BROCK UNIVERSITY

Final Examination:	**April 2004**	**Number of pages:**	**24**
Course:	**CHEM 1F92**	**Number of students:**	**430**
Date of Examination:	**Thursday 29 April 2004**	**Number of hours:**	**3**
Time of Examination:	**7:00pm -10:00pm**	**Instructors:**	**H.L. Gordon / M.F. Richardson**

TOTAL MARKS: 90

No examination aids other than those specified are permitted. Use or possession of unauthorized materials will automatically result in the award of a zero grade for this examination.

THE FOLLOWING INFORMATION IS PROVIDED:

Formula sheet.
Thermodynamic data.
List of physical constants and conversions.

CALCULATORS AND MODEL KITS ARE PERMITTED.

A minimum of 30% must be obtained on this final examination in order to achieve a passing grade in the course.

All questions are to be answered on the examination paper. If you need more space please write on blank pages at end of this paper.

Name:______________________________ **ID#:**________________

Lab section: ______________________________

Q. 1	Q. 2	Q. 3	Q. 4	Q. 5	Q. 6	Q. 7
/10	/10	/10	/10	/5	/10	/10
Q. 8	Q. 9	Q. 10	BONUS	TOTAL		
/10	/10	/5	/5	/90		

QUESTION 1. *(10 marks)*

Balance the following equation with the lowest whole-number coefficients:

_________ $C_5H_{12}O$ + _________ O_2 → _________ CO_2 + _________ H_2O

(a) What is the coefficient of O_2? ____________

(b) How many moles of CO_2 are produced for each mole of $C_5H_{12}O$ that reacts? ________

(c) How many moles of $C_5H_{12}O$ are there in 10.0 grams? ______________

(d) What mass of H_2O can be produced from combustion of 10.0 grams of $C_5H_{12}O$?

____

QUESTION 2. *(10 marks)*

Given the following species:

SO_3^{2-} XeF_5^+ $POCl_4^-$ NO_2^- SF_2

Answer the following questions.
Each question may have more than one correct answer! If there is NO correct answer, write NONE in the space provided. No marks will be awarded for a blank entry.

(a) Which of the above species have a central atom that is sp^3 hybridized?

____

(b) Which of the above species are linear?

____

(c) Which of the above species have at least one bond angle of approximately 120°?

____

(d) Which of the above species are square pyramidal molecules?

____

(e) Which of the above species have two lone pairs on the central atom?

____

(f) Which of the above species are tetrahedral molecules or ions?

____

(g) Which of the above species have no lone pairs on the central atom?

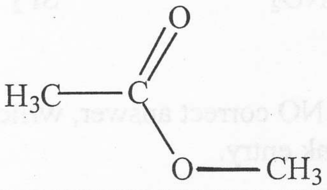
____

(h) Which of the above species has triangular planar electron pair geometry?

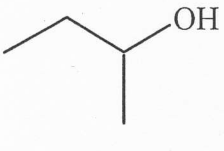
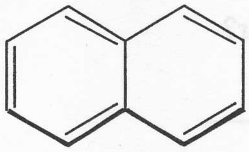
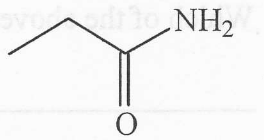
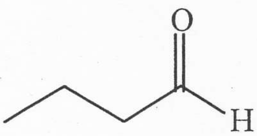
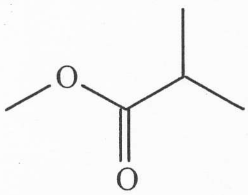
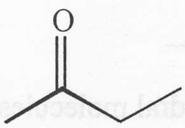
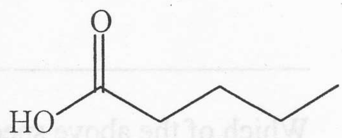
____

QUESTION 3. *(10 marks)*

Give **names** (not formulae!) for the acid and the alcohol needed to make the following ester:

	Name of acid: ________________ Name of alcohol: ________________

The following questions make use of the Figure shown below:

 **(a)**	 **(b)**	 **(c)**
 **(d)**	 **(e)**	 **(f)**
 **(g)**	 **(h)**	 **(i)**

Put the letter corresponding to the correct compound in the blanks below. If none of the compounds shown is a correct answer, state "NONE". No marks will be awarded for a blank entry.

