

NOTE:

- Write the version number of your question paper on the answer sheet.
- No clarifications or corrections will be provided during the exam. If you think there is an error/inconsistency/omission in the paper, please state your assumptions about it.

Information:  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ ,  $\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ ,  $dU = TdS - PdV$ ,  $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$ ,  $\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$ ,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

- The isomerization  $\text{trans-2-C}_4\text{H}_8(\text{g}) \rightleftharpoons \text{cis-2-C}_4\text{H}_8(\text{g})$  was performed with the following initial number of moles:  $n^0(\text{trans-2-C}_4\text{H}_8) = 2$ ,  $n^0(\text{cis-2-C}_4\text{H}_8) = 0$ , and  $n^0(\text{N}_2) = 2$ . Here nitrogen is an inert gas.
  - Calculate the equilibrium constant for this isomerization at 298.15 K. [5]
  - What is the Gibbs energy of the mixture at equilibrium, if the reaction occurs at a pressure of 1 bar? [10]
  - What is the equilibrium constant of the reaction at 600 K? [10]

The relevant thermodynamic data at 298.15 K ( $C_P$  is temperature independent) is given below:

Species	$C_P$ (J/mol K)	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)
<i>trans</i> -2-C <sub>4</sub> H <sub>8</sub> (g)	78.91	-11.17	65.95
<i>cis</i> -2-C <sub>4</sub> H <sub>8</sub> (g)	87.82	-6.99	63.06

- Decide, with a short justification, whether the following statements are true or false. Correct the false statements. [5 × 5]
  - The chemical potential of any species that can be exchanged between two phases will always be equal.
  - If a system is in equilibrium with a constant temperature reservoir and constant pressure reservoir, then that system is in equilibrium if there is at least one process that increases its Gibbs energy.
  - Only in a closed system is  $dU = dq + dw$ .
  - In a one-component system, when three phases coexist, one of the phases must be a gas, one must be a liquid, and one must be a solid.
  - The entropy of an isolated system increases when it undergoes an expansion.
- A reversible adiabatic process is an isentropic (constant entropy) process.
  - Show that the isentropic expansivity,  $\alpha_S = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_S$ , is  $-\frac{C_V \beta}{TV\alpha}$ . [10]
  - What is  $\alpha_S$  for an ideal gas? [5]
  - Consider the isentropic expansion of an ideal gas from  $(T_1, V_1)$  to  $(T_2, V_2)$ . Derive an expression for the final temperature  $T_2$  starting from the expression for  $\alpha_S$  you got in the previous part. [10]
- Ar has normal melting and boiling points of 83.80 K and 87.3 K; the triple point is at 83.806 K and 0.68 atm, and its critical temperature and pressure are 150.87 K and 48.3 atm. State whether Ar is a solid, liquid, or gas under each of the following conditions: (a) (0.9 atm, 90 K); (b) (0.7 atm, 80 K); (c) (0.8 atm, 88 K); (d) (1.2 atm, 83.5 K); (e) (0.5 atm, 84 K). [10]
  - One kilomole of an ideal gas is compressed isothermally at 400 K from 100 kPa to 1000 kPa. Calculate the entropy change of the gas, of the surroundings, and the total entropy change resulting from the process, if (a) the process is mechanically reversible; (b) the process is mechanically irreversible, requiring 20% more work than the mechanically reversible compression. [15]

1. The isomerization  $\text{trans-2-C}_4\text{H}_8(\text{g}) \rightleftharpoons \text{cis-2-C}_4\text{H}_8(\text{g})$  was performed with the following initial number of moles:  $n^0(\text{trans-2-C}_4\text{H}_8) = 2$ ,  $n^0(\text{cis-2-C}_4\text{H}_8) = 0$ , and  $n^0(\text{N}_2) = 2$ . Here nitrogen is an inert gas.

(a) Calculate the equilibrium constant for this isomerization at 298.15 K. [5]

(b) What is the Gibbs energy of the mixture at equilibrium, if the reaction occurs at a pressure of 1 bar? [10]

(c) What is the equilibrium constant of the reaction at 600 K? [10]

The relevant thermodynamic data at 298.15 K ( $C_P$  is temperature independent) is given below:

Species	$C_P$ (J/mol K)	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)
$\text{trans-2-C}_4\text{H}_8(\text{g})$	78.91	-11.17	65.95
$\text{cis-2-C}_4\text{H}_8(\text{g})$	87.82	-6.99	63.06

