Exam thermo 13/01/21

1) a) –
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b) no
yes
yes
no
yes

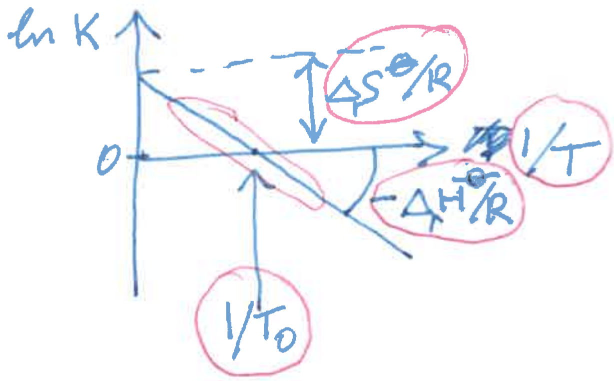
c) S entropy
Q^{rev} heat for a reversible alternative path (process)
T temperature
Q heat of the process
d infinitesimal small change

$dS = \frac{dQ^{rev}}{T}$: definition of entropy

$dQ^{rev} \geq dQ$: Clausius inequality
gives the maximal heat involved for an reversible alternative process

d) endo $\Rightarrow \Delta_r H^\ominus \underset{\uparrow}{=} Q^\ominus > 0$
$dp = 0$

$\Delta_r S^\ominus > 0$



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2] a] $q = \sum_i \exp[-\beta \varepsilon_i]$ $\qquad \beta = \frac{1}{kT}$

set $\varepsilon_0 = 0 \Rightarrow \left.\begin{array}{l} \varepsilon_1 = \mu_B H \\ H = 1\,T \end{array}\right\} \Rightarrow \left.\begin{array}{l} \varepsilon_1 = 9{,}27 \cdot 10^{-24}\,J/T \cdot 10\,T \\ \varepsilon_1 = 9{,}27 \cdot 10^{-23}\,J \end{array}\right\} \Rightarrow$

$\beta = \frac{1}{kT} = \frac{1}{1{,}38 \cdot 10^{-23} \cdot 300} = 2{,}415 \cdot 10^{20}$

$\Rightarrow \beta \mu_B H = 2{,}415 \cdot 10^{20} \cdot 9{,}27 \cdot 10^{-23} = 0{,}0224$

$q = \exp[-\beta \cdot 0] + \exp[-\beta \mu_B H]$

$\Rightarrow \underline{\underline{q = 1 + \exp[-\beta \mu_B H]}}$

b] $\frac{n_1}{N} = \frac{\exp[-\beta \varepsilon_1]}{q} = \frac{\exp[-\beta \mu_B H]}{1 + \exp[-\beta \mu_B H]} \Bigg\} \Rightarrow$

$\exp[-\beta \mu_B H] = \exp[-0{,}0224] = 0{,}978$

$\Rightarrow \underline{\underline{\frac{n_1}{N}}} = \frac{0{,}978}{1 + 0{,}978} = \underline{\underline{0{,}494}}$ $\qquad \left(\Rightarrow \frac{n_0}{N} = 0{,}506\right)$

c] $\langle u \rangle = N \sum_i \varepsilon_i \frac{n_i}{N}$

$\Rightarrow$ per electron $\langle u \rangle = \sum_i \varepsilon_i \frac{n_i}{N}$

$\Rightarrow \langle u \rangle = 0 \cdot \frac{n_0}{N} + \varepsilon_1 \frac{n_1}{N} = \varepsilon_1 \frac{n_1}{N}$

$\underline{\langle u \rangle} = 9{,}27 \cdot 10^{-23} \cdot 0{,}494 = \underline{\underline{4{,}58 \cdot 10^{-23}\,J}}$

or $-5{,}3 \cdot 10^{-25}\,J$ on original scale

d] entropy per electron

$s = \frac{S}{N} = -k \sum_i p_i \ln p_i = -k \sum_i \frac{n_i}{N} \ln \frac{n_i}{N}$

