Πανεπιστήμιο Κύπρου
Τμήμα Χημείας

ΛΥΣΕΙΣ ΤΕΛΙΚΗ ΕΞΕΤΑΣΗ ΦΥΣΙΚΟΧΗΜΕΙΑ Ι, ΧΗΜ 141

Μάθημα 2^{ου} έτους, Χειμερινό Εξάμηνο 2008

Διδάσκων: Δρ. Κωνσταντίνος Ζεϊναλιπούρ

1) $\Delta_{rxn}\bar{S}_{298} = 2\bar{S}_{298}(H_2O,g) - 2S_{298}(H_2,g) - \bar{S}_{298}(O_2,g)$

$= (2 \times 188.72 - 2 \times 130.57 - 205.03)\left(\frac{J}{K\,mol}\right)$

$= \underline{\underline{-88.73\ J/K\,mol}}$

$$\Delta_{rxn}\bar{S}_{400} = \Delta_{rxn}\bar{S}_{298} + \int_{298K}^{400K} \frac{\Delta C_p}{T}\,dT$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p}{T}\,dT \Rightarrow S(T_f) - S(T_i) = \int_{T_i}^{T_f} \frac{C_p\,dT}{T}$$

$$\Rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_p\,dT}{T} \Rightarrow \Delta S = \int_{T_i}^{T_f} \left(a + bT + \frac{c}{T^2}\right)\frac{dT}{T}$$

$$\Rightarrow \Delta S = a\int_{T_i}^{T_f} \frac{dT}{T} + b\int_{T_i}^{T_f} dT + c\int_{T_i}^{T_f} \frac{dT}{T^3}$$

$$\Rightarrow \Delta S = a \ln\left(\frac{T_f}{T_i}\right) + b(T_f - T_i) - \frac{c}{2}\left(\frac{1}{T_f^2} - \frac{1}{T_i^2}\right)$$

$$\Delta\bar{S}_{298\to400}(H_2) = 27.28\left(\frac{J}{K\,mol}\right) \cdot \ln\left(\frac{400}{298}\right) + 3.26\times10^{-3}\left(\frac{J}{K^2\,mol}\right) \cdot$$

$$(400-298)(K) - \frac{0.5\times10^5}{2}\left(\frac{J\,K}{mol}\right)\left(\frac{1}{400^2} - \frac{1}{298^2}\right)\left(\frac{1}{K^2}\right)$$

$$\Delta\bar{S}_{298\to400}(H_2) = 8.03\left(\frac{J}{K\,mol}\right) + 0.33\left(\frac{J}{K\,mol}\right) + 0.13\left(\frac{J}{K\,mol}\right)$$

$$= \underline{\underline{8.49\,(J/K\,mol)}}$$

$$\Delta\bar{S}_{298\to400}(O_2) = 29.96 \cdot \ln\left(\frac{400}{298}\right) + 4.18\times10^{-3}(400-298) + \frac{1.67\times10^{5}}{2}\left(\frac{1}{400^2} - \frac{1}{298^2}\right)$$

$$\Delta\bar{S}_{298\to400}(O_2) = 8.819 + 0.426 - 0.418 \Rightarrow \underline{\Delta\bar{S}_{298\to400}(O_2) = 8.83\left(\frac{J}{K\,mol}\right)}$$

$$\Delta\bar{S}_{298\to400}(H_2O) = 75.48\left(\frac{J}{K\,mol}\right)\ln\left(\frac{400}{298}\right) \Rightarrow \underline{\Delta\bar{S}_{298\to400}(H_2O) = 22.22\left(\frac{J}{K\,mol}\right)}$$

$$\begin{tikzcd}
T=298K & 2H_2(g) & + & O_2(g) \arrow[rr, "\Delta_r S_{298}"] & & 2H_2O(g) \arrow[d, "2\Delta\bar{S}_{298\to400}(H_2O)"] \\
T=400K & 2H_2(g) \arrow[u, "-2\Delta\bar{S}_{298\to400}(H_2)"'] & + & O_2(g) \arrow[u, "-\Delta\bar{S}_{298\to400}(O_2)"'] \arrow[rr, "\Delta_r S_{400}"] & & 2H_2O(g)
\end{tikzcd}$$

