

EXAM 1
20 September 1989

Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

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

$1 \text{ atm} = 101325 \text{ Pa}$

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

- (1) 10 points. *Only short answers (1 or 2 lines) are needed for full marks on this question.*
- What is *effusion*?
 - Explain the idea of the *collision number*.
 - What is meant by the term *mean free path*?
 - Define the three *classifications of systems*.
- (2) 10 points.
- Sketch a P versus V diagram for a real gas and label the axes. Show and label
 - The four areas corresponding to the *liquid, gas, liquid + vapor, and supercritical fluid phases*.
 - The *critical point*.
 - An *isotherm* corresponding to liquefaction of a gas by pressure.
 - Real gases can be better described by the van der Waals equation $(P + a n^2/V^2)(V - nb) = nRT$ than by the ideal gas equation. Explain the significance of *a* and *b* in terms of fundamental assumptions about ideal gases.
- (3) 6 points.
- Starting with the ideal gas equation, derive an expression for the density of an ideal gas as a function of the molar mass *M*.
 - An unknown gas has a density of 2 kg m^{-3} at a pressure of 10^5 Pa and a temperature of 0°C . What is its molar mass?
- (4) 14 points.
- Write down an expression for the mean square speed $\overline{u^2}$ of a molecule in an ideal gas in terms of molecular mass, pressure, volume and number of molecules.
 - Combine this expression with the ideal gas equation of state to prove that the average kinetic energy $\bar{\epsilon}$ of one molecule is given by $\bar{\epsilon} = 1.5 k_B T$, where k_B is the Boltzmann constant R/L .
 - Calculate $\bar{\epsilon}$ for H_2 gas at 500 K .
 - Use the molar mass of H_2 , $0.002 \text{ kg mol}^{-1}$, to find the molecular mass. Thus calculate the root mean square (rms) speed $(\overline{u^2})^{1/2}$ of the molecules.
 - Now consider atomic sulfur vapor, S, at 500 K . The molar mass is $0.032 \text{ kg mol}^{-1}$. Compare its $\bar{\epsilon}$ and rms speed to those for H_2 (*HINT: you do not need to work out (c) and (d) again from scratch*).
 - If the temperature is doubled, by what factor does the rms speed increase?

EXAM 2
12 October 1989

Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

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

$1 \text{ atm} = 101325 \text{ Pa}$

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

(1) 12 points. Only short answers (1 or 2 lines) are needed for full marks on this question.

- a) Define *enthalpy*.
- b) What are *endothermic* reactions? Are they permitted by the First Law of Thermodynamics.
- c) Explain the difference between *reversible* and *irreversible* processes.
- d) What is the point of the *Joule-Thompson experiment*?
- e) Define the *standard heat of formation* of a substance.
- f) Explain how the *average bond dissociation energy* of a molecule is related to the heats of formation of its constituent atoms.

(2) 12 points.

Diamonds are forever, but to prove that they are pure carbon some were burnt and only CO_2 was formed. The heat loss from the system (carbon plus oxygen) when this expensive reaction, $\text{C}(\text{diamond}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$, is carried out in a sealed calorimeter is $-395.4 \text{ kJ mol}^{-1}$.

Other data: $C_p(\text{diamond}) = 6 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_p(\text{O}_2) = 29 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_p(\text{CO}_2) = 37 \text{ J K}^{-1} \text{ mol}^{-1}$. The molar mass of C is 0.012 kg. The densities of diamond and graphite are 3500 and 2300 kg m^{-3} , respectively.

- a) Calculate $\Delta H(298 \text{ K})$ for this process.
- b) Calculate $\Delta H(2500 \text{ K})$ for this process.
- c) If graphite is burnt instead, we find that $\Delta H(298 \text{ K})$ for $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ is $-393.5 \text{ kJ mol}^{-1}$. Hence deduce $\Delta H(298 \text{ K})$ for the conversion $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$.
- d) Diamonds are formed at very high pressures deep underground. Assuming $P = 10^{10} \text{ Pa}$, calculate the work done on 1 mole of graphite during the conversion to diamond at 298 K.

(3) 16 points.

1 mole of an ideal gas, with $C_p = 29.4 \text{ J K}^{-1}$ and $C_v = C_p - R$, is initially at 10^5 Pa and 300 K. It can then be heated by 100 K in two different ways.

- A. Suppose it is heated at *constant pressure*.
 - a) How much heat is absorbed by the gas?
 - b) How much work is done on the gas?
 - c) What is ΔU for the gas?
 - d) What is ΔH for the gas?
- B. Suppose instead that it is heated at *constant volume*.
 - e) How much heat is absorbed by the gas?
 - f) How much work is done on the gas?
 - g) What is ΔU for the gas?
 - h) What is ΔH for the gas?

EXAM 3
November 3, 1989

Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$1 \text{ atm} = 101325 \text{ Pa}$

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

- (1) 8 points.
- Illustrate the Carnot cycle on a P-V diagram and label each of the four parts and the isotherms for two temperatures between which it works, T_h and T_c .
 - Suppose $T_h = 400 \text{ K}$, $T_c = 300 \text{ K}$ and the heat absorbed at T_h , q_h , is 100 J. How much heat is rejected at T_c ?
 - What is ΔS for the working fluid during the isothermal expansion at 400 K?
- (2) 12 points.
- Define the Helmholtz energy A . What is the condition that determines whether a constant volume system is at equilibrium?
 - Use the above definition plus the Maxwell relation $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ to prove that $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$. State any other results you use.
 - Hence calculate ΔU for the isothermal expansion of 1 mol of a van der Waals gas (which obeys $P = RT/(V-b) - a/V^2$; $a = 0.2 \text{ Pa m}^6$) from 0.01 to 1.0 m^3 .
- (3) 8 points.
- 1 mol of ethanol is evaporated at a constant 1 atm pressure, at its boiling point of 70 °C, and the volume increase is 28 dm^3 . The latent heat of evaporation is 84 kJ mol^{-1} . Calculate the work done on this system (w), ΔU , ΔG and ΔS .
- (4) 8 points.
- 1 mol of ideal gas at 300 K and $1.0 \times 10^5 \text{ Pa}$ is *irreversibly* and isothermally expanded to three times its original volume. The work performed by the gas is 500 J i.e. $w = -500 \text{ J}$. What are ΔH , ΔS and ΔG ? What work could have performed if the gas had been expanded *reversibly*?

EXAM 4
29 November 1983

Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ $1 \text{ atm} = 101325 \text{ Pa}$

IMPORTANT: Write clearly and neatly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a few words of explanation.

(1) 10 points.

Consider the partial dissolution of the slightly soluble salt MgF_2 (molar mass 0.062 kg) in water: $\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$.

- a) The solubility product K_s is $7.0 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$. What mass of MgF_2 dissolves in 1 dm^3 of pure water?
- b) Suppose $[\text{F}^{-}(\text{aq})]$ is fixed at 0.1 mol dm^{-3} . What then is the equilibrium $[\text{Mg}^{2+}(\text{aq})]$?

(2) 10 points

A gas reaction $\text{A} + \text{B} \rightleftharpoons \text{C}$ is exothermic and has $K_p = 1 \text{ atm}^{-1}$ at 298 K. With reference to a standard state of 1 atm,

- a) What is ΔG° at 298 K?
- b) What is the sign of ΔS° ? Why?
- c) Will K_p at 310 K be greater or less than 1 atm? Why?
- d) What will be the sign of ΔG° at 310 K? Why?
- e) Calculate K_c (standard state 1 mol dm^{-3}) at 298 K.

(3) 20 points.

- a) What is the relation between $d(\ln K_p)/d(1/T)$ and ΔH° ? Hence, assuming ΔH° is independent of T, derive an expression for $\ln(K_{p,1}/K_{p,2})$, the natural logarithm of the ratio of K_p at two temperatures T_1 and T_2 .

- b) Consider the process $\text{Br}_2 \rightleftharpoons 2 \text{Br}$. The following experimental data were obtained for an equilibrium mixture:

T	$p(\text{Br}_2)$	$p(\text{Br})$
500 K	1 atm	$1 \times 10^{-4} \text{ atm}$
600 K	1 atm	$3 \times 10^{-3} \text{ atm}$

Calculate K_p at each temperature.

- c) Calculate ΔH° .
- d) Calculate ΔG° at 600 K and hence ΔS° (standard state 1 atm).
- e) What is the degree of dissociation α of Br_2 at 600 K?
- f) If the system were changed by removing Br_2 i.e. lowering $p(\text{Br}_2)$, what does Le Chatelier's principle tell you about how the system would respond? Would α change, and if so, how?

EXAM 5
Take-home questions on Chapter 9
Due on Monday 4 December 1989 at 10 am

Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

(1) 15 points.

The composition of a solution initially containing pure A was measured as a function of time. A was consumed in a reaction that was second order with respect to A. The following data were obtained:

t/s	0	2	3	7	10
[A]/mol dm ⁻³	0.36	0.26	0.22	0.15	0.12

Find the rate constant by plotting a straight-line graph, and fit a straight line to the points by eye: a linear regression analysis is not required. Give the units of the rate constant.

ATTENTION: 5 of the points are for graphing style i.e. adherence to the following five essential rules for ANY scientific graph:

- i) Use only graph or squared paper.
- ii) Use a ruler for all straight lines: no freehand sketching.
- iii) Label both axes, and show the units.
- iv) Each axis must be at least 4" (10 cm) long: no micro drawings.
- v) No silly scales like 17.3 squares per unit.

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(2) 15 points.

The rate constant k of a first-order reaction has been measured as a function of temperature:

T/K	200	250	300	350	400
k/s ⁻¹	2×10^{-4}	3×10^{-3}	2×10^{-2}	1×10^{-1}	4×10^{-1}

Draw an Arrhenius plot of these data. Fit a straight line to the scattered points by eye: a regression analysis is not required. Find the A-factor and the activation energy E, and give their units. Again, there are 5 easy points for following the graph rules of Q.1.