THE UNIVERSITY of ADELAIDE

Semester 1, 2012

104311	Chemistry II A CHEM 2510
104312	Chemistry II A (Ecochemistry) CHEM 2512
104313	Chemistry II A (Molecular & Drug Design) CHEM 2514
104314	Chemistry II A (Nanoscience and Materials) CHEM 2516

Official Reading Time:	10 mins
Writing Time:	180 mins
Total Duration:	190 mins

Part	Questions	Time	Marks
A	Answer all of Q1, Q2 (a) or (b) and either (b) or (c), all of Q3.	45 mins	30 marks
B	Answer all questions	45 mins	30 marks
C	Answer all questions	45 mins	30 marks
D	Answer all questions	45 mins	30 marks
			120 Total

Instructions

- This is a Closed Book examination.
- Answers to Parts A, B, C and D are to be written in separate booklets provided.
- *In all your answers, indicate your reasoning and make clear (in words or by a diagram) the meaning of any symbols you introduce. Candidates are instructed to write in an easily legible, clearly expressed and grammatically correct manner. The mark given to your answer will depend on the quality of the reasoning displayed and on indications of conceptual understanding in addition to the factual material presented.*
- Examination materials must not be removed from the examination room.

Materials

- 4 Pink books.
- Calculators are permitted for the processing of numerical information. They must not be capable of remote communication, not have been programmed nor may they store additional information.
- Molecular models are permitted.
- Three tables are provided separately. These include (i) Selected Thermodynamic Data, (ii) Reference Formulae, Physical Constants and Dimensions, and (iii) a Periodic Table of the Elements.

DO NOT COMMENCE WRITING UNTIL INSTRUCTED TO DO SO

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Part A

Allow 45 minutes for this section of the paper. Answer in a separate booklet. Total marks = 30

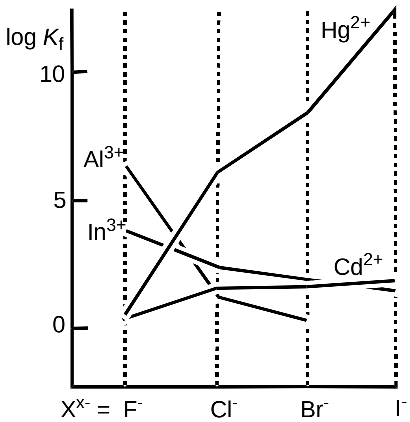
QUESTION 1. ANSWER (a) and (b)

(a) How is a Lewis acid and the Lewis base defined? The metal complex hexaamminenickel(II), $[Ni(NH_3)_6]^{2+}$, is often described as a Lewis acid-base complex. Explain this description and identify the Lewis acid and a Lewis base.

[2 marks]

(b) For the equilibrium: $M^{m+} + X^- \rightleftharpoons [MX]^{(m-x)+}$, where M^{m+} is a metal ion and X^- is a halide ion, the formation constant $K_f = [MX^{(m-x)+}]/\{[M^{m+}][X^-]\}$.

The variation of log K_f as the nature of M^{m+} and X^- changes is illustrated in the figure below. Explain why these variations occur for the four metal ions shown in terms of the hardness and softness of the Lewis acids and bases involved.



[6 marks]

[Total for question 1 = 8 marks]

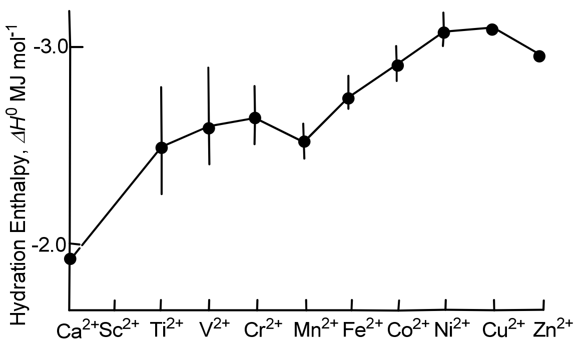
QUESTION 2. ANSWER EITHER (a) OR (b), AND EITHER (c) OR (d).

