(2025 / 2026)

Ex.1 4/4

① $PV_m = RT\left(1 + \frac{B(T)}{V_m}\right) \rightarrow \frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m}$

$B(T) = \frac{1}{V_m}\left(\frac{PV_m}{RT} - 1\right)$ (0,5)

$= \frac{1}{24}\left(\frac{1,5 \times 24}{0,082 \times 300} - 1\right)$ $B(T) = 11,12\ l/mol$ (0,5)

② $P = \frac{RT}{V_m}\left(1 + \frac{B(T)}{V_m}\right)$ (0,5), $B(T) = 11,12\ l/mol$, $V_m = 10\ l$

$P = 5,19$ atm (0,5)

③ Compressibility Factor $Z = \frac{(PV)_{real}}{(PV)_{ideal}} = \frac{(PV_m)_{real}}{RT} = 1 + \frac{B(T)}{V_m}$ (0,5)

$Z = 1 + \frac{11,12}{10} = 1,46$ (0,25)

$Z > 1 \Rightarrow$ Repulsive forces dominate (0,25)

④ $P = \frac{RT}{V_m}\left(1 + \frac{B(T)}{V_m}\right)$ $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V_m}\left(1 + \frac{B(T)}{V_m}\right)$ (0,5)

$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{P}\left(\frac{R}{V_m}\left(1 + \frac{B(T)}{V_m}\right)\right) = \frac{V_m}{RT}\left(\frac{1}{1 + \frac{B(T)}{V_m}}\right)\left(\frac{R}{V_m}\left(1 + \frac{B(T)}{V_m}\right)\right)$

$= \frac{1}{T} = \frac{1}{300} = 0,0033$ (0,5)

Ex.2 8/8

1) type of transformation

A → B isothermal. (0,5)

B → C isobaric (0,5)

C → D adiabatic (0,5)

2) Calcul of thermodynamic parameters:

from law of (perfect) ideal gaz:

$P_B V_B = nRT_B \Rightarrow V_B = \frac{nRT_B}{P_B} = \frac{1 \times 8,31 \times 275}{2\,10^5} = 11,42\,\ell = 0,01142\,m^3$ (0,25) (0,25)

$P_C V_C = nRT_C \Rightarrow V_C = \frac{nRT_C}{P_C} = \frac{1 \times 8,31 \times 335}{2\,10^5} = 0,01391\,m^3 = 13,91\,\ell$ (0,25) (0,25)

3) Calculate thermodynamic functions:

($\Delta T = 0$) $A \rightarrow B$ $\Delta U = Q + W$ (0,25) $\rightarrow \Delta U = nC_v \Delta T$ (0,25) $\rightarrow \Delta T = 0 \rightarrow \Delta U_{A\to B} = 0$ (0,25)

So $Q_{AB} + W_{AB} = 0 \rightarrow Q_{AB} = -W_{AB}$ (0,25)

(0,25) $W_{AB} = -\int_{V_A}^{V_B} P\,dV = -nRT_B \ln\left(\frac{V_B}{V_A}\right) = -1 \cdot 8,31 \cdot 275 \ln \frac{11,42}{2}$ (0,25)

$W_{AB} = -3,98\,kJ$ (0,25) $Q_{AB} = -W = 3,98\,kJ$ (0,25)

$\Delta S_{A\to B} = \frac{Q}{T} = \frac{3,98}{275} = 14,47\,kJ/K$ (0,25) (0,25)

($\Delta P = 0$) $B \rightarrow C$ $Q_{BC} = nC_p \Delta T = 1 \times 20,63 (335 - 275)$ (0,25) / $C_p = ?$ → $C_p - C_v = R$ → $C_p = 20,63\,J\,K^{-1}\,mol^{-1}$ (0,25)

$= 1,237\,kJ$ (0,25)

$W_{BC} = -P_C \int_{V_B}^{V_C} dV = -P_C (V_C - V_B) = -2\,10^5 (13,91 - 11,42)\,10^{-3} = -498\,J$ (0,25) (0,25)

$\Delta U_{BC} = Q_{BC} + W_{BC}$ or $\Delta U_{BC} = nC_v \Delta T$

$= 1,237 - 498 = 739\,J$ (0,25)

$\Delta S_{BC} = \int_{T_B}^{T_C} nC_p \frac{dT}{T} = nC_p \ln \frac{T_C}{T_B} = 1 \times 20,63 \ln \frac{335}{275} = 4,07\,J/K$ (0,25) (0,25)

