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Instituto de Ciências Exatas - ICEx
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Registration Number:

QUESTIONS BOOKLET

TEST OF GENERAL KNOWLEDGE ON CHEMISTRY FOR
APPLICANTS TO THE GRADUATE PROGRAM OF THE
DEPARTMENT OF CHEMISTRY – 1st TERM/2016

DECEMBER 14th, 2015

INSTRUCTIONS

- Read carefully the entire test.
- Each chosen question must be answered in the appropriate sheet of the answer booklet.
- Both question and answer booklets are required to be returned upon completion of the test.
- Any electronic device must be turned off during the test.

CANDIDATES FOR MASTER OF SCIENCE DEGREE

- Choose only two (02) questions in each area to answer. At the end, you will have answered eight (08) QUESTIONS.
- **WARNING:** If you answer THREE (03) questions of the same area, it will be evaluated only the TWO (02) formers.

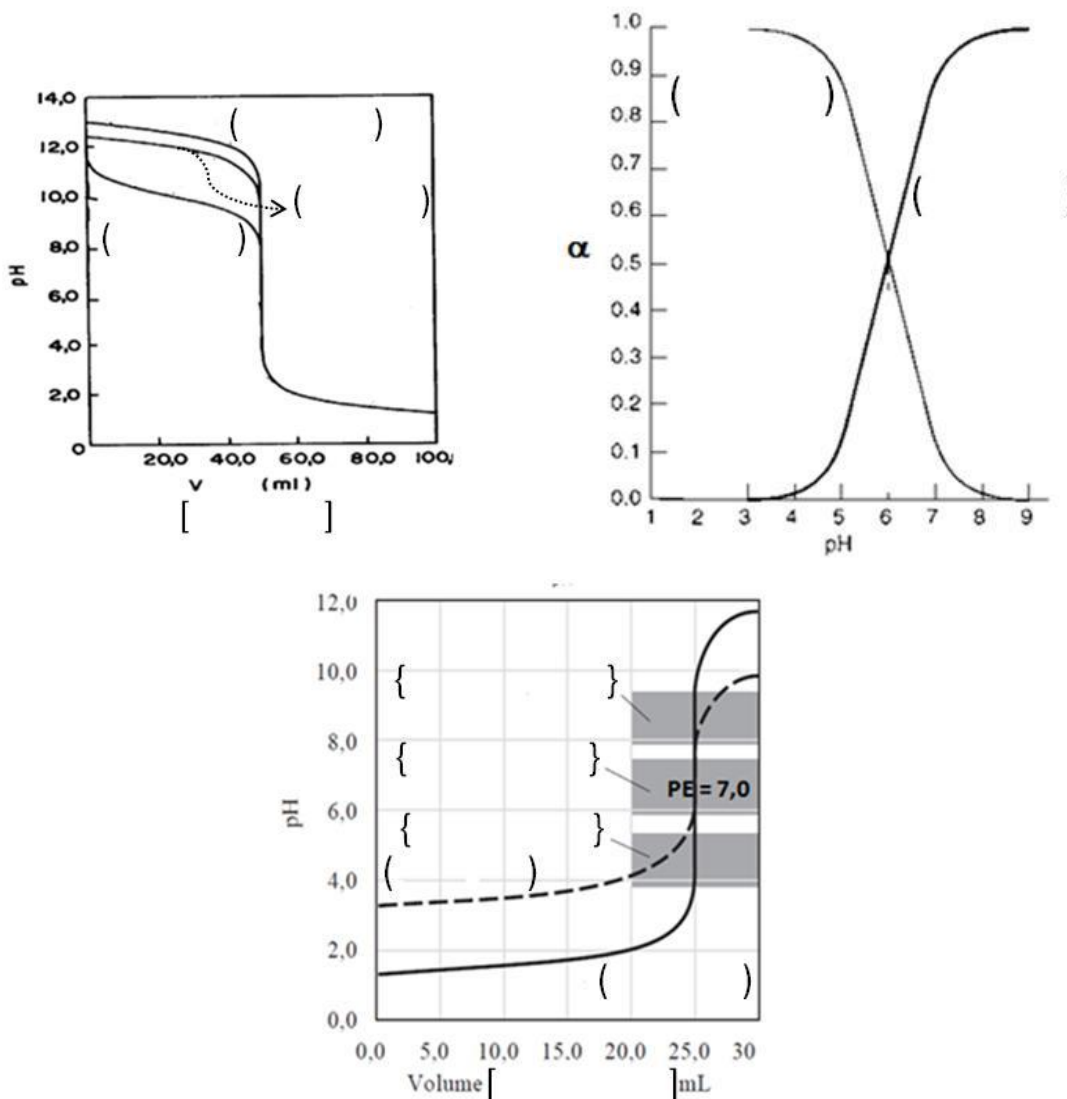
CANDIDATES FOR DOCTOR OF SCIENCE DEGREE

- Choose one (01) question in each area and other two (02) questions from any area to answer. At the end, you will have answered six (06) QUESTIONS.

