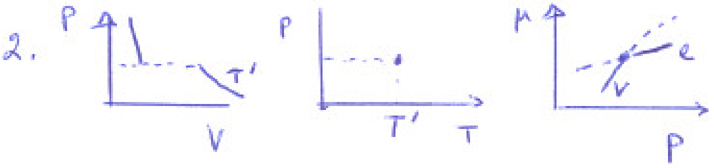
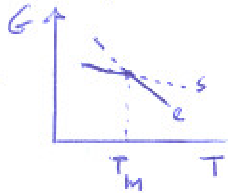
Θέματα Θερμοδυναμικής (13.1.12) 1

I. ισχύει : πρώτο, τρίτο, πέμπτο.

1. $dU = dw_{αδ.}$, για ιδαν. αέρ. $dU = C_v dT$ ή $w = C_v (T_2 - T_1) = \frac{C_v}{R}(P_2V_2 - P_1V_1)$

και $C_v/R = 1/(\gamma - 1)$ γιατί $\gamma = C_p/C_v$ και $C_p - C_v = R$

2. 

3. 

4. Γιατί $S_{solid} > S_{eq.}$!

5. Γιατί $\Delta H_{διαλ} < 0$

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II $\Delta U_{ολ} = 0$ (απομον. σύστημα), $\Delta V = 0 \Rightarrow q = (q_e + q_s) = 0$ $q_s = n_s \Delta H_m + n_s C (T_f - T_m)$

$\left\{ T_s\right.$: τελ. θερμ. n_s, n_e mol πάγου, νερού $\left.\right\}$ $q_e = n_e C (T_f - T_e) \Rightarrow$

$T_m = 273.15\,K$, $T_e = 363.15\,K$

$T_f = x_s T_m + x_e T_e - x_s \frac{\Delta H_m}{C}$ όπου $x_s = \frac{n_s}{n_s + n_e}$ και $x_e = 1 - x_s$; $x_s = 0.33$

$T_f = 306.4\,K \simeq 33.3\,°C$ $\Delta S = n_s \frac{\Delta H_m}{T_m} + \int_s \frac{dq}{T} + \int_e \frac{dq}{T} = 12.21 + C n_s \ln\frac{T_f}{T_m} + C n_e \ln\frac{T_f}{T_e} = 2.9 \frac{J}{K\,mol} > 0$

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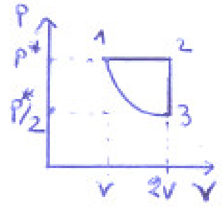
III 

$1 \to 2$ $w_{1\to2} = -P^*(2V - V) = -P^*V$, $q_{1\to2} = q_p = C_p(T_2 - T_1) = \frac{5}{2}P^*V > 0$

$\Delta S_{1\to2} = C_p \ln\frac{T_2}{T_1} = \frac{5}{2} R \ln\frac{V_2}{V_1} = \frac{5}{2} R \ln 2$

$2 \to 3$ $w_{2\to3} = 0$, $q_{2\to3} = q_v = C_v(T_3 - T_2) = \frac{C_v}{R}\left(\frac{P^*}{2} 2V - P^* 2V\right) = -\frac{3}{2} P^*V < 0$

$\Delta S_{2\to3} = C_v \ln\frac{T_3}{T_2} = \frac{3}{2} R \ln\frac{1}{2} = -\frac{3}{2} R \ln 2$

$3 \to 1$ $q_{3\to1} = w_{3\to1}$

$w_{3\to1} = -\int P dV = -RT_3 \ln\frac{1}{2} = RT_3 \ln 2 = P^*V \ln 2$

$q_{3\to1} = -P^*V \ln 2 < 0$, $\Delta S_{3\to1} = -(\Delta S_{1\to2} + \Delta S_{2\to3}) = -R\ln 2$

$\varepsilon = -\frac{w}{q_1}$, $w = -P^*V + P^*V \ln 2$ και απορροφούμενη $q_1 = \frac{5}{2} P^*V$

και $\varepsilon = P^*V(1 - \ln 2)/(\frac{5}{2}P^*V) = \frac{2}{5}(1 - \ln 2) \simeq 12.\%$

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IV : πρώτο σκέλος θεωρία. $H_2O(l) \rightleftharpoons H_2O(v)$ σε $T = 298\,K$: $\mu^v = \mu^l$