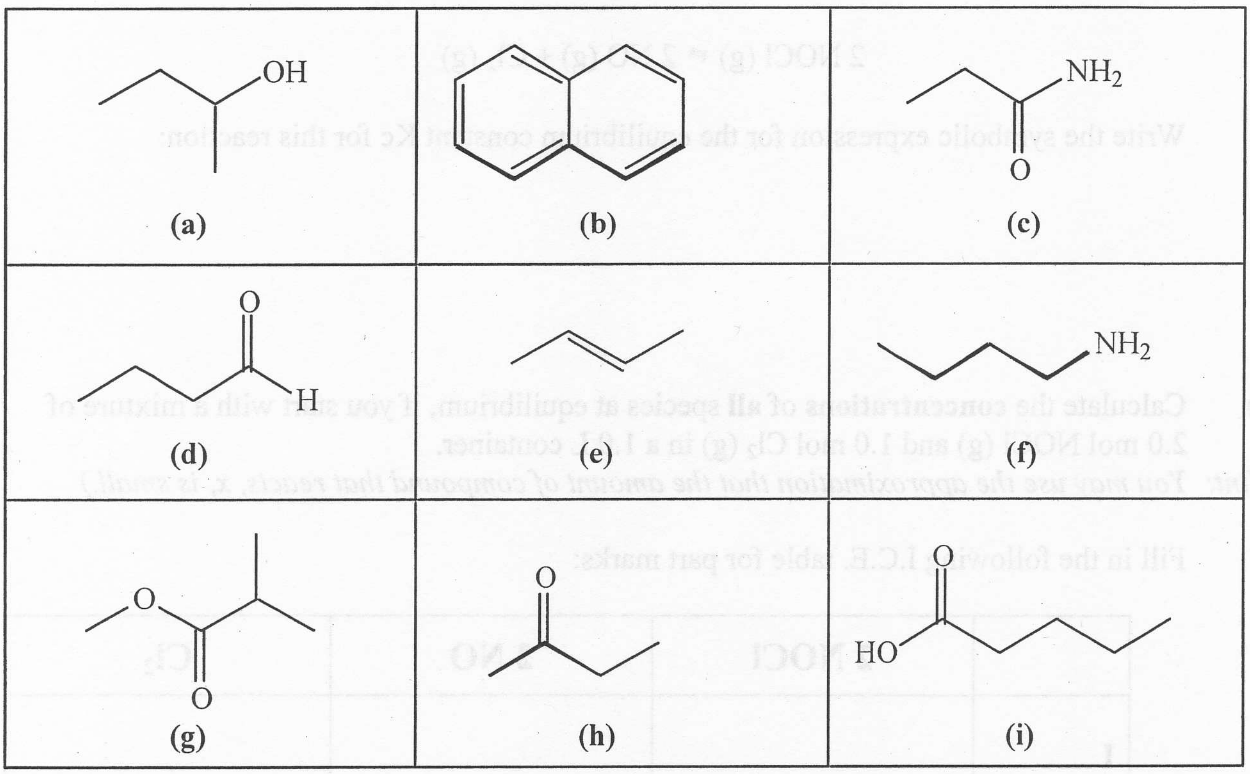
(i) Gives a basic reaction to pH paper. ________________

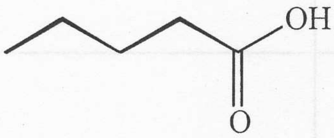
(ii) Reacts with Fehling's solution. ________________

(iii) Exists as a pair of optical isomers. ________________

QUESTION 3. *(continued ...)*

This Figure is repeated from page 4.