Από τον νόμο του Hess:

$$\Delta_r\bar{S}_{400} = \Delta_r\bar{S}_{298} - 2\Delta\bar{S}(H_2) - \Delta\bar{S}(O_2) + 2\,\Delta\bar{S}(H_2O)$$

$$(-88.73 - 2\times8.49 - 8.83 + 2\times22.22)\left(\frac{J}{K\,mol}\right)$$

$$\underline{\underline{\Delta_r\bar{S}_{400} = -70.1 \ J/K\,mol}}$$

2) a)

$$V = \frac{1}{4\pi\varepsilon_0}\left\{ -\frac{q_1 \cdot 2 \cdot q_2}{r+\ell} + \frac{q_1 \cdot 2 \cdot q_2}{r+2\ell} + \frac{2q_1 \cdot 2q_2}{r} - \frac{2q_1 \cdot 2q_2}{r+\ell} - \frac{q_1 \cdot 2q_2}{r-\ell} + \frac{q_1 \cdot 2 \cdot q_2}{r} \right\}$$

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0}\left\{ -\frac{2}{r+\ell} + \frac{2}{r+2\ell} + \frac{4}{r} - \frac{4}{r+\ell} - \frac{2}{r-\ell} + \frac{2}{r} \right\}$$

θέωντας $\ell = x \cdot r$

$$V = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0}\left\{ -\frac{2}{r+xr} + \frac{2}{r+2xr} + \frac{4}{r} - \frac{4}{r+xr} - \frac{2}{r-xr} + \frac{2}{r} \right\}$$

$$V = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0 \cdot r}\left\{ \frac{-2}{1+x} + \frac{2}{1+2x} + 4 - \frac{4}{1+x} - \frac{2}{1-x} + 2 \right\}$$

$$V = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0 \cdot r}\left\{ 6 - \frac{6}{1+x} + \frac{2}{1+2x} - \frac{2}{1-x} \right\}$$

$$V = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0 \cdot r}\left\{ 6 - 6(1-x+x^2-x^3) + 2(1-2x+4x^2-8x^3) - 2(1+x+x^2+x^3) \right\}$$

$$V = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0 r}\left\{ 6 - 6 + 6x - 6x^2 + 6x^3 + 2 - 4x + 8x^2 - 16x^3 - 2 - 2x - 2x^2 - 2x^3 \right\}$$

$$V = \frac{q_1 \cdot q_2}{4\pi\varepsilon_0 r}\left\{ -12x^3 \right\}$$

$$V = -\frac{3q_1 \cdot q_2 x^3}{\pi\varepsilon_0 \cdot r}$$

Αντικαθιστούμε την σχέση $x = \frac{\ell}{r}$

$$\Rightarrow V = \frac{-3q_1 q_2}{\pi\varepsilon_0 r}\frac{\ell^3}{r^3} \Rightarrow V = \frac{-3q_1 q_2 \ell^3}{\pi\varepsilon_0 r^4}$$

β) Αλληλεπίδραση τετραπόλου–διπόλου. $V<0$ συνεπώς η αλληλεπίδραση είναι ελκτικής φύσεως.

3) Βήμα $1 \to 2$: Ισοθερμοκρασιακή διεργασία

$$W_{12}' = +\int_{V_1}^{V_2} P\,dV = +\int_{V_1}^{V_2} \frac{nRT}{V}\,dV \Rightarrow W_{12}' = +nRT\ln\left(\frac{V_2}{V_1}\right)$$

όμως δεν γνωρίζουμε την θερμοκρασία στο σημείο 1 του ενδεικτικού διαγράμματος. Για να την υπολογίσουμε θα χρησιμοποιήσουμε την σχέση $P \cdot V^{\gamma} = \text{σταθερά}$ που ισχύει για το αδιαβατικό βήμα $3 \to 1$.

$$\Rightarrow P_3 \cdot V_3^{\gamma} = P_1 \cdot V_1^{\gamma} \qquad \gamma = \frac{5}{3} \Rightarrow$$

$$P_3 \cdot V_3^{5/3} = P_1 \cdot V_1^{5/3} \Rightarrow P_1 = 100\,kPa\left(\frac{20}{2}\right)^{5/3}$$

$$\Rightarrow P_1 = 4641.58\ kPa$$

Ιδανικό αέριο $P_1 = \frac{nRT_1}{V_1} \Rightarrow T_1 = \frac{P_1 \cdot V_1}{nR}$