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY AREA 1

QUESTION 1A

Titration and molar fraction curves (α) are represented below. Indicate between parenthesis "(.....)", the compound which was titrated. Indicate between brackets "[.....]", the compound which was used as titrant. Moreover, indicate between braces "{.....}" the reagent used as indicator.



(a) NaCH_3COO , $K_a = 1.0 \times 10^{-10}$	[h] NaOH	{j} bromothymol blue, $pK_a = 7.1$
(b) HCl 0.050 mol L^{-1}	[i] HCl	{k} bromocresol green, $K_a = 2 \times 10^{-5}$
(c) A^- , $K_h = 1.0 \times 10^{-8}$		{l} phenolphthalein, $K_a = 5.01 \times 10^{-10}$
(d) NaOH		
(e) HCl $0.0050 \text{ mol L}^{-1}$		
(f) HA, $pK_a = 6.0$		
(g) MOH, $K_b = 1.0 \times 10^{-2}$		

Note: the analytical concentration of NaCH_3COO , NaOH and MOH are the same.

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY AREA 1

QUESTION 1B

Consider an aqueous solution composed of two cations Tl^+ 0.15mol L^{-1} and Zn^{2+} 0.20mol L^{-1} which should be separated by the addition of sodium sulfide.

- a) Which cation will precipitate first? Explain presenting calculations to prove your answer.
- b) Is it possible to precipitate these species selectively? Present all the calculations that prove your answer.

Important: To achieve an efficient separation it is necessary that the remaining concentration of the first cation does not exceed 0.1% of its analytical concentration when the precipitation of the second cation initiate.

Important information: $K_{\text{sp}} \text{Tl}_2\text{S} = 6.0 \times 10^{-22}$ $K_{\text{sp}} \text{ZnS} = 3.0 \times 10^{-23}$

AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY AREA 1

QUESTION 1C

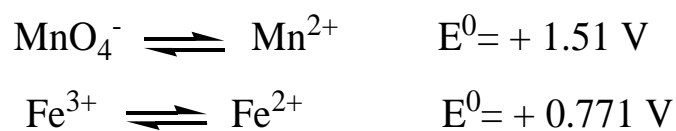
The total iron content in an ore sample was determined by redox titration. The sample was prepared according to the procedure below:

- i. 12.00 g of ore were weighed;
- ii. An aliquot of hydrochloric acid was added to the ore;
- iii. The mixture was heated until complete solubilization of the ore;
- iv. The solution volume was made up to 1 L.

After that, 5.00 mL of the solution was reduced to Fe(II), acidified with sulfuric acid and titrated with 5.80 mL of potassium permanganate 0.0200 mol L⁻¹ solution.

- a) Write the oxidation and reduction half-reactions and the global equation of the titration process.
- b) Determine the total content of iron in the ore (% w/w).
- c) Explain why the iron content determined in this titration is total iron.

Data



AREA OF KNOWLEGDE: ANALYTICAL CHEMISTRY AREA 1

List of Equations:

$K' = \frac{K}{\alpha_M \alpha_L}$	$\alpha_0 = \frac{1}{(1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n)}$
$\alpha_1 = \beta_1 \alpha_0 [L]$	$\alpha_n = \beta_n \alpha_0 [L]^n$
$\alpha_M = [M] / c_T$	$\beta_n = \frac{[ML_n]}{[M][L]^n} = K_1 K_2 \dots K_n$
$[H^+]^2 + K_a [H^+] - K_a C_a = 0$	$[H^+] = \sqrt{K_a C_a}$
$[H^+] = K_a \left(\frac{C_a}{C_b} \right)$	$pH = pK_a - \log \left(\frac{C_a}{C_b} \right)$
$K_w = K_a K_b = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$	$S = \frac{K_{ps}}{[M]} \left(1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1} K_{a2}} \right)$
$\log K = \frac{n(E_{cathode}^0 - E_{anode}^0)}{0.0592}$	$E = E^0 - \frac{0.0592}{n} \log \frac{[Red]}{[Ox]}$

QUESTION 2A

The hexacyanoferrate(II) ion has an absorption band at 310.5 nm, related to the *d-d* transition. The pairing energy, for the iron ion, is 177.6 kJ mol⁻¹.