(iv) Structural isomer of 

____

(v) This compound is a ketone. ____________________

(vi) This compound has geometric isomers. _______________

(vii) Reacts with sodium hydroxide to give a salt _________________

(viii) Reacts with Br_2 to give 1,2-dibromobutane _________________

(ix) Reacts with HCl to give a salt _________________

QUESTION 4. *(10 marks)*

At 35°C, Kc = 1.6×10^{-5} for the following reaction:

$$2\ NOCl\ (g) \rightleftarrows 2\ NO\ (g) + Cl_2\ (g)$$

(a) Write the symbolic expression for the equilibrium constant Kc for this reaction:

(b) Calculate the **concentrations** of **all** species at equilibrium, if you start with a mixture of 2.0 mol NOCl (g) and 1.0 mol Cl_2 (g) in a 1.0 L container.
(Hint: You may use the approximation that the amount of compound that reacts, x, is small.)

Fill in the following I.C.E. table for part marks:

	2 NOCl	**2 NO**	**Cl_2**
I			
C			
E			

QUESTION 4. *(continued ....)*

(c) Given the following equilibrium:

$$UO_2\,(s) + 4\,HF\,(g) \rightleftharpoons UF_4\,(g) + 2\,H_2O\,(g)$$

(i) Write down the symbolic expression for the equilibrium constant for this reaction.

(ii) **Circle** which way the equilibrium will shift under the following circumstances:

(1) Additional UO_2 (s) is added to the system.

Shifts towards reactants *Shifts towards products* *Does not change*

(2) Volume of container is decreased.

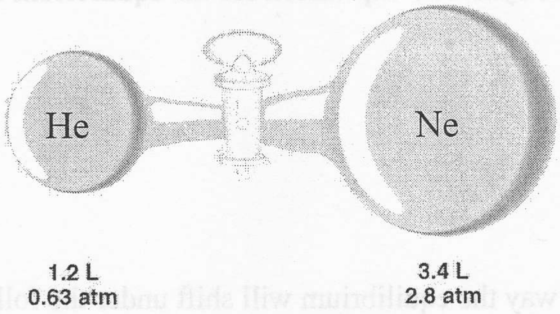
Shifts towards reactants *Shifts towards products* *Does not change*

(3) Water vapour is removed.

Shifts towards reactants *Shifts towards products* *Does not change*

QUESTION 5. *(5 marks)*

Initially the He (g) and Ne (g) are stored separately in the following apparatus at 16°C:



(a) What are the partial pressures of He (g) and Ne (g) in this apparatus after the stopcock is opened? *(Show your work! Do not forget units!)*

P_{He}: ____________________

P_{Ne}: ____________________

(b) What is the total pressure in the apparatus? ____________________________

(c) What is the mole fraction of Ne (g)? ______________________________

QUESTION 6. *(10 marks)*

The ice calorimeter was originally developed by two French scientists Lavoisier and Laplace. It uses the density change of water as it changes from the solid (ice) to liquid state, and the heat of fusion to compute enthalpies of reactions. The heat given off by a chemical reaction occurring in the ice calorimeter is absorbed by a surrounding bath of crushed ice and water. The temperature of the ice bath remains constant at 0.0 °C.

Metallic Mg reacts with hydrochloric acid according to the following equation:

$$Mg\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$$

In a particular experiment, 14.59 g of ice are melted when 0.2675 g of Mg reacts with excess HCl.

(a) Calculate the heat absorbed by the ice.

(b) What is the heat given off by the reaction of 0.2675 g Mg with HCl?

(c) Calculate ΔH°_{rxn} for the reaction of 1 mole of Mg (s) with 2 moles of HCl (aq).

(d) The density of ice at 0°C is 0.915 g cm^{-3}; the density of liquid water at 0°C is 0.9999 g cm^{-3}. Does the volume of the ice-bath increase or decrease when the ice melts?