EITHER

(a) The hydration enthalpy, ΔH^o for the reaction:

$$M^{2+}(\text{gas}) + 6H_2O\ (\text{liquid}) \xrightarrow{\Delta H^o} [M(H_2O)_6]^{2+}\ (\text{in water})$$

varies with the nature of M^{2+} as shown in the figure below. Explain how this variation arises.



[6 marks]

OR

(b) The molecular orbitals of octahedral first row *d*-metal complexes [ML_6] (in which there is no π bonding) have the following order of descending energy: $t_{1u} > a_{1g} > e_g > t_{2g} > e_g > t_{1u} > a_{1g}$.

Construct a molecular orbital energy level diagram showing the energies of the molecular orbitals of the complex [ML_6] *and* the energies and identities of the metal and ligand orbitals from which they were formed. Identify the molecular orbitals of the complex as antibonding, nonbonding and bonding. Identify the LUMO and HOMO molecular orbitals of the complex. Indicate the ligand field splitting, Δ_o, on your molecular orbital energy level diagram.

[6 marks]

AND

EITHER

(c) The complex [$Ir(Cl)_3(PPh_3)_3$] exists as two geometric isomers (PPh_3 is triphenylphosphine). Draw and name these isomers. One isomer possesses a C_2 axis of symmetry and the other a C_3 axis of symmetry. Show these axes on your drawings of the isomers and explain what the symbols C_2 and C_3 signify.

[4 marks]

OR

(d) The complex $[Cr(ox)_3]^{3-}$ (where ox^{2-} is oxalate, $^-O_2C\text{-}CO_2^-$) exists as two enantiomers. Name them, draw them and explain their relationship to each other. Each enantiomer possesses a C_3 axis of symmetry. Show this C_3 axis on the drawings of each of the enantiomers and explain what the symbol C_3 signifies.

[4 marks]

[Total for question 2 = 10 marks]

QUESTION 3. ANSWER (a), (b) and (c).

(a) Draw the catalytic scheme for the Monsanto synthesis of acetic acid from methanol using the [$RhI_2(CO)_2$] catalyst in the presence of CO. Identify the oxidative addition step and the reductive elimination step. Explain why [$RhI_2(CO)_2$] is described as a 16 electron system.

[6 marks]

(b) Describe with an annotated drawing the structure of methyllithium. Methyllithium is electron deficient. Explain this in terms of the valence electrons available and the type of bonding present.

[3 marks]

(c) Describe with an annotated drawing the structure of trimethylaluminium. Trimethylaluminium is electron deficient. Explain this in terms of the valence electrons available and the type of bonding present.

[3 marks]

[Total for question 3 = 12 marks]

[Total for Part A = 30 marks]

- - - END of PART A - - -

Part B

Allow 45 minutes for this section of the paper. Answer in a separate booklet. Total marks = 30

QUESTION 1

(a) Calculate the entropy change for burning 1 kg of *n*-octane(g) to H_2O(l) and CO_2(g) at 298 K and 1 atm.

[3 marks]

(b) One mole of an ideal monatomic gas is expanded from an initial state of 2 atm and 400 K to a final state of 1 atm and 300 K. Calculate ΔS for the following paths:

Isothermal expansion against 1 atm at 400 K, followed by an isobaric decrease in T to 300 K.

[5 marks]

[Total for question 1 = 8 marks]

QUESTION 2

(a) Calculate the work done at 298.15 K when 1 mole of an ideal gas expands isothermally from 400 kNm^{-2} to 150 kNm^{-2} in one stage by a sudden direct reduction in pressure to 150 kNm^{-2}.

[2 marks]

(b) Calculate the work done at 298.15 K when 1 mole of an ideal gas expands isothermally by having a large series of infinitesimal decreases of pressure over a long period from 400 kNm^{-2} to 150 kNm^{-2}.

[2 marks]

[Total for question 2 = 4 marks]

QUESTION 3

(a) One mole of an ideal monatomic gas is expanded from an initial state of 4 atm and 300 K to a final state of 2 atm and 300 K. Calculate ΔG for this expansion.