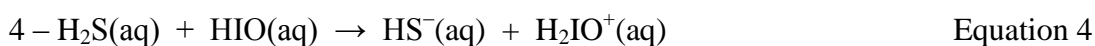
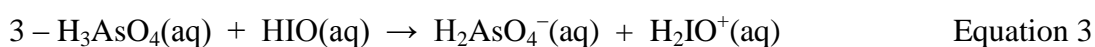
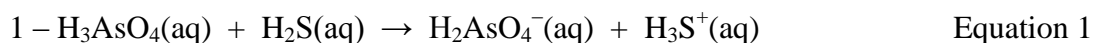
- a) **Calculate** the value of 10 Dq (Δ_o) (in kJ mol⁻¹) for this complex.
- b) Considering the information presented, the complex ion is a low-spin or high-spin compound? **Justify** your answer.
- c) **Draw** the energy diagram of Crystal Field Theory (CFT) and **calculate** the value of the Crystal Field Stabilization Energy (CFSE), in kJ mol⁻¹, involved in the formation of the complex.

AREA OF KNOWLEGDE: INORGANIC CHEMISTRY **AREA 2**

QUESTION 2B

Do what you are asked in each item below.

a) Consider the following equations involving the species: H_3AsO_4 , H_2S , HClO_4 and HIO . Order these species in ascending order of strength.



b) Consider the following equation: $\text{AsF}_3(\text{g}) + \text{SbF}_5(\text{g}) \rightarrow [\text{AsF}_2]^+[\text{SbF}_6]^- (\text{s})$.

b.1) Classify the AsF_3 and SbF_5 species as acid or base.

SbF_5 () Acid () Base

AsF_3 () Acid () Base

b.2) Justify the classification presented in the previous item for SbF_5 specie.

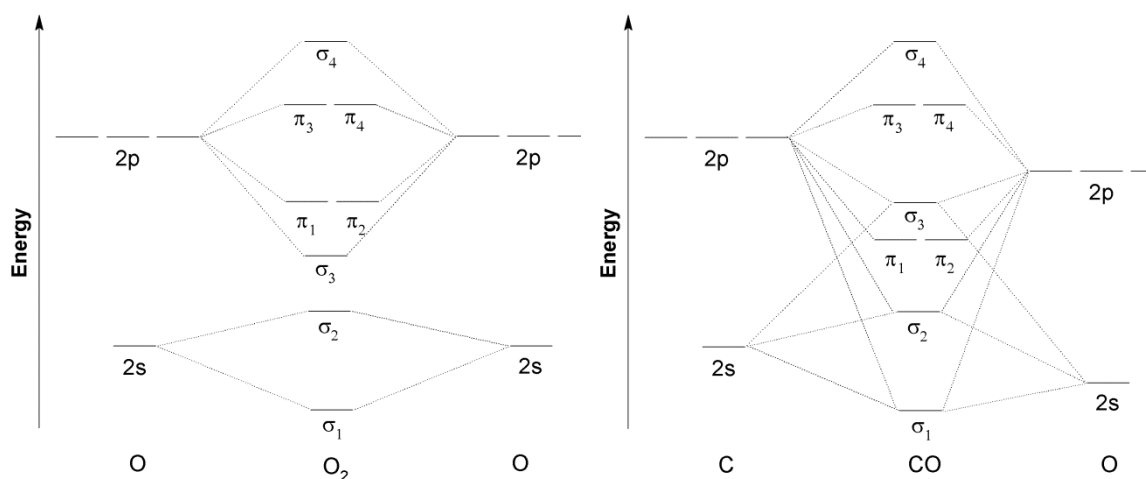
c) Aluminium fluoride is insoluble in liquid hydrofluoric acid, but dissolves in this solvent when sodium fluoride is added in the medium. When boron trifluoride is added to the solution (aluminium fluoride + hydrofluoric acid + sodium fluoride), the aluminum fluoride precipitates from the solution. Justify the experimental observations presented considering the Pearson classifications for acids and bases.

AREA OF KNOWLEGDE: INORGANIC CHEMISTRY **AREA 2**

QUESTION 2C

Do what you are asked in each item below.

