Populate the atomic orbitals and the molecular orbitals with electrons.

You do NOT have to draw pictures of the orbitals on your diagram. Just show the energy levels and which atomic orbitals combine to make each molecular orbital.

(d) Write the valence orbital occupancy (i.e., electron configuration) in line notation for BF. *[1 mark]*

(e) What bond order does your molecular orbital diagram predict for BF? *[1 mark]*

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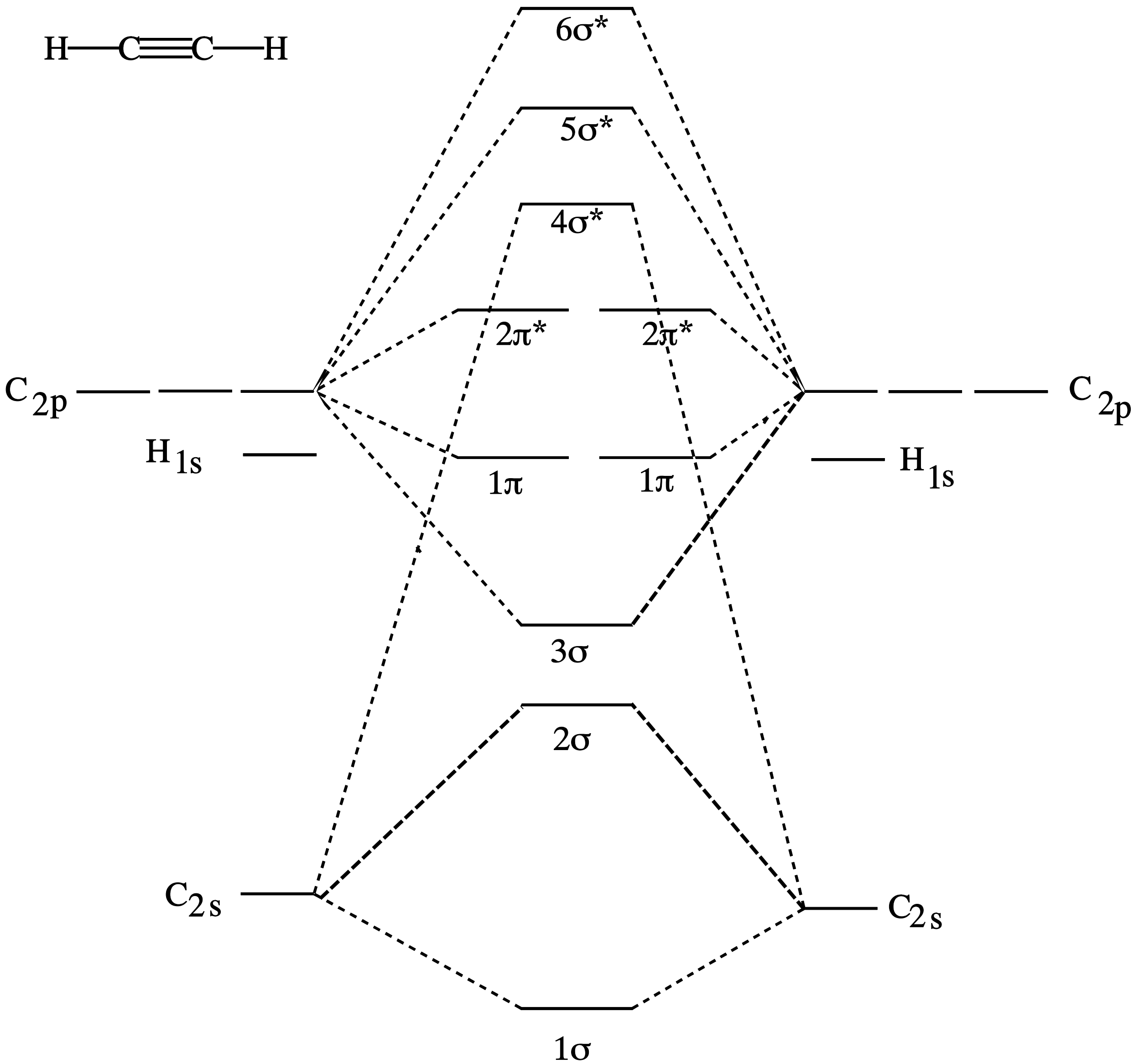
7. The figure below shows a molecular orbital energy level diagram for ethyne (formerly known as acetylene). The energy levels for the atomic orbitals of each half of the molecule (one carbon atom and one hydrogen atom) are shown on the left and right. ***Lines connecting the atomic orbitals of the <u>hydrogen</u> atoms to the corresponding molecular orbitals have been omitted for clarity. There is a line (not shown) from each H(1s) to every sigma MO.*** **[15 marks]**