[3 marks]

(b) Using the thermodynamic information provided, determine which set of products will be most favoured? Show your work clearly to receive full credit.

$$2OH(g) \rightarrow \begin{cases} H_2O_2(g) & (a) \\ H_2O(g) + 0.5O_2(g) & (b) \\ OH^-(g) + OH^+(g) & (c) \end{cases}$$

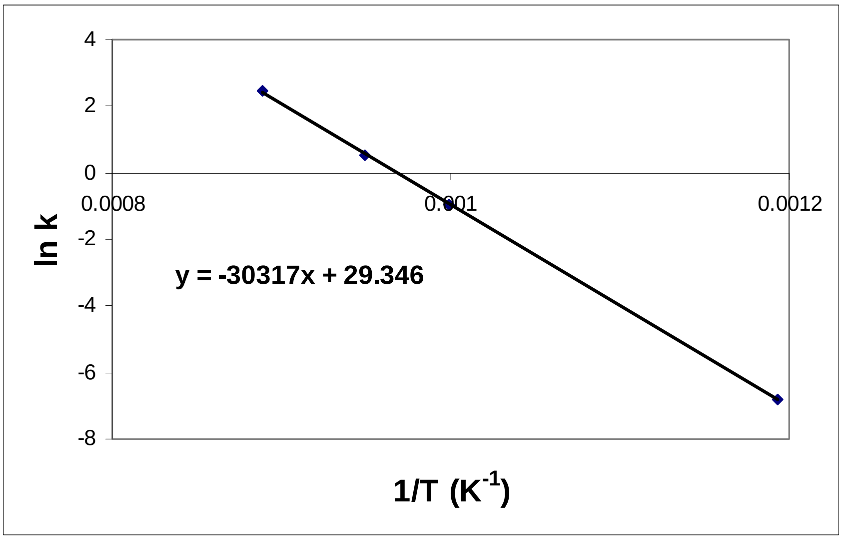
	ΔG^o_f(298 K) $kJmol^{-1}$
$H_2O(g)$	-228.572
H_2O_2 (g)	-105.57
OH(g)	34.23
$OH^-(g)$	-138.698
$OH^+(g)$	1306.437
$O_2(g)$	0

[5 marks]

[Total for question 3 = 8 marks]

QUESTION 4

The natural logarithm of the rate constant (ln *k*) is plotted against the reciprocal of the absolute temperature for the decomposition of N_2O. The best-fit linear curve has an equation shown below in the plot.



What is the value of the activation energy of this reaction?

[Total for question 4 = 3 marks]

QUESTION 5

(a) Briefly explain why the following rate law for the chemical reaction below is unlikely.

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

Rate = $k[NO_2]^2[F_2]$, where k is the rate constant

[1 mark]

(b) In fact, the experimentally determined rate law for the reaction is Rate = $k[NO_2][F_2]$. Propose a simple and acceptable mechanism that satisfies the rate law.

[2 marks]

[Total for question 5 = 3 marks]

QUESTION 6

The decomposition of hydrogen iodide,

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

has rate constants of 9.51×10^{-9} L/mol·s at 500 K and 1.10×10^{-5} L/mol·s at 600 K. Calculate the activation energy. Hint: the frequency factor A is independent of temperature.

[Total for question 6 = 4 marks]

[Total for Part B = 30 marks]

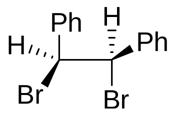
- - - END of PART B - - -

Part C

Allow 45 minutes for this section of the paper. Answer in a separate booklet. Total marks = 30

QUESTION 1

The following wedge-and-dash structure illustrates a conformation for one of the stereoisomers of 1,2-dibromo-1,2-diphenylethane.



(a) Assign the configuration of the stereocentre(s) as either *R* or *S*.

(b) Draw a Newman projection, viewed along the bond between C1 and C2, for this conformation.

(c) Draw the wedge-and-dash structure that illustrates the conformation where the bromo groups are antiperiplanar.

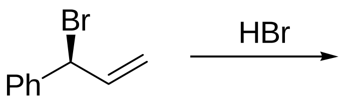
(d) Is this compound optically active? Provide a reason for your answer.