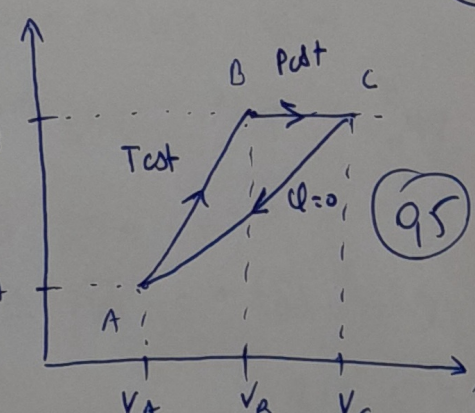
$Q=0$ $C \rightarrow A$ $Q_{C-A} = 0$ and $\Delta S_{C-A} = 0$ (0,25)

(0,25) $\Delta U = W_{CA} = nC_v \Delta T = nC_v (T_A - T_C)$

$= 1 \cdot 12,32 (275 - 335)$

$= +739,2\,J$ (0,25)

4) Clapeyron diagram



(0,5) (2)

Ex03

(1) at $T = 298K$: $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(\ell)$

$a = 1 \quad b = 5 \quad c = 3 \quad d = 4$ (0,5)

(2) $\Delta H^\circ_R = \Delta U^\circ_R + (\Delta n)_{gas} RT$ (0,5) with $\Delta n = \Sigma n^\circ_{pro} - \Sigma n^\circ_{reac} = 3 - (1+5) = -3$ (0,5)

$\Delta H^\circ_R = -2052 \cdot 10^3 - 3 \cdot 8,31 \cdot 298 = -2059429,14\ J$ (0,25)

(0,25) $\Delta H^\circ_R < 0 \Rightarrow$ exothermic reaction (0,25)

(3) ΔS°_R calculation : $\Delta S^\circ_R = \Sigma_i S^\circ(prod) - \Sigma_i S^\circ(react)$ (0,5)

$= 4S^\circ(H_2O_\ell) + 3S^\circ(CO_2,g) - S^\circ(C_3H_8,g) - 5S^\circ(O_2,g)$

$= -375,03\ J/K$ (0,5)

(4) $\Delta G^\circ_R = \Delta H^\circ_R - T\Delta S^\circ_R$ at 298 K (0,5)

$= -2059429,14 - 298(-375,03) = -1947670,2\ J$ (0,5)

(0,25) $\Delta G^\circ_R < 0 \Rightarrow$ yes, the reaction is spontaneous in direction → 1 (0,25)

(5) $\Delta H^\circ_R(T_2) = \Delta H^\circ_R(T_1) + \int_{T_1}^{T_2} \Delta C_p\, dT$ (0,5) $\quad T_1 = 298K$. $\quad T_2 = 333K$.

$= -2059429,14 + 192(333 - 298)$ $\quad \Delta C_p = \Sigma n_i C_{p\,pror} - \Sigma n_i C_{p\,reac}$ (0,25)

$= -2052704,59\ J$ (0,5) $\quad = 3C_p(CO_2,g) + 4C_p(H_2O,\ell) - C_p(C_3H_8,g) - 5C_p(O_2,g)$

$= 192,13\ J/K\,mol$ (0,25)

(6) $\Delta G^\circ_R = -RT \ln K_p \Rightarrow K_p = e^{-\Delta G^\circ_R/RT}$ (0,25)

$K_p = \exp\left(\frac{1947670,2}{8,31 \cdot 298}\right) = 3,73 \cdot 10^{341}$ (0,25)

(0,25) $K_p = K_c(RT)^{\Delta n}$ $\quad \Delta n = -3$ $\quad K_p = K_c(RT)^{-3} \Rightarrow K_c = \frac{K_p}{(RT)^{-3}} = \frac{3,73\,10^{341}}{(8,31 \cdot 298)^{-3}}$

$K_c = 5,66\,10^{351}$ (0,25)

(7) the variance (0,25) $v = n + 2 - r + p$ $\quad n=4 \;/\; r=1 \;/\; p=2$

(0,25) $v = 4 + 2 - 1 - 2 = 3$.

(8) A) the equilibrium will shift to direction 2 if we decrease P_{O_2} (0,25)

2 if we increase T (0,25)

B) " " " " " "