(a) Complete the diagram above by adding electrons to the molecular orbitals. *[1 mark]*

(b) Which orbital is the HOMO? *[1 mark]*

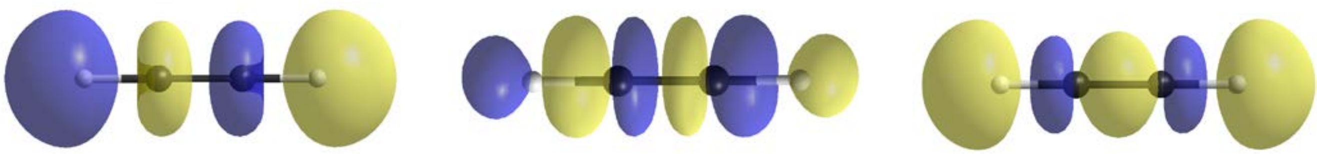
(c) Which orbital is the LUMO? *[1 mark]*

(d) If ethyne were to act as a nucleophile in a reaction, which orbital(s) would be involved in the reaction? *[1 mark]*

7. *continued…*

(e) In the space below, sketch the three sigma bonding molecular orbitals for ethyne. You may sketch the molecular orbital or sketch the superposition of the atomic orbitals. Clearly label each sketch so that we know which molecular orbital it shows. *[3 marks]*

(f) The pictures below show the calculated σ* orbitals for ethyne. *[3 marks]*
Underneath each picture, label the orbital as 4σ*, 5σ* or 6σ*.



(g) If ethyne were considered according to valence bond model, what would be the hybridization of the C atoms? *[1 mark]*

(h) In comparing the the MO and VB models of the bonding in ethyne, what is the same? *[2 marks]*

(i) In comparing the the MO and VB models of the bonding in ethyne, what is different? *[2 marks]*

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8. A common demonstration is to generate carbon dioxide in a test tube by heating a sample of solid magnesium carbonate: **[6 marks]**

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$$

(a) Is $\Delta_r G$ positive, negative or zero for this reaction? Briefly, justify your answer. *[2 marks]*

(b) Is $\Delta_r S$ positive, negative or zero for this reaction? Briefly, justify your answer. *[2 marks]*

(c) Is $\Delta_r H$ positive, negative or zero for this reaction? Briefly, justify your answer. *[2 marks]*

9. Consider the equilibrium expression below: **[8 marks]**

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Is this reaction favoured in the forward or reverse direction if the partial pressures of the initial mixture are 0.123 bar (PCl_5), 0.456 bar (PCl_3), and 0.789 bar (Cl_2) and the temperature is 25.00 °C?

10. Briefly demonstrate how the formula $\Delta_r G° = -RT ln K$ is derived from $\Delta_r G = \Delta_r G° + RT ln Q$. Your logic must be clear (which may require you to define terms). **[3 marks]**

11. Zinc metal can be used to convert VO_2^+ into VO^{2+} in aqueous acid. **[5 marks]**
An incomplete and unbalanced equation for this process is shown below:

$$VO_2^+(aq) + Zn(s) \rightarrow VO^{2+}(aq) + Zn^{2+}(aq)$$

(a) What is the oxidation state of V in VO_2^+? *[1 mark]*

(b) What is the oxidation state of V in VO^{2+}? *[1 mark]*

(c) Is Zn acting as an oxidizing agent or a reducing agent in this reaction? How do you know? *[1 mark]*

(d) Write a balanced chemical equation for this process. *[2 marks]*

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12. One of your professors received an email from a "Dr. Chem. Sorin Cosofret" containing the following statement: **[9 marks]**

> "Have you ever seen or heard about a battery having both electrodes identically and at both electrodes the very same chemical processes take place? Could such battery deliver an electric current into an electric circuit? … Although the answer of modern science is a categorically no, the experiments say a definitely yes."

"Dr." Cosofret is categorically wrong.

Such batteries are well known and are called concentration cells.

Such a cell might, for example, have Cu metal electrodes and Cu^{2+} cations in both cells.