Volume increases *Volume decreases*

QUESTION 7. *(10 marks)*

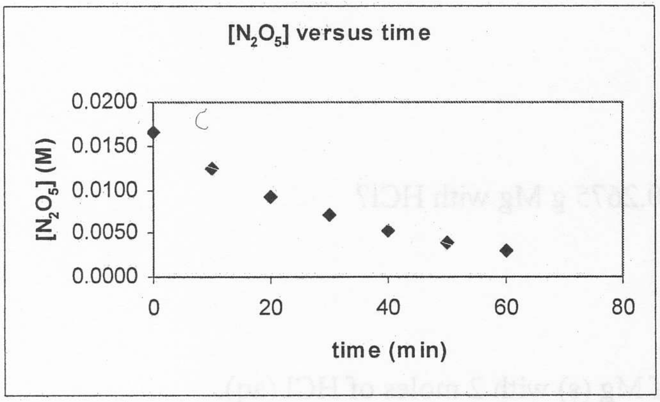
The decomposition of dinitrogen pentoxide is described by the following stoichiometric equation:

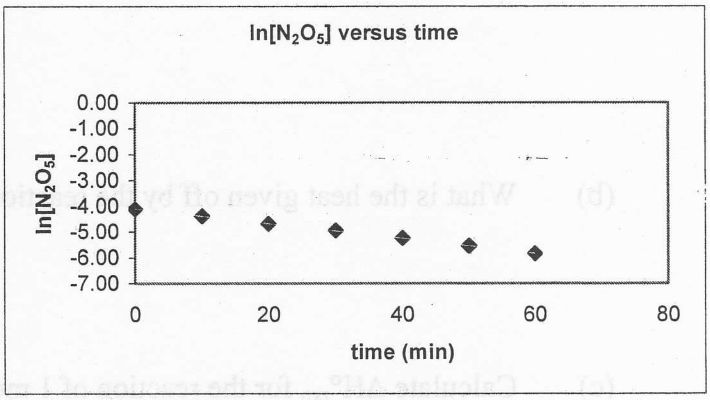
$$2N_2O_5\,(g) \rightarrow 4NO_2(g) + O_2(g)$$

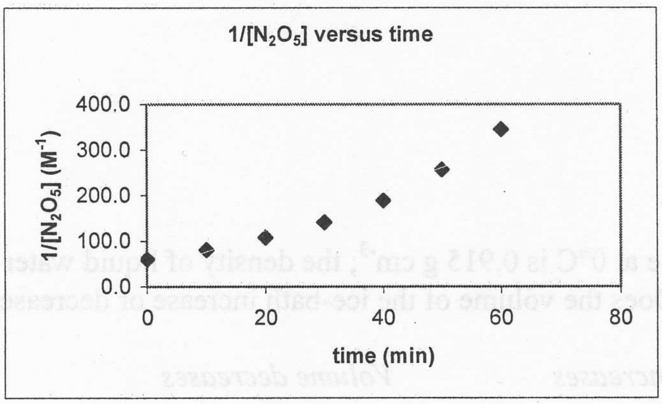
Given a starting concentration of N_2O_5 of 0.0165 M, the following graphs were produced to show how the concentration of N_2O_5 changed with time.

(a) **Circle** the correct answer:
The graphs below show that the decomposition of N_2O_5 (g) is

(a) zero order with respect to N_2O_5
(b) first order with respect to N_2O_5
(c) second order with respect to N_2O_5
(d) complex order with respect to N_2O_5







QUESTION 7. *(continued ...)*

The decomposition of dinitrogen pentoxide (MW = 108.010) is described by the following stoichiometric equation:

$$2N_2O_5\,(g) \rightarrow 4NO_2(g) + O_2(g)$$

(b) Calculate the total volume of gas collected at 760 torr and 25 °C from the complete decomposition of 35.2 g dinitrogen pentoxide.

(c) Compute $\Delta H°_{rxn}$ for the decomposition of exactly 2 moles of dinitrogen pentoxide.

(d) Compute $\Delta S°_{rxn}$ for the decomposition of exactly 2 moles of dinitrogen pentoxide.

(e) Compute $\Delta G°_{rxn}$ for the decomposition of exactly 2 moles of dinitrogen pentoxide at 25°C.

QUESTION 7. *(continued ...)*

$$2N_2O_5\ (g) \rightarrow 4NO_2(g) + O_2(g)$$

Circle the correct answer in parts (f) – (i) below:

(f) Is the decomposition of dinitrogen pentoxide endothermic or exothermic?

Endothermic *Exothermic*

(g) Does the decomposition of dinitrogen pentoxide represent an increase or decrease in entropy?