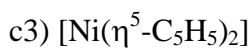
a) Consider the simplified diagrams of Orbital Molecular Theory for O₂ and CO molecules, shown below. Explain why CO is a stronger-field ligand than O₂.



b) Justify the observed values of the stretching frequencies of CO bond in the complex listed in the table below (Free CO ν_{\max} 2147 cm⁻¹).

Complex	$\nu_{\max.}$ (cm ⁻¹)
[Ni(CO) ₄]	2060
[Co(CO) ₄] ⁻	1890
[Fe(CO) ₄] ²⁻	1790

c) Make the electron counting of the coordination compounds bellow.



Form:

$$E = \frac{hc}{\lambda}$$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$N = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$c = 2.998 \times 10^8 \text{ m s}^{-1}$$

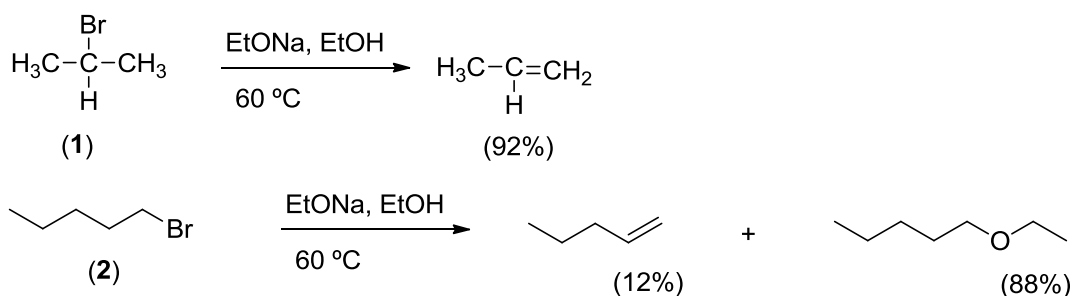
$$1 \text{ nm is equal to } 1 \times 10^{-9} \text{ m}$$

QUESTION 3A

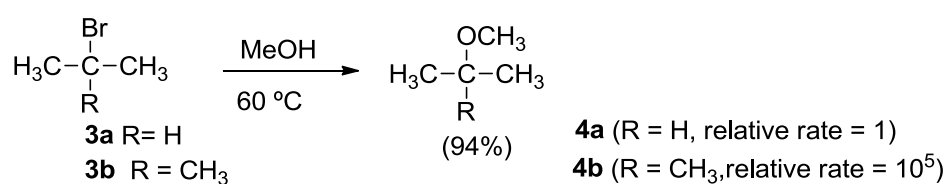
The equations for some substitution and elimination reactions are illustrated bellow.

Answer the proposed questions.

- a) Explain why compound (1) when treated with EtONa affords 92% of elimination product, while the compound (2) under the same conditions, affords the ether as main product. Represent the mechanism for this reaction, showing how alkenes and ether are formed.