(a) These cells always have the same value of E°. What is the value for E° for all concentration cells? *[1 mark]*

(b) Using the Cu/Cu^{2+} concentration cell as an example, write an equation for the half-reaction that takes place at the anode. *[1 mark]*

(c) Using the Cu/Cu^{2+} concentration cell as an example, write an equation for the half-reaction that takes place at the cathode. *[1 mark]*

(d) Consider the following list of possible concentration cells. *[1 mark]*

Circle **<u>all</u>** of the examples listed that would have a positive cell potential, E.

i. $Cu_{(s)}\left|Cu^{2+}_{(aq)}(0.020\ M)\right\|Cu^{2+}_{(aq)}(0.060\ M)\left|Cu_{(s)}\right.$

ii. $Cu_{(s)}\left|Cu^{2+}_{(aq)}(0.040\ M)\right\|Cu^{2+}_{(aq)}(0.060\ M)\left|Cu_{(s)}\right.$

iii. $Cu_{(s)}\left|Cu^{2+}_{(aq)}(0.060\ M)\right\|Cu^{2+}_{(aq)}(0.060\ M)\left|Cu_{(s)}\right.$

iv. $Cu_{(s)}\left|Cu^{2+}_{(aq)}(0.080\ M)\right\|Cu^{2+}_{(aq)}(0.060\ M)\left|Cu_{(s)}\right.$

v. $Cu_{(s)}\left|Cu^{2+}_{(aq)}(0.100\ M)\right\|Cu^{2+}_{(aq)}(0.060\ M)\left|Cu_{(s)}\right.$

(e) For one of the answers you circled in part (d), calculate E at 25.00 °C. *[5 marks]*

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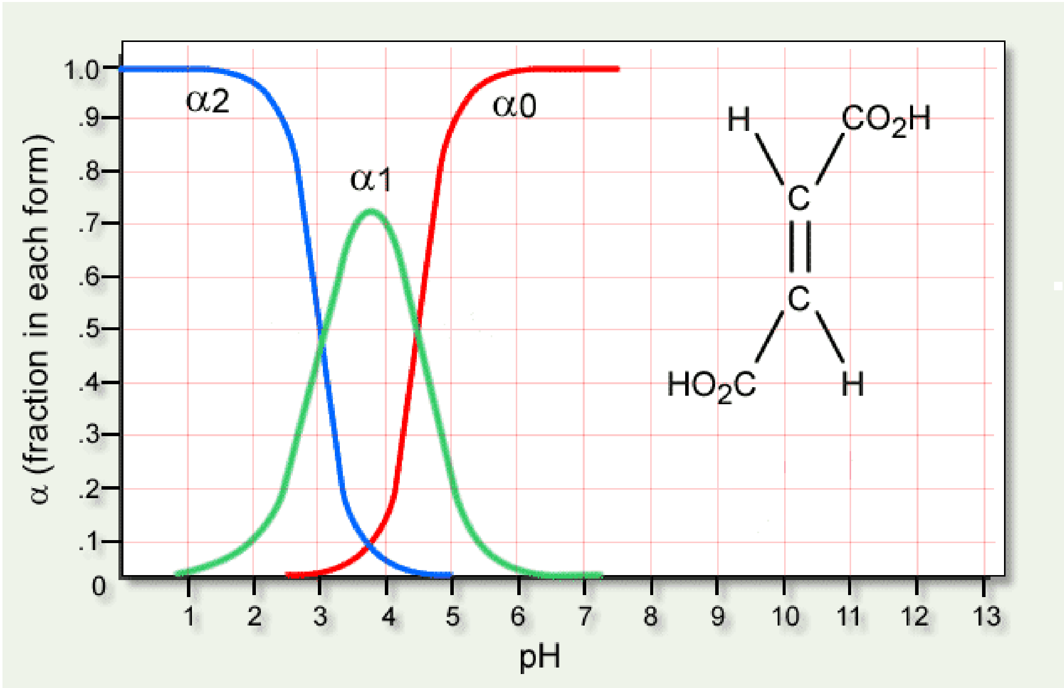
13. The following diagram shows the distribution curve for fumaric acid: **[6 marks]**



Fractional composition diagram (distribution curves) for fumaric acid (*trans*-butenedioic acid).