**Answer:**

$$\Delta_r G^\circ = -RT \ln K \quad [3]$$

$$\Delta_r G^\circ = 63060 \text{ J mol}^{-1} - 65950 \text{ J mol}^{-1} = -2890 \text{ J mol}^{-1} \quad [1]$$

$$-2890 \text{ J mol}^{-1} = -RT \ln K = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} 298.15 \text{ K} \ln K$$

$$K = 3.21 \quad [1]$$

(a)

$$K = 3.21 = \frac{\xi}{2 - \xi} \quad [3]$$

$$\xi = 1.524$$

$$G = n_t \mu_t + n_c \mu_c + n_{\text{N}_2} \mu_{\text{N}_2}, \quad [2]$$

where  $n_t$ ,  $n_c$ , and  $n_{\text{N}_2}$  are the number of moles at equilibrium of  $\text{trans-2-C}_4\text{H}_8$ ,  $\text{cis-2-C}_4\text{H}_8$ , and nitrogen respectively.

$$n_t = 2 - \xi = 0.476 \quad n_c = 1.524 \quad n_{\text{N}_2} = 2$$

$$\mu = \mu^\circ + RT \ln \frac{P}{P^\circ} \quad [2]$$

$$G = 0.476 \left( \mu_t^\circ + RT \ln \frac{0.476}{4} \right) + 1.524 \left( \mu_c^\circ + RT \ln \frac{1.524}{4} \right) + 2 \left( \mu_{\text{N}_2}^\circ + RT \ln \frac{2}{4} \right)$$

$$G = 0.476 \times (65950 + 8.314 \times 298.15 \ln 0.119) + 1.524 \times (63060 + 8.314 \times 298.15 \ln 0.381) + 2 \times (8.314 \times 298.15 \ln 0.5)$$

$$G = 28880 + 92458 - 3436 \text{ J} = 117.58 \text{ kJ} \quad [3]$$

(b)

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ(T)}{RT^2} \quad [2]$$

$$\begin{aligned} \Delta_r H^\circ(T) &= \Delta_r H^\circ(298.15) + \Delta C_p(T - 298.15) \\ \Delta_r H^\circ(298.15) &= -6.99 + 11.17 \text{kJ mol}^{-1} = 4180 \text{J mol}^{-1} \quad \Delta C_p = (87.82 - 78.91) \text{J mol}^{-1} \text{K}^{-1} \end{aligned} \quad [3]$$

$$\begin{aligned} \int_1^2 d \ln K &= \int_{T_1=298.15}^{T_2=600} \frac{1523.5 + 8.91T}{RT^2} dT \\ \ln \frac{K_2}{K_1} &= -183.2 \left( \frac{1}{600} - \frac{1}{298.15} \right) + 1.072 \ln \frac{600}{298.15} = 0.3091 + 0.7494 \end{aligned} \quad [3]$$

$$K_2 = 3.21 \times 2.882 = 9.25 \quad [3]$$

2. Decide, with a short justification, whether the following statements are true or false. Correct the false statements. [5 × 5]

- The chemical potential of any species that can be exchanged between two phases will always be equal.
- If a system is in equilibrium with a constant temperature reservoir and constant pressure reservoir, then that system is in equilibrium if there is at least one process that increases its Gibbs energy.
- Only in a closed system is  $dU = dq + dw$ .
- In a one-component system, when three phases coexist, one of the phases must be a gas, one must be a liquid, and one must be a solid.
- The entropy of an isolated system increases when it undergoes an expansion.

**Answer:** NO/WRONG JUSTIFICATION, NO CREDIT

- FALSE. The chemical potentials are equal ONLY at equilibrium.
- FALSE. The criterion for equilibrium at constant  $T$  and  $P$  is  $dG_{T,P} = 0$ , which implies that  $G$  is a global minimum at equilibrium. Hence from an equilibrium state, ALL processes would involve an increase in  $G$ .
- TRUE. This is the statement of the first law for a closed system.
- FALSE. If the substance has only one type of solid phase, the statement is true. In general, you could have a triple point involving two solid phases and a liquid phase, for example.
- TRUE.  $dS = \left( \frac{\partial S}{\partial V} \right)_U dV$  From the combined first and second law,  $dU = TdS - PdV$  or  $dS = \frac{dU}{T} + \frac{P}{T}dV$ . For an isolated system  $\left( \frac{\partial S}{\partial V} \right)_U = \frac{P}{T}$ . If the denominator of the left hand side is positive, so should the numerator because the RHS is positive.