Entropy increases *Entropy decreases*

(h) Is the decomposition of dinitrogen pentoxide spontaneous at 25°?

Spontaneous *Not spontaneous*

(i) Would increasing the pressure favour the products or the reactants?

Products favoured *Reactants favoured*

(j) **Compute** the **range** of temperatures, if any, over which this decomposition is spontaneous.

QUESTION 8. *(10 marks)*

(a) The rate law for the decomposition of phosphine, PH_3, is:

$$rate = -\frac{d[PH_3]}{dt} = k[PH_3]$$

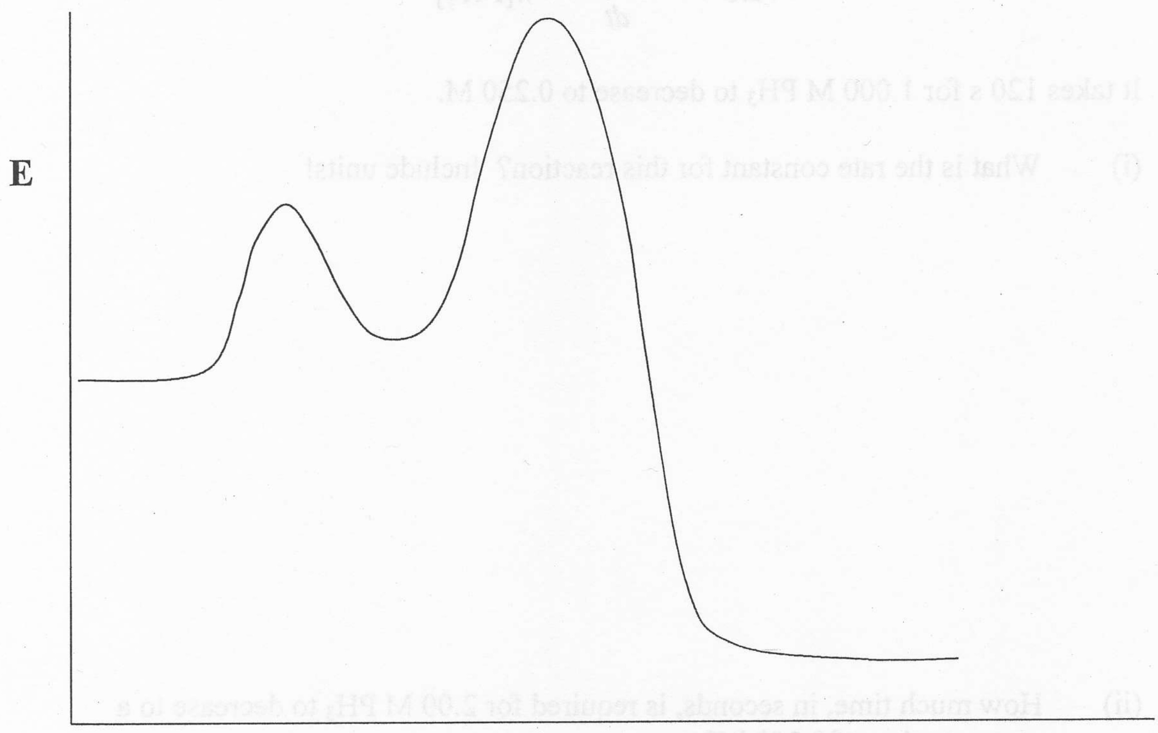
It takes 120 s for 1.000 M PH_3 to decrease to 0.250 M.

(i) What is the rate constant for this reaction? Include units!

(ii) How much time, in seconds, is required for 2.00 M PH_3 to decrease to a concentration of 0.350 M?