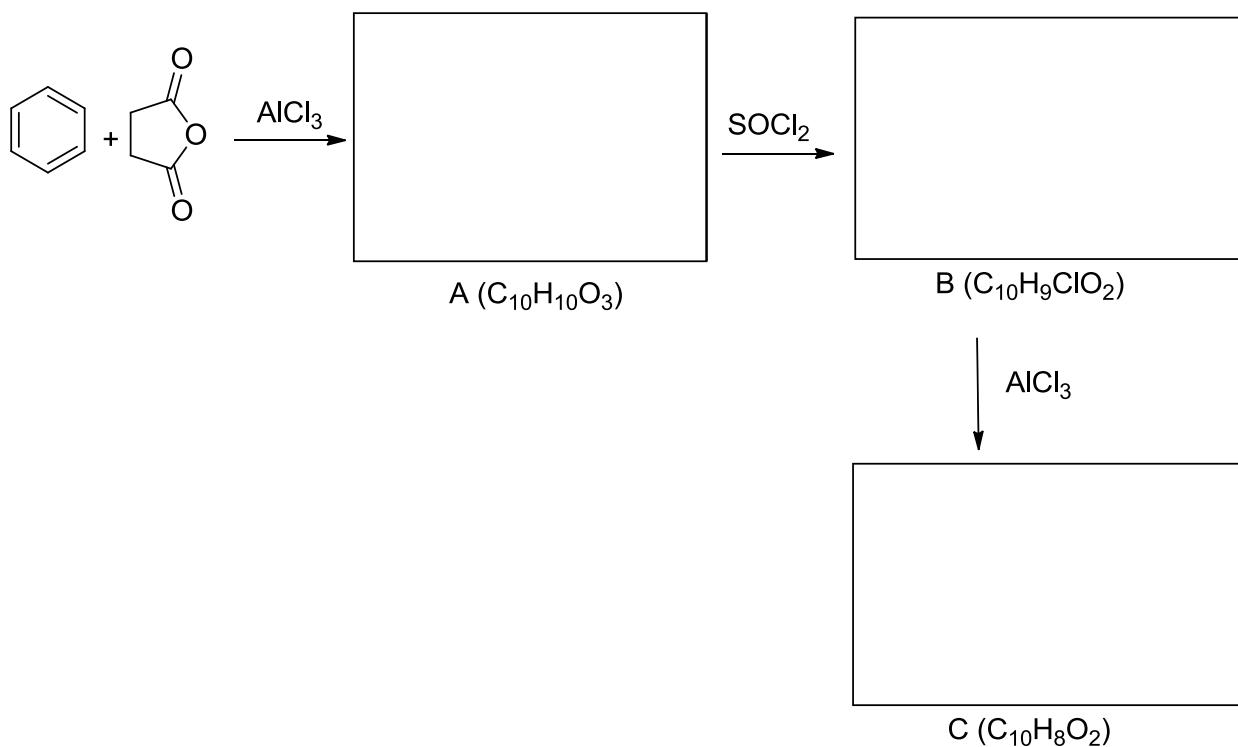


- b) Note that the reaction of the compound **3** (R = H or Me) in methanol under heating only provides the product of nucleophilic substitution. Explain why the conversion of **3a** to **4a** occurs much slower than the conversion of **3b** into **4b**.



QUESTION 3B

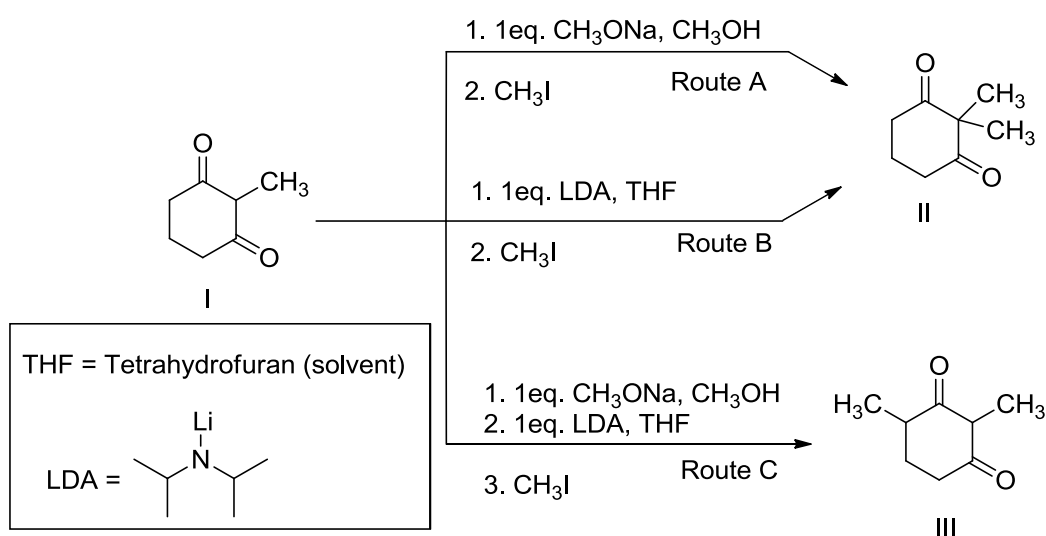
The reaction of benzene with succinic anhydride affords compound **A**. This compound is converted into product **B** upon treatment with SOCl_2 . Further reaction of **B** with AlCl_3 results in the formation of compound **C** as illustrated in the following scheme.



- a) Complete the scheme above with the structural formulas of compounds **A**, **B** and **C**.
- b) Represent all the steps for the mechanism of conversion of benzene and succinic anhydride into compound **A**.

QUESTION 3C

When compound **I** is treated with 1.0 equivalent of sodium methoxide in methanol, followed by addition of 1.0 equivalent of iodomethane, product **II** is formed. When the same compound **I** is treated with 1.0 eq. of LDA in tetrahydrofuran (THF), followed by addition of 1.0 eq. of CH_3I it also provides the same product **II**. However, when compound **I** is treated with 1.0 eq. of CH_3ONa in methanol followed by treatment with 1 eq. of LDA in THF and addition of 1.0 eq. of CH_3I , the only product isolated is **III**.