[Total for question 1 = 6 marks]

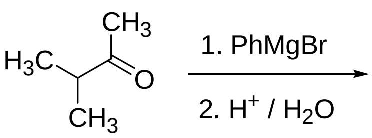
QUESTION 2

For the following reactions, draw the major product(s). If the products can exist as stereoisomers, show which stereoisomers are obtained. Also indicate whether the final product(s) for each reaction is/are chiral.

(a)



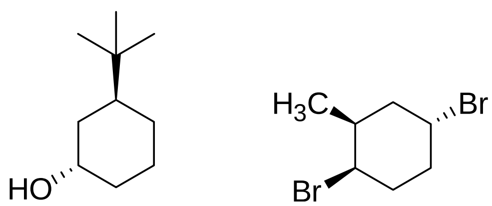
(b)



[Total for question 2 = 6 marks]

QUESTION 3

For each of the following molecules:



(a) draw clear chair conformation structures.

(b) draw the alternate (ring-flipped) chair conformation for each compound.

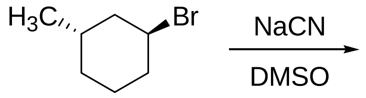
(c) circle the chair conformation that you predict to be the more stable for each compound. Provide a reason for your decision in each case.

[Total for question 3 = 6 marks]

QUESTION 4

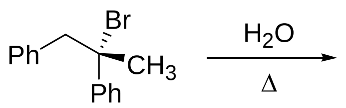
(a) By considering the reagents and conditions for each reaction below, determine if a **substitution** reaction would proceed. If yes, give a detailed mechanism for the formation of **all** possible products, clearly showing stereochemistry where applicable.

(i)



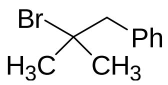
[3 marks]

(ii)



[3 marks]

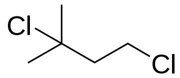
(b) Two alkenes are formed from the E1 reaction of bromide X. Draw the structures of these alkenes, indicate which one would be the major product and provide a reason for your choice.



X

[4 marks]

(c) The molecule below contains two halogens. Which halogen would be more reactive in an S_N1 reaction? Provide a reason for your answer.



[2 marks]

[Total for question 5 = 12 marks]

[Total for Part C = 30 marks]

- - - END of PART C - - -

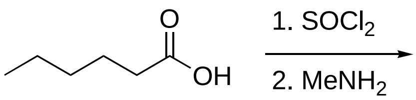
Part D

Allow 45 minutes for this section of the paper. Answer in a separate booklet. Total marks = 30

QUESTION 1

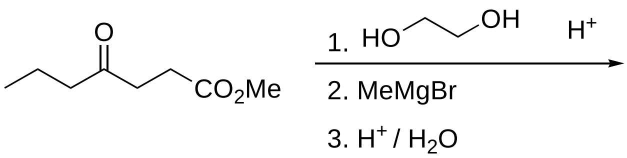
In each reaction below, identify the product(s) formed and give a detailed mechanism for their formation

(a)



[3 marks]

(b)

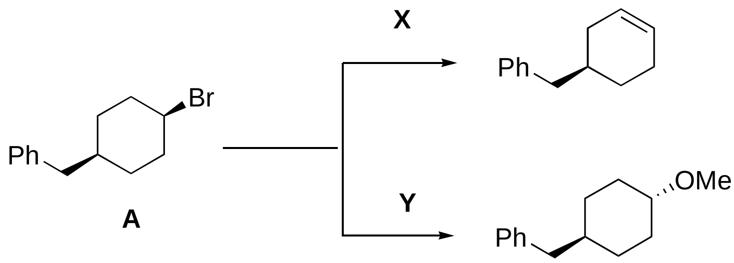


[5 marks]

[Total for question 1 = 8 marks]

QUESTION 2

Answer questions (a) to (d) given the following information



(a) Draw two chair conformations for A.

[2 marks]

(b) Suggest reagents and conditions for X and Y, with detailed reasons.