QUESTION 8. *(continued ...)*

(b) Most reactions occur by a series of steps. The reaction progress diagram for a certain reaction is given below:



Reaction progress →

(i) **Clearly and neatly** label the following on the graph:

(1) positions of reactants and products

(2) position of activated complex

(3) position of stable intermediate (if any)

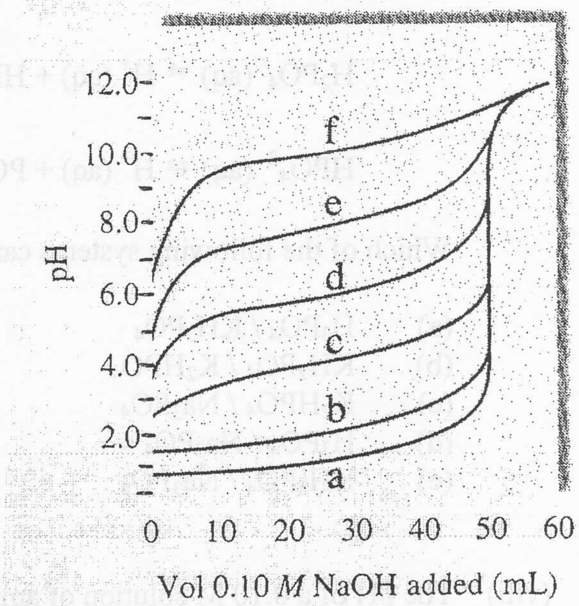
(4) ΔH_{rxn}

(5) E_a for rate-determining step

(ii) Is this reaction endothermic or exothermic? ______________________

QUESTION 9. *(10 marks)*
No calculations are required for these questions. Think CAREFULLY.

The following plot shows the pH curves for several acid-base titrations. In each case, 50.00 mL monoprotic acid is titrated with 0.1000 M NaOH.



Taken from Zumdahl and Zumdahl, "Chemistry", Houghton Mifflin, 2003.

(i) Which curve corresponds to the **weakest** acid?

(ii) Which curve corresponds to the **strongest** acid? ____________

(iii) Which curve corresponds to the acid with $K_a = 1\times10^{-6}$? ____________

(iv) Which of the following acid-base colour indicator(s) would be most appropriate to use for titration curve **e**?

____

Colour Indicator:	Thymol blue	Thymolphthalein	Phenolphthalein	Methyl Red
pH range of colour change:	1.2-2.8	9.5-10.5	8.3-10.0	4.2-6.3

(v) What is the pH (correct to ±0.5 units) at the equivalence point of titration curve **d**?

____

(vi) All of the acids depicted above are at the **same** initial concentration. What is the initial acid concentration?

____

QUESTION 9. *(continued ...) NONE of these questions require extensive calculations!!!*

(vii) Phosphoric acid has three acid-dissociation equilibria:

H_3PO_4 (aq) ⇄ H^+ (aq) + $H_2PO_4^-$ (aq) Ka = 7.5×10^{-3}

$H_2PO_4^-$ (aq) ⇄ H^+ (aq) + HPO_4^{2-} (aq) Ka = 6.2×10^{-8}

HPO_4^{2-} (aq) ⇄ H^+ (aq) + PO_4^{3-} (aq) Ka = 4.8×10^{-13}

Which of the following systems can be used as a buffer for pH values between 7.0 – 7.4?

(a) H_3PO_4 / KH_2PO_4
(b) KH_2PO_4 / K_2HPO_4
(c) K_2HPO_4 / Na_3PO_4
(d) H_3PO_4 / Na_3PO_4
(e) KH_2PO_4 / Na_3PO_4

(viii) The pH of a 0.10 M solution of ammonium chloride (NH_4Cl), pK_a = 9.26, is:
(Hint: Although you can do a calculation here, it actually isn't necessary; write down the species existing in solution when you dissolve NH_4Cl in water and the correct hydrolysis reaction. Only one of the following pH values makes sense.)
(a) 5.12
(b) 0.512
(c) 9.26
(d) 0.926
(e) 51.2

(ix) A student prepared a 0.100 M CH_3COOH/ 0.091 M CH_3COONa solution and measured its pH to be 4.70. The K_a for CH_3COOH is 6.5×10^{-5}. Can this solution be used as a buffer?
(a) No: buffers should have a pH close to 7.
(b) Yes: buffers should have a pH close to their pKa.
(c) No: buffer solutions have to have higher concentrations of conjugate acid and base than this.
(d) Yes: but it will only resist addition of base, because its pH is below 7.

