Examination

Thermodynamics

(NWI-MOL135)

Monday, 16th January 2023, 08:30 – 11:30
Time allowed: **three hours**.

Please hand in your answers to each question on SEPARATE sheets.

Clearly write your name and student number on each sheet.

There are 4 questions and the marks in square brackets are only indicative of the approximate weight given to each part of the question.

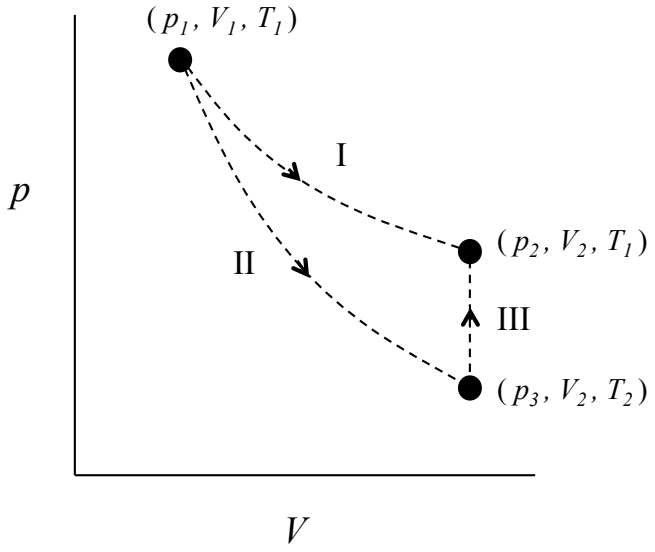
A list of constants (below) and a formula sheet (at the end) are included.

List of constants

Elementary charge	e	1.602×10^{-19} C
Faraday's constant	F	9.648×10^{4} C mol^{-1}
Boltzmann's constant	k_B	1.381×10^{-23} J K^{-1}
Planck's constant	h	6.626×10^{-34} J s
Atomic mass constant	m_u	1.661×10^{-27} kg
Avogadro's constant	N_A	6.022×10^{23} mol^{-1}
Gas constant	R	8.314 J K^{-1} mol^{-1}
Gravitational acceleration	g	9.807 m s^{-2}
Unit of energy		1 cal = 4.184 J
Standard pressure	$p^{\ominus}$	1 bar = 1×10^{5} Pa = 0.9869 atm
Unit of pressure		1 atm = 101.3 kPa

1. (a) Describe what is meant by the term *state function*. **[1]**

Consider the diagram below that shows two alternative paths for the expansion of a monoatomic perfect gas from (p_1, V_1, T_1) to (p_2, V_2, T_1). The first path consists of a reversible isothermal expansion (I); the second path involves a reversible adiabatic expansion (II), followed by reversibly heating at constant volume (III).



(b) (i) For each of the processes I, II, and III, find w_{rev}, q_{rev} and ΔU in terms of V_1, V_2, C_V, T_1, T_2, and n. **[9]**

(ii) Consider the values of w_{rev}, q_{rev} and ΔU for the two alternative paths from (p_1, V_1, T_1) to (p_2, V_2, T_1), to explain that ΔU is a state function and w_{rev} and q_{rev} are not. **[3]**

(c) One mole of a monoatomic perfect gas is expanded reversibly and adiabatically to 100 times its initial volume. Calculate the final temperature if the initial temperature is 298 K. **[4]**

(d) Given that $\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$, derive the following Maxwell relation: **[3]**

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T .$$

2. (a) Starting from the First Law of Thermodynamics and the thermodynamic definition of the entropy, show that the reversible change in entropy for a closed system at constant volume is given by **[4]**

$$T\mathrm{d}S = C_V \mathrm{d}T.$$

(b) Two quantities of water each of mass 216 g are mixed together in a vessel (at constant volume). The temperatures of the two quantities before mixing are 303 K and 333 K. The entire system is isolated from its surroundings and the vessel has a negligible heat capacity. Calculate the change in entropy after equilibrium has been established, and comment on your result in the light of the Second Law of Thermodynamics. **[5]**

$C_\mathrm{V} = 75.5$ J K^{-1} mol^{-1} for water in this temperature range and $M = 18$ g mol^{-1}.