3. A reversible adiabatic process is an isentropic (constant entropy) process.

- Show that the isentropic expansivity,  $\alpha_S = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_S$ , is  $-\frac{C_V \beta}{TV\alpha}$ . [10]
- What is  $\alpha_S$  for an ideal gas? [5]
- Consider the isentropic expansion of an ideal gas from  $(T_1, V_1)$  to  $(T_2, V_2)$ . Derive an expression for the final temperature  $T_2$  starting from the expression for  $\alpha_S$  you got in the previous part. [10]

**Answer:** (a)

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

At constant  $S$ , the LHS is zero, which implies that

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

Remember that  $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$  and  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$  - a Maxwell relation.  
Now we may write

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T &= -1 \\ \left(\frac{\partial T}{\partial V}\right)_P &= \frac{1}{V\alpha} \quad \left(\frac{\partial V}{\partial P}\right)_T = -V\beta \end{aligned}$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$$

$$\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S = \alpha_S = -\frac{1}{V} \frac{C_V}{T} \frac{\beta}{\alpha}$$

(b) For an ideal gas  $V = \frac{RT}{P}$ . Thus

$$\alpha = \frac{1}{V} \frac{R}{P} = \frac{1}{T}$$

$$\beta = -\frac{1}{V} \frac{-RT}{P^2} = \frac{1}{P}$$

$$\alpha_S = -\frac{C_V}{TV} \frac{T}{P} = -\frac{C_V}{RT}$$

(c) For an ideal gas, from the earlier part we know

$$\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{RT}$$

$$\frac{dV}{V} = -\frac{C_V}{R} \frac{dT}{T}$$

$$\int_{V_1}^{V_2} \frac{dV}{V} = -\frac{C_V}{R} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\frac{R}{C_V} \ln \frac{V_1}{V_2} = \ln \frac{T_2}{T_1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}}$$

4. (a) Ar has normal melting and boiling points of 83.80 K and 87.3 K; the triple point is at 83.806 K and 0.68 atm, and its critical temperature and pressure are 150.87 K and 48.3 atm. State whether Ar is a solid, liquid, or gas under each of the following conditions: (a) (0.9 atm, 90 K); (b) (0.7 atm, 80 K); (c) (0.8 atm, 88 K); (d) (1.2 atm, 83.5 K); (e) (0.5 atm, 84 K). [10]
- (b) One kilomole of an ideal gas is compressed isothermally at 400 K from 100 kPa to 1000 kPa. Calculate the entropy change of the gas, of the surroundings, and the total entropy change resulting from the process, if (a) the process is mechanically reversible; (b) the process is mechanically irreversible, requiring 20% more work than the mechanically reversible compression. [15]

**Answer:**  $5 \times 2$

- (a) (0.9 atm, 90 K) - below atmospheric pressure, above the normal boiling point  $\Rightarrow$  vapour  
 (b) (0.7 atm, 80 K) - slightly above the triple point pressure and below the triple point temperature  $\Rightarrow$  solid  
 (c) (0.8 atm, 88 K) - below atmospheric pressure, above the normal boiling point  $\Rightarrow$  vapour  
 (d) (1.2 atm, 83.5 K) - above atmospheric pressure, below the melting point  $\Rightarrow$  solid  
 (e) (0.5 atm, 84 K) - well below atmospheric pressure, below the melting point  $\Rightarrow$  vapour.

$$w = -(1 \text{ kmol})(8.314 \text{ kJ kmol}^{-1} \text{ K}^{-1})(400 \text{ K}) \ln \frac{100}{1000} = -7657 \text{ kJ} \quad [2]$$

$$\Delta U = 0 = q_{\text{rev}} + w_{\text{rev}} \Rightarrow q_{\text{rev}} = -w_{\text{rev}} = 7657 \text{ kJ} \quad [2]$$

$$\Delta_{\text{sys}}S = \frac{q_{\text{rev}}}{T} = \frac{-7657}{400} \text{ kJ K}^{-1} = -19.144 \text{ kJ K}^{-1} \quad [1]$$

$$\Delta_{\text{surr}}S = -\Delta_{\text{sys}}S \quad [1]$$

$$\Delta_{\text{tot}}S = 0 \quad [1]$$

(b)

$$w = 1.20 * w_{\text{rev}} = 9188 \text{ kJ} = -q_{\text{sys}} \quad [2+2]$$

$$\Delta_{\text{sys}}S = -19.144 \text{ kJ K}^{-1}$$

$$\Delta_{\text{surr}}S = \frac{-q_{\text{sys}}}{T} = \frac{9188}{400} \text{ kJ K}^{-1} = 22.97 \text{ kJ K}^{-1} \quad [2]$$

$$\Delta_{\text{tot}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S = -19.144 + 22.97 \text{ kJ K}^{-1} = 3.83 \text{ kJ K}^{-1} \quad [1]$$