(a) Fumaric acid undergoes two ionizations. What are its pKa values? *[2 marks]*

pK_{a1} = ______________ pK_{a2} = ______________

(b) What species are present in solution at pH = 3.5? *[2 marks]*
You do not need to list any species present in lower concentration than 1%.
Your answers must be either chemical formulas or structures.

major species: minor species:

(c) What species are present in solution at pH = 5.5? *[2 marks]*
You do not need to list any species present in lower concentration than 1%.
Your answers must be either chemical formulas or structures.

major species: minor species:

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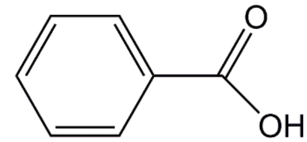
14. What is the pH of a 0.27 M aqueous solution of benzoic acid ($pK_a = 4.20$) at 25.00 °C? **[8 marks]**

benzoic acid = 

15. What was the most interesting and/or useful thing you learned in CHEM 2000? **[1 mark]**

…AND THAT'S ALL FOR CHEM 2000.
HAVE A GREAT SUMMER!

DATA SHEET
Some Useful Constants and Formulae

Fundamental Constants and Conversion Factors

Atomic mass unit (u)	$1.660\,539 \times 10^{-27}$ kg	Kelvin temperature scale	0 K = -273.15 ˚C
Avogadro's number (N_A)	$6.022\,141 \times 10^{23}$ mol^{-1}	K_w (at 25 °C)	10^{-14}
Boltzmann constant (k_B)	$1.380\,649 \times 10^{-23}$ J·K^{-1}	Planck's constant (h)	$6.626\,070 \times 10^{-34}$ J·Hz^{-1}
Charge of electron	$-1.602\,176 \times 10^{-19}$ C	Speed of light in vacuum (c)	$2.997\,925 \times 10^{8}$ m·s^{-1}
Faraday's constant (F)	96 485 C·mol^{-1}	Volume conversion	1000 L = 1 m^3
Ideal gas constant (R)	8.314 462 J·mol^{-1}·K^{-1} 8.314 462 m^3·Pa·mol^{-1}·K^{-1}	Pressure conversions	1 bar = 100 kPa 1 atm = 1.01325 bar

Formulae

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}RT \qquad v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} \qquad PV = nRT$$

$$S = k_B \ln\Omega \qquad \Delta S = \frac{q_{rev}}{T} \qquad \Delta_r G = \Delta_r H - T\Delta_r S \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\Delta_r G = \Delta_r G^\circ + RT\ln Q \qquad \Delta_r G^\circ = -RT\ln K \qquad \ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$P_A = X_A P_A^\bullet \qquad [A] = k_H P_A \qquad X = \frac{n}{\sum n} \qquad \Delta_r G = -\upsilon_e FE \qquad E = E^\circ - \frac{RT}{\upsilon_e F}\ln Q$$

$$pH = -\log a_{H^+} \qquad pK_a = -\log K_a \qquad pK_b = -\log K_b \qquad K_w = K_a \cdot K_b \qquad pH = pK_a + \log\left(\frac{a_{A^-}}{a_{HA}}\right)$$

$$\Delta H^0_{rxn} = \sum(\Delta H^0_f(products) - \sum(\Delta H^0_f(reactants) \qquad \Delta S^0_{rxn} = \sum(S^0(products) - \sum(S^0(reactants)$$

$$\Delta G^0_{rxn} = \sum(\Delta G^0_f(products) - \sum(\Delta G^0_f(reactants)$$

Activities

Solid	$a = 1$
Pure liquid	$a = 1$
Ideal Solvent	$a = X$
Ideal Solute	$a = \frac{c}{c^\circ}$
Ideal Gas	$a = \frac{P}{P^\circ}$

DATA SHEET

CHEM 2000 Standard Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1.0079 **H** 1																	4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12											26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Nh** 113	(289) **Fl** 114	(288) **Mc** 115	(293) **Lv** 116	(294) **Ts** 117	(294) **Og** 118

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2016)

Some Useful Thermodynamic Properties

Substance	$\Delta_f H° \left(\frac{kJ}{mol}\right)$	$\Delta_f G° \left(\frac{kJ}{mol}\right)$	$S° \left(\frac{J}{mol \cdot K}\right)$
PCl_3 (g)	-287	-268	312
PCl_5 (g)	-402	-323	353

Half Reaction	$E°(V)$
$Cu^{2+}_{(aq)} + 2\,e^- \rightarrow Cu_{(s)}$	+0.34
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^{+}_{(aq)}$	+0.15