- Explain why reaction of compound **I** under conditions given by routes **A** and **B** produces the same compound **II**.
- Explain why the reaction of compound **I** under the conditions of route **C** produces only compound **III** and compound **II** is not formed.

QUESTION 4A

The specific Heat Capacity of nitrogen above room temperature is:

$$C_p = 28,90 - 1,57 \times 10^{-3}T - 8,08 \times 10^{-6}T^2 \quad \left(J \text{ mol}^{-1} K^{-1} \right)$$

- (a) Obtain the enthalpy as a function of temperature, $H(T)$. Use room temperature enthalpy $H_{(298)}$, as the reference level.
- (b) In addition, obtain the entropy, $S(T)$, referred to room temperature $S_{(298)}$.
- (c) Calculate ΔH and ΔS when the nitrogen is submitted to heating from room temperature to 698K.

QUESTION 4B

Consider helium at 350 K and $0.75 \text{ m}^3 \text{ kg}^{-1}$ as its specific volume. Determine the change in pressure corresponding to an increase of:

- (a) 1% in temperature at constant specific volume.
- (b) 1% in specific volume at constant temperature.
- (c) 1% in both, temperature and specific volume.

QUESTION 4C

Calculate the boiling point variation of water as a function of pressure change (dT/dP).

Assume that water vapor behaves ideally at 100 °C. The density of liquid water at 100

°C is 0.95835 g mL⁻¹ and the vaporization enthalpy of water $\Delta H_{vap} = 40.625 \text{ kJ mol}^{-1}$.

Form

$$R = 0.082057 \text{ atm L mol}^{-1} \text{ K}^{-1} = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1} = 1.98717 \text{ cal K}^{-1} \text{ mol}^{-1} = 2.0769 \text{ kPa m}^3 \text{ kg}^{-1} \text{ K}^{-1}$$

$$N_A = 6.02252 \times 10^{23} \text{ particles mol}^{-1}$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2} = 10^{-5} \text{ bar} = (1 \times 10^{-5} / 1.01325) \text{ atm} \qquad 1 \text{ atm} = 760 \text{ mmHg}$$

$$1 \text{ atm L} = 101.325 \text{ Joule}$$

$$Z = pV_m/RT \qquad pV_m = RT \qquad (p + a/V_m^2)(V_m - b) = RT$$

$$pV_m = RT[1 + B(T)/V_m + C(T)/V_m^2 + D(T)/V_m^3 + \dots]$$

$$dU = \delta Q + \delta W \qquad H = U + pV \qquad dQ_{\text{rev}} = C_p dT$$

$$C_V = (\partial U / \partial T)_V \qquad C_P = (\partial H / \partial T)_P \qquad C_{P,m} - C_{V,m} = R$$

$$pV^\gamma = \text{cte} \qquad T_2 = T_1(V_1/V_2)^{\gamma R/C_V}$$

$$\alpha = (1/V)(\partial V / \partial T)_P \qquad \kappa_T = -(1/V)(\partial V / \partial P)_T$$

$$dS = \delta Q_{\text{rev}} / T$$

$$G = H - TS \qquad A = U - TS \qquad dG = Vdp - SdT$$

$$dH = Vdp + TdS \qquad \Delta_{\text{transition}} S = \frac{\Delta_{\text{transition}} H}{T_{\text{transition}}}$$

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) = C_V \ln \left(\frac{T_f}{T_i} \right) = C_P \ln \left(\frac{T_f}{T_i} \right) \quad \text{For solid and liquids}$$

$$\int d \ln P = \frac{\Delta H}{R} \frac{1}{T^2} dT$$

If *f* is a function of *x* and *y*, then:

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

$$\ln \left(\frac{P}{P'} \right) = - \frac{\Delta_{\text{transition}} H_m^\ominus}{RT} + \frac{\Delta_{\text{transition}} S_m^\ominus}{T} \quad \text{ou} \quad \ln \left(\frac{P}{P'} \right) = - \frac{\Delta_{\text{transition}} H_m^\ominus}{RT} + \frac{\Delta_{\text{transition}} H_m^\ominus}{RT'}$$

Gibbs Phase rule: $F = C - P + 2$ *F*, freedom, *C*, components, *P*, phases.

Periodic Table of the Elements

1 IA 1A																	18 VIIIA 8A	
1 H Hydrogen 1.008	2 IIA 2A												13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180	
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948	
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 68.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80	
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29	
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018	
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown	

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]