[4 marks]

(c) Give detailed mechanisms for each reaction, with reference to your structures in part (a).

[4 marks]

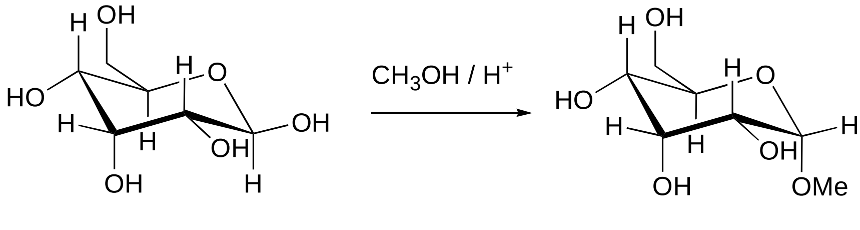
(d) Suggest a competing reaction for step Y.

[1 mark]

[Total for question 2 = 11 marks]

QUESTION 3

Answer this question with reference to the following reaction Scheme:



β-D-glucose

(a) Define the terms β and D.

[2 marks]

(b) Identify the anomeric centre in β-D-glucose.

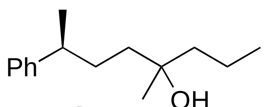
[1 mark]

(c) Give a mechanism for the reaction and explain why the OMe group prefers to be in the axial position.

[3 marks]

[Total for question 3 = 6 marks]

QUESTION 4



A

(a) Give a detailed retrosynthetic analysis of Compound A based on Grignard chemistry and in the process identify two possible routes for its synthesis.

[3 marks]

(b) Give all reagents and conditions for a synthesis of A based on your answer to part (a).

[2 marks]

[Total for question 4 = 5 marks]

[Total for Part D = 30 marks]

- - - END of PART D - - -

- - - END OF EXAMINATION PAPER - - -

THE UNIVERSITY OF ADELAIDE AUSTRALIA

Examination for the Ordinary Degrees of
B.Sc., B.Sc.(Ecochem.), B.Sc.(Mol. Biol.), B.Sc.(Mol. Drug Des.), B.Sc.(Nanosci. Mat.)

Semester 1, 2012

104311	Chemistry II A CHEM 2510
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104314	Chemistry II A (Nanoscience and Materials) CHEM 2516

Three tables are provided.
These include (i) Selected Thermodynamic Data,
(ii) Reference Formulae, Physical Constants and Dimensions (4 pages), and
(iii) a Periodic Table of the Elements.

Selected Thermodynamic Data at 1 atm and 25°C

	ΔH^o_f(kJ/mol)	ΔG^o_f(kJ/mol)	S^o(J/K.mol)
$Al_{(s)}$	0	0	28.3
$Al_2O_{3(s)}$	-1669.8	-1576.4	50.99
$Be_{(s)}$	0	0	9.5
$BeO_{(s)}$	-610.9	-581.58	14.1
$Br_{2(l)}$	0	0	152.3
$CH_3CHO_{(g)}$	-166.35	-139.08	264.2
$CH_{4(g)}$	-74.85	-50.8	186.19
$C_2H_{2(g)}$	226.6	209.2	200.8
$C_2H_{4(g)}$	52.3	68.1	219.45
$C_2H_5OH_{(g)}$	-276.98	-174.18	161.04
$C_2H_5OH_{(l)}$	-235.10	-168.49	282.70
$C_2H_{6(g)}$	-84.7	-32.89	229.49
$C_3H_{6(g)}$	53.30	104.45	237.55
$C_3H_{8(g)}$	-103.9	-23.49	269.91
$C_4H_{8(g)}$	-0.13	71.39	305.71
$C_4H_{10(g)}$	-126.15	-17.03	310.23
$C_5H_{12(g)}$	-146.44	-8.20	348.40
$C_6H_{6(g)}$	82.93	129.72	269.31
$C_6H_{6(l)}$	49.04	124.5	123.5
$C_6H_{12(l)}$	-156	26.8	-