QUESTION 10 *(5 marks)*

Balance the following redox equation (*show your work!*):

$$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2 \qquad \text{(acidic solution)}$$

EXTRA PAGE FOR CALCULATIONS .....

PHYSICAL CONSTANTS and CONVERSION FACTORS:

Avogadro's Number		**6.022×10^{23} mol^{-1}**	
Planck's Constant	**h**	**6.6256×10^{-34} J s**	
Speed of light	**c**	**2.998×10^{8} m s^{-1}**	
Rydberg constant	**R_H**	**2.18×10^{-18} J**	
Ideal Gas Constant	**R**	**0.08205 L atm / K mol** **8.314 J / K mol**	
Pressure		**1 atm = 760 mmHg** **1 mm Hg = 1 torr**	
Energy		**1 L atm = 101.3 J**	
Molar heat capacity $H_2O(l)$		**75.4 J K^{-1} mol^{-1}**	**between 0°C and 100°C**
Specific heat capacity $H_2O(l)$		**4.183 J K^{-1} g^{-1}**	**between 0°C and 100°C**
Molar heat capacity $H_2O(g)$		**33.76 J K^{-1} mol^{-1}**	**at constant pressure**
Specific heat capacity $H_2O(g)$		**1.874 J K^{-1} g^{-1}**	**at constant pressure**
Molar heat capacity $H_2O(s)$		**38.07 J K^{-1} mol^{-1}**	**at constant pressure**
Specific heat capacity $H_2O(s)$		**2.113 J K^{-1} g^{-1}**	**at constant pressure**
Heat of vaporization $H_2O(l)$		**2257 J g^{-1}** **40.79 kJ mol^{-1}**	**at 100°C** **at 100°C**
Heat of condensation $H_2O(g)$	**=**	**- Heat of vaporization H_2O(l)**	
Heat of fusion (melting) $H_2O(l)$		**333.4 J g^{-1}**	**at 0°C**
For H_2O (*l*)		**K_f = -1.86 °C kg/mol** **K_b = 0.52 °C kg/mol**	

Thermodynamic data at 25°C.

Species (state)	*ΔH°_f (kJ mol^{-1})*	*S°_f (J K^{-1} mol^{-1})*
Ag (s)	0	42.55
Ag^+ (aq)	105.579	72.68
AgCl (s)	-127.068	96.2
C (s, graphite)	0	5.740
C (s, diamond)	1.895	2.377
Ca (s)	0	41.42
$CaCO_3$ (s, calcite)	-1206.92	92.9
Cl_2 (g)	0	223.066
Cl^- (aq)	-167.159	56.5
CO (g)	-110.525	197.674
CO_2 (g)	-393.509	213.74
HCO_3^- (aq)	-691.99	91.2
CO_3^{2-} (aq)	-677.14	-56.9
Fe (s)	0	27.28
Fe_2O_3 (s)	-824.2	87.40
H_2 (g)	0	130.684
H_2O (g)	-241.818	188.825
H_2O (l)	-285.830	69.91
H^+ (aq)	0	0
OH^- (aq)	-229.994	-10.75
H_2O_2 (aq)	-191.17	143.9
H_2S (g)	-20.63	205.79
N_2 (g)	0	191.61
NH_3 (g)	-46.11	192.45
NH_3 (aq)	-80.29	111.3
NO (g)	90.25	210.761
NO_2 (g)	33.18	240.06
N_2O_5 (g)	11.30	346.55
NO_3^- (aq)	-205.0	146.4
Na^+ (aq)	-240.12	59.0
NaCl (s)	-411.153	72.13
NaCl (aq)	-407.27	115.5
NaOH (s)	-425.609	64.455
O_2 (g)	0	205.138
O_3 (g)	142.7	238.93
S (rhombic)	0	31.80
SO_2 (g)	-296.830	248.22
SO_3 (g)	-395.72	256.76