$\mu^v = \mu^* + RT \ln\frac{P^o}{P^*} = \mu^l(T) \Rightarrow \mu^*(T) - \mu^l(T) = \Delta G^o(T = 298K) \Rightarrow$

$-RT \ln\frac{P^o}{P^*} = \Delta G^o = -RT \ln K_{eq}$ (από το πρώτο σκέλος) $\Rightarrow$

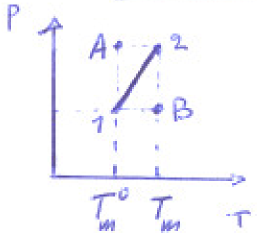
$K_{eq} = P^o/P^* = 0.03$

Θέματα Θερμοδυναμικής (13.1.12) ②

V. $\left(\frac{dP}{dT}\right)_{s\to l} = \frac{\Delta H_m}{T\,\Delta V_{s\to l}}$ $\Delta V = V_l - V_s$; $V_l = 89.65\ cm^3/mole$, $V_s = 87.65\ cm^3/mole$ $\Rightarrow \Delta V = 2\ cm^3/mole$

$$\Delta P = \frac{\Delta H_m}{\Delta V}\ln\frac{T_m}{T_m^o} \Rightarrow \ln\frac{T_m}{T_m^o} = \frac{\Delta P\,\Delta V}{\Delta H_m} = \frac{999\ Atm\cdot 2\ cm^3}{10\cdot 10^3\ J \times 9.87\ \frac{Atm\ cm^3}{J}} = 0.02 \Rightarrow$$

$\underline{T_m = 284.7\ K}$ (1000 Atm) από $T_m^o = 279\ K$ (1 Atm).



Συνύπαρξη $l \leftrightarrow s$ στην 1−2 ή $\mu_l(1)=\mu_s(1)$ και $\mu_l(2)=\mu_s(2)$

A: $\Delta G_{s\to l}(T_m^o, P) = \mu_l(A) - \mu_s(A) = \mu_l(1) + V_l\,\Delta P - (\mu_s(1) + V_s\,\Delta P)$

$\Delta G_{s\to l} = \Delta V\,\Delta P \simeq 0.2\ kJ > 0$ solid C_6H_6 μόνο

B: $\Delta G_{s\to l}(T_m, P^*) = \mu_l(B) - \mu_s(B) = \mu_l(2) - V_l\,\Delta P - (\mu_s(2) - V_s\,\Delta P)$

$(-\Delta P = P^* - P)$

$\Delta G_{s\to l} = (V_s - V_l)\,\Delta P = -\Delta V\,\Delta P \simeq -0.2\ kJ < 0$ liquid C_6H_6 μόνο

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VI A/B, x_B σε $T_2 = 363K$ $P = P^*$ (διότι βράζει σε εξωτερική πίεση P^*)

$$P = P_A(T_2) + P_B(T_2) = x_A P_A^o(T_2) + x_B P_B^o(T_2) = P_A^o(T_2) + x_B\left[P_B^o(T) - P_A^o(T)\right] \quad (1)$$

P_A καθαρό υγρό: $P_A^o(T_2) = P^* \exp\left\{-\frac{\Delta H_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_A^o}\right)\right\}$ 2a (εξίσωση Clausius/Clapeyron)

$P_B^o(T_2) = P^* \exp\left\{-\frac{\Delta H_B}{R}\left(\frac{1}{T_2} - \frac{1}{T_B^o}\right)\right\}$ 2b

Υπολογισμός των ΔH_A, ΔH_B (ενέργεια εξάτμισης): οι εξισώσεις 2a,b αλλά με T_1 αντί T_2 και $P_A^o(T_1)$, $P_B^o(T_1)$ που δίδονται με $T_1 = 343K$

$\frac{\Delta H_A}{R} = 3977\ K$ και $\frac{\Delta H_B}{R} = 4394\ K$. Αντικατάσταση των στις 2a,b

$\Rightarrow P_A^o(T_2) = 1.363\,P^*$ και $P_B^o(T_2) = 0.548\,P^*$ και από την (1)

$\Rightarrow \underline{x_B = 0.445}$. Από την αντίστοιχη (1'): $P = \frac{P_A^o P_B^o}{P_B^o - (P_B^o - P_A^o)\,y_B} \Rightarrow$

$\Rightarrow \underline{y_B = 0.244}$