	ΔH^o_f(kJ/mol)	ΔG^o_f(kJ/mol)	S^o(J/K.mol)
$C_8H_{18(l)}$	-249.9	6.4	361.1
$Cl_{2(g)}$	0	0	223.0
$CO_{(g)}$	-110.5	-137.3	197.9
$CO_{2(g)}$	-393.5	-394.4	213.6
$Fe_{(s)}$	0	0	27.2
$Fe_2O_{3(s)}$	-822.2	-741.0	90.0
$H_{(g)}$	218.2	203.2	114.6
$H_{2(g)}$	0	0	131.0
$HBr_{(g)}$	-36.2	-53.2	198.48
$HCl_{(g)}$	-92.3	-95.27	187.0
$H_2O_{(g)}$	-241.8	-228.6	188.7
$H_2O(l)$	-285.8	-237.2	69.9
$N_{2(g)}$	0	0	191.5
$NH_{3(g)}$	-46.3	-16.6	193.0
$O_{(g)}$	249.4	230.1	160.95
$O_{2(g)}$	0	0	205.0
$O_{3(g)}$	142.2	163.4	237.6
$SO_{2(g)}$	-296.1	-300.4	248.5
$ZnO_{(s)}$	-348.0	-318.2	43.9
$ZnS_{(s)}$	-202.9	-198.3	57.7

Reference Formulae, Physical Constants and Dimensions

General & Calculus:

$e^a \times e^b = e^{a+b}$, $\frac{1}{e^a} = e^{-a}$, $ln(e^a) = a$, $ln\left(\frac{a}{b}\right) = lna - lnb$

$$\int_{x_1}^{x_2} \frac{1}{x} dx = \ln \frac{x_2}{x_1}$$

Ideal Gas Law:

$$pV = nRT$$

Pressure-Volume Work:

From classical mechanics, $dw = -Fdx$

For a gas, in general $w = -\int_{V_i}^{V_f} pdV$

which gives $dw = -p_{ex} \times dV$ for an irreversible expansion and

$w_{rev} = -nRT \int_{V_i}^{V_f} \frac{1}{V} dV = -nRT \ln \frac{V_f}{V_i}$ for a reversible expansion.

First Law of Thermodynamics:

Internal energy is a state function and any change is given by $\Delta U = q + w$

In the infinitesimal limit $dU = dq + dw_{\text{exp}} + dw_{\text{other}}$ but we mostly ignore the last term.

Constant Volume Conditions:

$dU = dq$ or $\Delta U = q$ at constant Volume (no expansion work)

The Heat Capacity is defined as $C_V = \frac{dU}{dT}$

So if C_V is approximately constant over the temperature range of interest then

$$\Delta U = q = C_V \times \Delta T$$

Constant Pressure Conditions:

If the pressure can change (*i.e*. non-constant Volume) then some expansion work can be done and

$$dU < dq$$

Enthalpy is defined as $H = U + pV$ which becomes $H = U + nRT$ for an ideal gas.

$dH = dq$ or $\Delta H = q$ at constant Pressure.

The Heat Capacity is defined as $C_{\mathrm{P}} = \frac{dH}{dT}$

So if C_P is approximately constant over the temperature range of interest then

$$\Delta H = q = C_{\mathrm{P}} \times \Delta T$$

For a perfect monatomic gas $C_{\mathrm{V}} = \frac{3}{2}R$ and $C_{\mathrm{P}} = C_{\mathrm{V}} + nR$

The Temperature-dependence of reaction enthalpies $\Delta H^0_{T_2} = \Delta H^0_{T_1} + \Delta C_{\mathrm{P}} \Delta T$

where $\Delta C_{\mathrm{P}} = \sum_{\text{products}} nC_{\mathrm{P}}(\text{products}) - \sum_{\text{reactants}} nC_{\mathrm{P}}(\text{reactants})$

is known as Kirchoff's Law.

Entropy (S):

For a spontaneous change $dS = \frac{dq_{rev}}{T}$ hence $\Delta S = \int_i^f \frac{dq_{rev}}{T}$

At constant Temperature and for a reversible process this gives $\Delta S = \frac{q_{rev}}{T}$

For an irreversible process this becomes $\Delta S > \frac{q}{T}$

Since for a spontaneous process, $dS + dS_{surroundings} \geq 0$

it follows that $dS \geq \frac{dq}{T}$ or $\Delta S \geq \frac{q}{T}$ in its non-infinitesimal notation. This is known as the Clausius Inequality.