Relationship between energy and wavelength or frequency of light: $E = h\nu$ or $E = hc/\lambda$	Energy of an electron in the nth shell of Bohr model of hydrogen-like atom: $E_n = -R_H\left(1/n^2\right)$
Charles' Law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$	Heat change due to change of phase: $q = \Delta H_{vap} m$ $q = \Delta H_{fus} m$
Boyle's Law: $P_1V_1 = P_2V_2$	Heat change due to change of temperature at constant P: $q = C_P(T_2 - T_1)$ or $q = m\overline{C_P}(T_2 - T_1)$
Ideal Gas Law: $PV = nRT$	Standard enthalpy change for a reaction: $\Delta H^o_{rxn} = \sum n\Delta H^o_f(products) - \sum m\Delta H^o_f(reactants)$
Dalton's Law of Partial Pressures: $P_{total} = P_A + P_B + P_C + \ldots$	Standard entropy change for a reaction: $\Delta S^o_{rxn} = \sum nS^o_f(products) - \sum mS^o_f(reactants)$
Relationship of partial pressure to mole fraction: $P_A = X_A \cdot P_{total}$	Standard free energy change for a reaction: $\Delta G^o_{rxn} = \sum n\Delta G^o_f(products) - \sum m\Delta G^o_f(reactants)$
Relationship between equilibrium constant and ΔG: $\Delta G^o = -RT\ln K_P$ or $\Delta G^o = -RT\ln K_C$	Gibbs free energy: $\Delta G = \Delta H - T\Delta S$
van der Waal's equation: $\left[P + \frac{an^2}{V^2}\right][V - nb] = nRT$	Internal energy: $\Delta E = q + w$
Pressure-volume work: $w = -P_{ext}(V_2 - V_1)$	Enthalpy change for constant pressure process: $\Delta H = \Delta E + P(V_2 - V_1)$
Average kinetic energy of gas molecules: $\overline{KE} = \frac{1}{2}m\overline{u^2}$	Henry's Law: $c = kP$

Root-mean-square speed of gas molecules: $u_{rms} = \sqrt{\frac{3RT}{M}}$	Vapour pressure lowering: $P_{solution} = X_{solvent} P^o_{solvent}$
Simple cubic cell: 1 atom/cell; cell length = 2r	Freezing point lowering: $T^o_{fp} - T_{fp} = K_f im$
Body-centred cubic cell: 2 atoms/cell; cell length = $\frac{4}{\sqrt{3}} r$	Boiling point elevation: $T_{bp} - T^o_{bp} = K_b im$
Face-centred cubic cell: 4 atoms/cell; cell length = $\sqrt{8}r$	Osmotic pressure: $\pi = iMRT$ and $\pi = (mass)RT / FW$
Clausius-Clapeyron equation: $\ell n \left\{ \frac{P_1}{P_2} \right\} = \frac{\Delta H_{vap}}{R} \left\{ \frac{T_1 - T_2}{T_1 T_2} \right\}$	$k = Ae^{-Ea/RT}$ Arrhenius equation: or $\ln k = \ln A - \frac{E_a}{RT}$
$\ln[A] - \ln[A]_o = -kt$ First order rate equation: $\ln \left\{ \frac{[A]}{[A]_o} \right\} = -kt$	Second order rate equation: $\frac{1}{[A]} - \frac{1}{[A]_o} = kt$
Half-life for first order reaction: $t_{1/2} = \frac{\ln(2)}{k} = \frac{0.623}{k}$	Half-life for second order reaction: $t_{1/2} = \frac{1}{k[A]_o}$
pH = -log [H$^+$]; pOH = -log [OH$^-$]; $K_w = K_a K_b = 10^{-14}$	Solution to quadratic equation: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
Standard emf of electrochemical cell: $E^o_{cell} = E^o_{cathode} - E^o_{anode}$ Relationship between ΔG° and standard emf: $\Delta G^o = -nFE^o_{cell}$	Relationship between standard emf of cell and K: $E^o_{cell} = \frac{RT}{nF} \ln K$ Nernst equation: $E = E^o_{cell} - \frac{RT}{nF} \ln Q$

PERIODIC TABLE OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9062	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.905	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La ★ 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac ◆ 227.028	104 Rf (261)	105 Ha (262)	106 Sg (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)									

★ Lanthanide series	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
◆ Actinide series	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (260)	102 No (259)	103 Lr (262)