

Preparatory material for Incoming Students: Physical Chemistry

1. The Physical Chemistry tutorials at St Edmund Hall are given by David Manolopoulos.
2. There will be three first year Physical Chemistry tutorials in the Michaelmas term, one in week 1, one in week 3, and one in week 6.
3. The physical chemistry lecture courses in the Michaelmas term are as follows:

Classical Mechanics (6 lectures)

The Role of Charge (4 lectures)

Properties of Gases (4 lectures)

Chemical Thermodynamics (13 lectures)

The first three of these lecture courses are regarded as “physics for chemistry” and will be covered in classes with a doctoral student. The last is a major physical chemistry course which will be the focus of the first term’s tutorials.

To prepare yourself for these courses, please buy a copy of Atkins’ Physical Chemistry, by Peter Atkins, Julio de Paula, and James Keeler (12th Edition, Oxford University Press, 2022, available from [amazon.co.uk](https://www.amazon.co.uk) for £59.99), study Chapter 1 on the Properties of Gases and Chapter 2 on The First Law, and answer the 5 questions on the sheet below before you arrive in Oxford. You will be expected to hand in your answers to these questions when you arrive so that they can be marked before the first tutorial in week 1.

Atkins’ Physical Chemistry is the only physical chemistry textbook you will need to buy for your first year at Oxford. It is quite expensive at £59.99. However, College Grant funds are available to support the purchase of essential course materials, currently at the rate of £300 per year, of which £100 may be used to purchase books.

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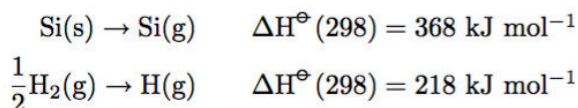
Problems

A. THE FIRST LAW

- A1. (a) Calculate the work done when 1 mole of an ideal gas (initial volume V_1) expands isothermally and reversibly to a final volume $V_2 = 3V_1$ at 298 K.
 (b) Calculate the work done when 1 mole of an ideal gas (initial volume V_1) expands isothermally into an evacuated space to a final volume $V_2 = 3V_1$ at 298 K.
 (c) The initial and final states of the gas are the same in parts (a) and (b), so the change in internal energy is the same in both cases. Reconcile your results for (a) and (b) with the First Law.
 (d) One mole of $\text{CaCO}_3(\text{s})$ was heated in an open vessel at 1 atm pressure to 700 °C when it decomposed into $\text{CaO}(\text{s})$ and $\text{CO}_2(\text{g})$. Calculate the work done during the decomposition assuming that CO_2 may be regarded as an ideal gas.

- A2. A 0.825 g sample of benzoic acid was ignited in a bomb calorimeter in the presence of excess oxygen. The temperature of the calorimeter rose by 1.940 K from 298 K. In two separate experiments in the same apparatus, 0.498 g of fumaric acid and 0.509 g of maleic acid were ignited and gave temperature rises of 0.507 K and 0.528 K respectively. Calculate (a) the molar internal energy of combustion; (b) the molar enthalpy of combustion and (c) the molar enthalpy of formation of (i) fumaric acid and (ii) maleic acid. Comment on the difference between the enthalpies of formation of the two isomers. The standard enthalpy of formation of water is $-285.8 \text{ kJ mol}^{-1}$ and of CO_2 $-393.5 \text{ kJ mol}^{-1}$. The internal energy of combustion of benzoic acid is $-3251 \text{ kJ mol}^{-1}$. The relative molecular masses of benzoic, fumaric and maleic acids are 122, 116 and 116 respectively.

- A3. Calculate the average bond dissociation enthalpy of the Si-H bonds in SiH_4 from the following data. The molar enthalpy of combustion of $\text{SiH}_4(\text{g})$ to $\text{SiO}_2(\text{s})$ and $\text{H}_2\text{O}(\text{l})$ is $-1367 \text{ kJ mol}^{-1}$. The standard enthalpies of formation of SiO_2 and H_2O are -858 kJ mol^{-1} and -286 kJ mol^{-1} respectively. Also:



- A4. At 298 K, the standard enthalpy of formation ($\Delta_f H^\ominus$) of $\text{NH}_3(\text{g})$ is $-46.11 \text{ kJ mol}^{-1}$. Assuming that the molar heat capacities can be represented by expressions of the form $C_{p,m} = A + BT$, with the coefficients A and B given below, calculate $\Delta_f H^\ominus$ at 1000 K.

	N_2	H_2	NH_3
$A/\text{J K}^{-1} \text{ mol}^{-1}$	28.58	27.28	29.75
$10^3 B/\text{J K}^{-2} \text{ mol}^{-1}$	3.77	3.26	25.1

- A5. One mole of a perfect monatomic gas (with $C_v = \frac{3}{2}R$) is expanded adiabatically and reversibly to twice its initial volume, from an initial temperature of 298 K. Calculate (a) the final temperature of the gas and (b) the work done on the gas during the expansion.