$$\Rightarrow T_1 = \frac{4641.58\,(kPa) \cdot 2\,(\ell) \qquad (1\,atm)}{\left(\frac{0.03\,Kg}{0.02802\,Kg/mol}\right) \cdot 0.0821\left(\frac{\ell \cdot atm}{K\,mol}\right) \quad 101.325\,(kPa)}$$

$$\Rightarrow T_1 = \underline{\underline{1042\ K}}$$

$$W'_{12} = + \frac{0.03\,Kg}{0.02802\left(\frac{Kg}{mol}\right)} \cdot 8.314\left(\frac{J}{Kmol}\right) \cdot 1042(K)\,\ln\left(\frac{20}{2}\right)$$

$$W'_{12} = \underline{\underline{+21357\ J}}$$

Το έργο του βήματος $2 \to 3$: $W'_{23} = 0$ για $\Delta V = 0$

Το έργο του βήματος $3 \to 1$

$$W'_{31} = -\int_{V_3}^{V_1} P\,dV \qquad P = ?$$

$$P \cdot V^{\gamma} = P_3 \cdot V_3^{\gamma} \Rightarrow P = \frac{P_3 \cdot V_3^{\gamma}}{V^{\gamma}}$$

$$P = \frac{100\,KPa\,(20L)^{5/3}}{V^{5/3}} \cdot \frac{1 atm}{101.325\ KPa} \Rightarrow P = \frac{145.43\ atm \cdot \ell^{5/3}}{V^{5/3}}$$

$$W'_{31} = -\int_{V_3}^{V_1} \frac{145.43\ atm \cdot \ell^{5/3}}{V^{5/3}} \cdot dV = -145.43\ atm\,\ell^{5/3} \Big|_{V_3}^{V_1} \left(-\frac{3}{2}\right) V^{-\frac{2}{3}}$$

$$\Rightarrow W'_{31} = -218.15\,(atm \cdot \ell^{5/3})(0.629 - 0.136)(\ell^{-2/3})$$

$$\Rightarrow W'_{31} = -107.55\,(atm \cdot \ell)\,\frac{101325\left(\frac{N}{m^2}\right)}{1 atm} \cdot \frac{10^{-3}\,m^3}{1\,\ell}$$

$$\Rightarrow W'_{31} = \underline{\underline{-10897\ J}}$$

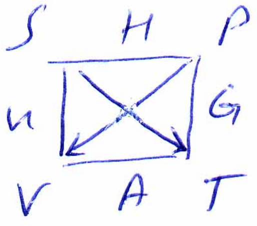
Το συνολικό έργο

$$W'_{tot} = W'_{12} + W'_{23} + W'_{31} = (+21357 + 0 - 10897)\ J$$

$$\Rightarrow W'_{tot} = \underline{\underline{+10460\ J}}$$

β) Η εσωτερική ενέργεια είναι μια καταστατική συνάρτηση οπότε $\oint dU = 0 \Rightarrow \underline{\underline{\Delta U_{tot} = 0}}$

4) a)



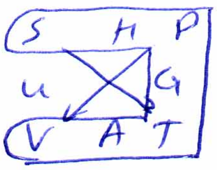
$$dH = TdS + VdP$$

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}(TdS)\right]_T + \left[\frac{\partial}{\partial P}(VdP)\right]_T$$

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\cancel{\left(\frac{\partial P}{\partial P}\right)_T}^{=1}$$

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\underbrace{\left(\frac{\partial S}{\partial P}\right)_T}_{?} + V \quad (1)$$

Με χρήση των εξισώσεων Maxwell πάλι από το "SHP UG VAT"



$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

$$(1) \,\&\, (2) \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

πολλαπλασιάζοντας και διαιρώντας με V

$$\left(\frac{\partial H}{\partial P}\right)_T = -\underbrace{\frac{T\cdot V}{V}\left(\frac{\partial V}{\partial T}\right)_P}_{\alpha} + V \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = V - \alpha V T$$

β) $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Ιδ. αέριο $V = \frac{nRT}{P}$

$$\Rightarrow \alpha = \frac{1}{V}\left[\frac{\partial\left(\frac{nRT}{P}\right)}{\partial T}\right]_P = \frac{nR}{V\cdot P} = \frac{1}{T}$$

έτσι $\left(\frac{\partial H}{\partial P}\right)_T = V - \alpha V T = \cancel{V} - \frac{1}{\cancel{T}}\cancel{V}\cancel{T} \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = 0$