For phase transitions (pt) at constant pressure, the entropy change is $\Delta S_{pt} = \frac{\Delta H_{pt}}{T_{pt}}$

For an iso-thermal expansion, $q = -w$ and so $\Delta S = nR\ln(\frac{V_2}{V_1}) = nR\ln(\frac{P_1}{P_2})$

The Temperature dependence of entropy is $\Delta S = \int_i^f \frac{dq_{rev}}{T}$

$\therefore$ at constant Pressure, $S_{T_2} = S_{T_1} + \int_{T_1}^{T_2} \frac{C_P}{T} dT$ which approximates to $\Delta S = C_P \ln(\frac{T_2}{T_1})$

$\therefore$ at constant Volume, $S_{T_2} = S_{T_1} + \int_{T_1}^{T_2} \frac{C_V}{T} dT$ which approximates to $\Delta S = C_V \ln(\frac{T_2}{T_1})$

Helmholtz (A) and Gibbs (G) Free Energy:

$A = U - TS$ therefore, $dA = dU - TdS$ or, $\Delta A = \Delta U - T\Delta S$ at constant T & V.

$G = H - TS$ therefore, $dG = dH - TdS$ or, $\Delta G = \Delta H - T\Delta S$ at constant T & P.

For a spontaneous (or equilibrium) process $dA_{T,V} \leq 0$ and $dG_{T,P} \leq 0$

The Pressure and Temperature dependence of Gibbs Free Energy is $dG = Vd\mathrm{p} - Sd\mathrm{T}$

At constant Temperature, $dT = 0$, the Gibbs Free Energy becomes $G_{P_2} = G_{P1} + \int_{P_1}^{P_2} VdP$

For solids and liquids, assuming zero volume change $G_{P_2} = G_{P1} + V\Delta P$

For gases, assuming Ideal Gas Law $G_{P_2} = G_{P_1} + nRT\, ln\frac{P_2}{P_1}$

Reaction Kinetics:

For 1st order kinetics: $[\mathrm{A}] = [\mathrm{A}]_0 \exp(-kt)$ or $\ln[\mathrm{A}] = -k\,t + \ln[\mathrm{A}]_0$ and $t_{1/2} = \frac{\ln 2}{k}$

For 2nd order kinetics 2A $\rightarrow$ B: $\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + k\,t$

Arrhenius equation: $k = A\exp\left(-\frac{E_a}{RT}\right)$ or $\ln k = -\frac{E_a}{RT} + \ln A$

J ≡ kg m^2 s^{-2}	N ≡ kg m s^{-2} ≡ J m^{-1}
W ≡ kg^2 m s^{-3} ≡ J s^{-1}	Pa ≡ kg m^{-1} s^{-2} ≡ N m^{-2}
W ≡ J s^{-1}	A ≡ C s^{-1}
J ≡ V C	Ω ≡ V A^{-1}
e = –1.6022 × 10^{-19} C	F = 96485.31 C mol^{-1}
h = 6.626 × 10^{-34} J s	c = 2.998 × 10^{8} m s^{-1}
k = 1.381 × 10^{-23} J K^{-1}	N = 6.023 × 10^{23} mol^{-1}
R = 8.314 J K^{-1} mol^{-1}	R = 0.08206 L atm. K^{-1} mol^{-1}
R = 0.08314 L bar K^{-1} mol^{-1}	R = 62.36 L Torr K^{-1} mol^{-1}
1 amu = 1.66024 × 10^{-27} kg	0 °C = 273.15 K
1 atm. = 101,325 Pa	1 atm. = 760 mm Hg (or Torr)
1 mmHg = 133.322 Pa	1 bar = 1 × 10^{5} Pa

Periodic Table of the Elements

1																	18
1 H 1.008	2											13	14	15	16	17	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114		116	117	

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr