

**EXAM 1**  
**12 September 1990**

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) 8 points

- a) What is Graham's Law of Effusion? Explain how it is related to microscopic properties of gases.
- b) Consider two bulbs of He and Ar, at identical P and T. Ar atoms weigh 10 times as much as He atoms. What are the ratios of (i) the average molecular velocities, and (ii) the average molecular kinetic energies?

(2) 22 points

- a) What are the three postulates or assumptions of the kinetic-molecular model for ideal gases?
- b) 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. Briefly explain the significance of  $a$  and  $b$  in terms of your answer to (a).
- c) Sketch a P versus V diagram for a real gas and label the axes. Show and label
- (i) The four areas corresponding to the *liquid, gas, liquid + vapor, and supercritical fluid phases.*
  - (ii) The *critical point.*
  - (iii) An *isotherm* corresponding to liquefaction of a gas by pressure.

(3) 20 points

- Imagine that  $N$  molecules of gas, with diameter  $d$ , are confined in a volume  $V$ , and that the mean relative velocity is  $\sqrt{2} \bar{u}$ .
- a) Explain what the separation between centers of a pair of colliding molecules is.
- b) Considering a single molecule, what volume does it sweep out in one second? How many other molecules were in that volume?
- c) Hence calculate the number of collisions a single molecule experiences per second. What is the name of this quantity?
- d) What is the mean time between collisions? Show that the molecule will travel a distance  $\lambda = V / [\sqrt{2} \pi d^2 N]$  between collisions. What is the special name for this distance?
- e) 1 mol of pure  $\text{N}_2$  ( $d = 3 \times 10^{-10} \text{ m}$ ) is held at 298 K in  $24 \text{ dm}^3$ . Calculate  $\lambda$ .

EXAM 2  
5 October 1990

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

- a) What are the definitions of  $C_V$  and  $C_p$ , in terms of  $P$ ,  $V$ ,  $T$ ,  $H$  and  $U$ ?
- b) A general result is  $C_p - C_V = [P + (\frac{\partial U}{\partial V})_T] (\frac{\partial V}{\partial T})_P$   
Use this to calculate  $C_p - C_V$  for 1 mole of an ideal gas.
- c) Give an industrial application of the Joule-Thomson effect.
- d) Define the average bond dissociation energy of a molecule.

(2) 22 points

Consider 1 mole of ideal gas in a cylinder volume  $V_1$  at a pressure  $P_1$  and temperature  $T$ . A piston is pushed in to compress the gas to a volume  $V_2$  at pressure  $P_2$ .

- a) Write down an expression for  $dw$ , the work done on the gas if the volume is changed by an infinitesimal amount  $dV$ .
- b) Suppose the gas is compressed isothermally and reversibly.
  - (i) Derive an expression for the total work done on the gas,  $w$ .
  - (ii) What is  $\Delta U$  for the gas?
  - (iii) What is the heat absorbed by the gas,  $q$ ?
- c) Suppose instead that the gas is compressed irreversibly by immediately increasing the pressure to  $P_2$ , and finishing at the same final state.
  - (i) Derive an expression for the total work done on the gas,  $w$ .
  - (ii) What is  $\Delta U$  for the gas?
  - (iii) What is the heat absorbed by the gas,  $q$ ?
- d) Sketch the two compressions on a PV diagram.
- e) Which of the quantities  $w$ ,  $U$  and  $q$  are functions of state, and why?

(3) 20 points

Suppose 1 mole of  $\text{H}_2(\text{g})$  is burnt in a calorimeter at 298 K, to form 1 mole of liquid  $\text{H}_2\text{O}$ . The heat released is 250 kJ.

- a) Use the data to calculate  $\Delta_f H^\circ(\text{H}_2\text{O}(l))$  at 298 K.
- b)  $\Delta H^\circ$  for the evaporation of water is  $40 \text{ kJ mol}^{-1}$ . Use this to show that  $\Delta H^\circ$  for the reaction  $\text{H}_2(\text{g}) + 0.5 \text{ O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$  is  $-214 \text{ kJ mol}^{-1}$  at 298 K.
- c) The heat capacities of  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}(\text{g})$  are 27, 30 and  $40 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. Calculate  $\Delta H^\circ$  for the reaction in part (b) at 1000 K.
- d) Estimate the maximum temperature of an  $\text{H}_2/\text{O}_2$  flame.
- e) Give one reason why your answer to (d) is likely to be an overestimate.

EXAM 3  
2 November 1990

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

1 atm = 101325 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) 16 points

Initially at 400 K and 2 atm, 1 mole of an ideal gas undergoes an irreversible isothermal expansion to 3 times its original volume. The work performed on the gas is -600 J.

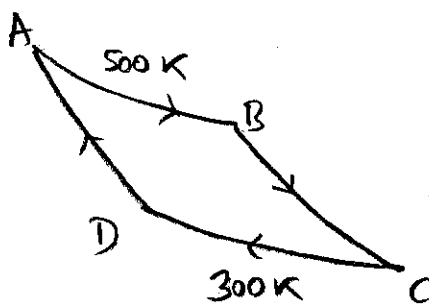
- What are the values of  $q$ ,  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $\Delta A$  and  $\Delta G$  for the gas?
- Is  $\Delta S$  for the entire universe positive, negative or zero, and why? Suppose instead the expansion had been reversible: what then could you say about  $\Delta S$  for the universe?

(2) 16 points

- Starting with  $dU = -PdV + TdS$  and the definition of Helmholtz energy  $A$ , derive an expression for the differential  $dA$  in terms of state functions. Would you expect this differential to be "exact" or not, and why?
- Use this expression to prove that  $(\partial A/\partial V)_T = -P$  and  $(\partial A/\partial T)_V = -S$ .
- Use the result of (b) to prove that  $(\partial P/\partial T)_V = (\partial S/\partial V)_T$ .
- Hence determine  $(\partial S/\partial V)_T$  for 1 mole of an ideal gas.

(3) 18 points

Here is a reversible Carnot cycle for 1 mole of an ideal gas, which has  $C_p = 40 \text{ J K}^{-1}$ :



- What is thermodynamic efficiency of this engine?
- 100 J of heat are absorbed at the higher temperature. How much work is performed by the engine? How much heat is rejected at 300 K?
- What are  $\Delta S$  and  $\Delta G$  for the gas going from A to B?
- What are  $\Delta S$  and  $\Delta G$  for the gas going from B to C?

SOLUTIONS TO EXAMS, 11-2-90

1 a) ISOTHERMAL  $\therefore \Delta U = \Delta H = 0$ .  
 $\Delta U = q + w = q - 600 \text{ J} \therefore q = 600 \text{ J}$ .  
 $\Delta S = R \ln \left( \frac{V_2}{V_1} \right) = R \ln 3 = 9.13 \text{ JK}^{-1}$ .  
 $\Delta A = \Delta U - T\Delta S = 0 - 400 \times 9.13 = -3654 \text{ J}$ .  
 $\Delta G = \Delta H - T\Delta S = 0 - 400 \times 9.13 = -3654 \text{ J}$ .

f)  $\Delta S_{\text{uni}} > 0$  for all spontaneous processes. If the process had been reversible then  $\Delta S_{\text{surr}}$  would cancel  $\Delta S_{\text{system}}$  to leave  $\Delta S_{\text{uni}} = 0$ .

2 a)  $A = U - TS$   
 $\therefore dA = dU - Tds - SdT$   
 $= -PdV + Tds - Tds - SdT$   
 $= -PdV - SdT$ .

This is exact because  $A$  is a state function  $\therefore \oint dA = 0$ .

f)  $dA$  is also  $\left( \frac{\partial A}{\partial V} \right)_T dV + \left( \frac{\partial A}{\partial T} \right)_V dT$

$\therefore$  by comparing the terms for  $dV$  and  $dT$ ,  $\left( \frac{\partial A}{\partial V} \right)_T = -P$   
and  $\left( \frac{\partial A}{\partial T} \right)_V = -S$ .

c)  $\left( \frac{\partial P}{\partial T} \right)_V = \frac{\partial \left[ - \left( \frac{\partial A}{\partial V} \right)_T \right]_V}{\partial T} = \frac{\partial \left[ - \left( \frac{\partial A}{\partial T} \right)_V \right]_T}{\partial V} = \left( \frac{\partial S}{\partial V} \right)_T$ .

d)  $P = \frac{RT}{V} \therefore \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V}$ .

$$3a) \quad \varepsilon = \frac{T_h - T_c}{T_h} = \frac{800 - 300}{800} = 0.625$$

$$b) \quad \text{Work performed} = 0.625 \times 100 \text{ J} = 62.5 \text{ J}$$

$$\text{Heat rejected} = 100 \text{ J} - 62.5 \text{ J} = 37.5 \text{ J}$$

$$c) \quad \Delta S = \frac{q_{\text{rev}}}{T} = \frac{100 \text{ J}}{800 \text{ K}} = 0.125 \text{ J K}^{-1}$$

$\Delta G = \Delta H - T\Delta S$  and  $\Delta H = 0$  for an isothermal change on an ideal gas

$$\therefore \Delta G = 0 - 800 \times 0.125 \text{ J} = -100 \text{ J}$$

d) Here,  $dq_{\text{rev}} = 0$  (ADIABATIC)  $\therefore \Delta S = 0$ .

$$\begin{aligned} \Delta H &= C_p \Delta T = 40 \text{ J K}^{-1} \times (300 - 800) \text{ K} \\ &= -20 \text{ 000 J} \end{aligned}$$



MODEL ANSWERS FOR EXAM 4, FALL 1990.

- 1a) The partial molar Gibbs energy,  $\mu = \left( \frac{\partial G}{\partial n_A} \right)_{n_B, n_C, \dots, T, P}$ .
- b)  $K_p = K_c (RT)^{\Delta \nu}$
- c)  $a = \gamma c$  where  $\gamma$  is the activity coefficient.
- 2a) The activity of a pure liquid = 1 by convention, so  $K_p = P$ .

b)  $\frac{d \ln K_p}{d(1/T)} = \frac{d \ln K_p}{dT} \cdot \frac{dT}{d(1/T)} = \frac{\Delta H}{RT^2} \div -\frac{1}{T^2} = -\frac{\Delta H}{R}$

$\therefore \ln K_p = -\frac{\Delta H}{RT} + \text{const}$ , by integration.

Alternatively,  $\Delta G = \Delta H - T\Delta S = -RT \ln K_p$

$\therefore \ln K_p = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$ .

Either way,  $\ln (K_{p1}/K_{p2}) = -\frac{\Delta H}{RT_1} - \left( -\frac{\Delta H}{RT_2} \right) = \frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

and  $K_{p1}/K_{p2} = P_1/P_2$  here.

c)  $\ln \left( \frac{0.9}{0.1} \right) = \frac{\Delta H}{R} \left( \frac{1}{298} - \frac{1}{350} \right) \therefore 2.197 = \frac{\Delta H}{R} (0.0004986)$

$\therefore \Delta H = 3663 \text{ kJ mol}^{-1}$ .

At 298 K,  $K_p = 0.1 \therefore \Delta G = -RT \ln K_p = -8.314 \times 298 \times \ln 0.1$   
 $= 5705 \text{ J mol}^{-1}$

but  $\Delta G = \Delta H - T\Delta S \therefore \Delta S = \frac{\Delta H - \Delta G}{T} = 10.38 \text{ JK}^{-1} \text{ mol}^{-1}$ .

Check: at 350 K,  $K_p = 0.9 \therefore \Delta G = 307 \text{ J mol}^{-1}$ .

$36630 - 350 \times 103.8 = 300$  which agrees within rounding errors.  
 $\Delta H - T \Delta S = \Delta G$

$$3a) K_p^u = e^{-\frac{\Delta G}{RT}} = e^{-\frac{19000}{8.314 \times 1000}} = 0.102$$

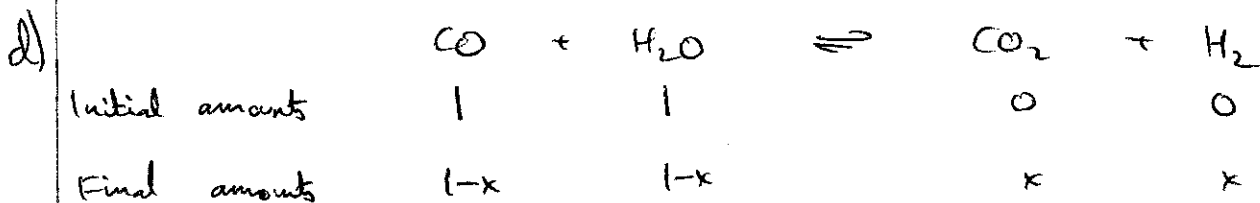
or  $K_p = 0.102 \text{ atm}$ .

$$b) \Delta G = \Delta H - T\Delta S \quad \therefore \Delta H = \Delta G + T\Delta S$$

$$= 19000 + 1000 \times -40$$

$$= -21000 \text{ J mol}^{-1}$$

c)  $\Delta H < 0$  so  $K_p$  decreases if  $T$  goes up. By Le Chatelier's Principle, reaction equilibrium will shift to oppose an applied change.



For a fixed volume,  $P \propto$  amount

$$\therefore K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{x^2}{(1-x)^2} \quad \therefore \frac{x}{1-x} = \sqrt{K_p}$$

$$\therefore x = \frac{\sqrt{K_p}}{1 + \sqrt{K_p}} \approx 0.24 \text{ here}$$

Thus the equilibrium amounts of CO, H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub> are 0.76, 0.76, 0.24 and 0.24 mol, respectively.

e) Because  $\sum \nu_i = 0$ ,  $K_p = K_c$  and  $K_c$  is dimensionless.

Alternatively,  $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$  so concentration units cancel.



EXAM 5

Take-home questions on Chapter 9  
Due on Monday, December 3, 1990 at 10 am

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

(1) 15 points.

The rate constant  $k$  of an elementary gas-phase bimolecular reaction has been measured as a function of temperature:

T/K	300	350	400	450	500
$k/\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$	2.5	$2.5 \times 10^2$	$2.2 \times 10^3$	$2.0 \times 10^4$	$6.4 \times 10^4$

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.

**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.

**PENCIL IS PERFECTLY ACCEPTABLE AND LETS YOU CORRECT MISTAKES.**

(2) 12 points.

A solution reaction is first order, and has a rate constant at 300 K of  $20 \text{ s}^{-1}$ . The pre-exponential A factor is  $2 \times 10^5 \text{ s}^{-1}$ . Calculate the activation energy  $E$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  all at 300 K.