(c) Sketch and fully label the phase diagram for H_2O. **[2]**

(d) Use the Clapeyron equation

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}},$$

to explain why (i) the solid-liquid boundary is negative for H_2O and (ii) the solid-gas boundary is always steeper than the liquid-gas boundary. **[4]**

3. Measurements performed on the following electrochemical cell

$$\mathrm{Mg(s)} \mid \mathrm{MgSO_4(aq,}\ a_1) \parallel \mathrm{CuSO_4(aq,}\ a_2) \mid \mathrm{Cu(s)}$$

yielded the values $E^\ominus_\mathrm{cell} = 2.71$ V and $\mathrm{d}E^\ominus_\mathrm{cell}/\mathrm{d}T = 7.2 \times 10^{-5}$ V K^{-1} at 298 K.

(a) Write down the half reactions and the cell reaction. **[3]**

(b) Determine $\Delta_r G^\ominus$, and the equilibrium constant for the cell reaction at 298 K. Comment on the value for the equilibrium constant. **[3]**

(c) Determine $\Delta_r S^\ominus$ and $\Delta_r H^\ominus$ for the cell reaction at 298 K. **[2]**

(d) Calculate E_cell at 298 K when the activities are respectively $a_1 = 1.0 \times 10^{-4}$ and $a_2 = 1.0 \times 10^{-2}$. **[2]**

4. Methanol is produced commercially by passing a mixture of carbon monoxide and hydrogen over a zinc oxide/copper oxide catalyst:

$$\mathrm{CO(g)} + 2\mathrm{H_2(g)} \leftrightharpoons \mathrm{CH_3OH(g)}.$$

You may assume that the gases behave as perfect gases. The table below shows the standard enthalpies and Gibbs free energies of formation of the species at 298 K.

	$\Delta_f H^{\ominus}$/kJ mol^{-1}	$\Delta_f G^{\ominus}$/kJ mol^{-1}
CO(g)	-110.5	-137.2
$\mathrm{CH_3OH(g)}$	-200.7	-162.0

(a) Calculate the equilibrium constant K_p for this reaction at 298 K. **[3]**

(b) Starting from the relationship between the equilibrium constant, K_p, and the standard Gibbs free energy, $\Delta_r G^{\ominus}$, derive the Van 't Hoff equation

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H^{\ominus}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

where $K_2 = K_p(T_2)$ and $K_1 = K_p(T_1)$, clearly stating any assumption you make.

Hint: you will need the Gibbs-Helmholtz equation: $\left(\dfrac{\partial(G/T)}{\partial T}\right)_p = -\dfrac{H}{T^2}$. **[6]**

(c) A commercial reactor is operated at a temperature of 600 K. Calculate the equilibrium constant K_p at this temperature, assuming that $\Delta_r H^{\ominus}$ is independent of temperature, and *briefly* explain how this is consistent with Le Chatelier's principle. **[5]**

(d) The gas flowing into the reactor contains two moles of $\mathrm{H_2}$ for each mole of CO. If the mole fraction of methanol in the exhaust gas from the reactor is 0.25, what is the total pressure in the reactor at 600 K? You may assume that equilibrium is established in the reactor. **[6]**

[Use $K_2 = 3.0 \times 10^{-4}$ if you did not find an answer in part (c).]

Formulae

$$pV = nRT = Nk_\mathrm{B}T$$

$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_\mathrm{B}T \qquad \text{(monatomic perfect gas)}$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \quad \text{or} \quad \Delta U = q + w$$

$$\mathrm{d}q_\mathrm{V} = C_\mathrm{V}\mathrm{d}T \quad \text{and} \quad C_\mathrm{V} = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\mathrm{d}q_\mathrm{p} = C_\mathrm{p}\mathrm{d}T \quad \text{and} \quad C_\mathrm{p} = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\mathrm{d}S = \frac{\mathrm{d}q_\mathrm{rev}}{T} \geq \frac{\mathrm{d}q}{T}$$

$$\mathrm{d}S_\mathrm{tot} = \mathrm{d}S + \mathrm{d}S_\mathrm{surr} \geq 0$$

$$S = k_\mathrm{B}\ln W$$

$$H = U + pV$$

$$A = U - TS$$

$$G = H - TS$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{p,T} = \Delta_r G^\ominus + RT\ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$\Delta_r G^\ominus = -RT\ln K_p \quad \text{with} \quad K_p = \prod_i a_i^{\nu_i}$$

$$\Delta_r G = -\nu F E$$

$$E = E^\ominus - \frac{RT}{\nu F}\ln Q$$