$\Rightarrow s = -1{,}38 \cdot 10^{-23} [0{,}506 \ln 0{,}506 + 0{,}494 \ln 0{,}494]$

$= -1{,}38 \cdot 10^{-2} \cdot (-0{,}6931)$

$= 9{,}56 \cdot 10^{-24}\,J/K$

$\Rightarrow \underline{\underline{s = 9{,}56 \cdot 10^{-24}\,J/K}}$

$\Rightarrow S_m = 9{,}56 \cdot 10^{-24} \cdot 6{,}022 \cdot 10^{23} = \underline{\underline{5{,}76\,J/molK}}$

Uitwerking tentamen thermo 13/01/21

3 a) adiabatisch $\Rightarrow Q^{omg} = 0$, $W = 0$ $\Rightarrow Q^{eth} = -Q^{H_2O}$

$$\Rightarrow \int dQ^{eth} = -\int dQ^{H_2O} \Rightarrow C_p^{eth}\Delta T = C_p^{H_2O}\Delta T$$

$$\Rightarrow 0{,}57\, cal/gK \cdot 1000g\,(T_2 - 75{,}0) = -1{,}00\cdot 1000\,(T_2 - 25{,}0)$$

$$\Rightarrow 0{,}57 \cdot 75{,}0 + 25{,}0$$

$$\Rightarrow T_2(0{,}57 + 1{,}00) = 0{,}57 \cdot 75{,}0 + 25{,}0$$

$$\Rightarrow T_2 = \frac{67{,}8}{1{,}57} = 43{,}2\,°C = 316\,K$$

alternatief met „hefboom": $T_2 = \dfrac{C_{p_1} T_{0_1} + C_{p_2} T_{0_2}}{C_{p_1} + C_{p_2}}$

b) i) warmte uitwisselen zonder te mengen

ii) vervolgens mengen bij T_2

ad i) $\Delta S_{H_2O} = \int \frac{dQ}{T} = C_p^{H_2O} \int \frac{dT}{T} = 1{,}00 \cdot 10^3 \ln \frac{316}{298{,}2} = 58{,}0\, cal/K = 244\, J/K$

$\Delta S_{eth.} = 0{,}57 \cdot 10^3 \ln \frac{316}{348{,}2} = -55\, cal/K = -230\, J/K$

ad ii) $\Delta_{mix} S = -nR\,[x_A \ln x_A + x_B \ln x_B]$

$n_{H_2O} = \frac{10^3}{M_{H_2O}} = 55{,}5\, mol$, $n_{eth} = \frac{10^3}{M_{eth}} = 21{,}7\, mol$ $\Rightarrow n = 77{,}2\, mol$

$\Rightarrow x_{H_2O} = \frac{55{,}5}{77{,}2} = 0{,}719$ en $x_{eth} = \frac{21{,}7}{77{,}2} = 0{,}281$

$\Rightarrow \Delta_{mix} S = -77{,}2 \cdot 8{,}314\,[0{,}719 \ln 0{,}719 + 0{,}281 \ln 0{,}281]$
$= -641{,}8 \cdot [-0{,}594] = 381\, J/K$

$\Rightarrow \Delta S = 381 + (244 - 230) = 395\, J/K$

c) ideaal mengsel $\Rightarrow \Delta_{mix} H = 0$

d) $Q^{omg} = 0 \Rightarrow \Delta S^{omg} = 0$

$\Rightarrow \Delta S^{tot} = \Delta S^{omg} + \Delta S = 395\, J/K > 0$

klopt met spontaan mengen

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4 a) $Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)$

$$E_0 = E^{\ominus} - \frac{RT}{\nu F}\ln Q = E^{\ominus}_{Cu^{2+}/Cu} - E^{\ominus}_{Zn^{2+}/Zn} - \frac{RT}{\nu F}\ln\frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$$E_0 \approx 0{,}34 + 0{,}76 - \frac{8{,}314 \cdot 298}{2 \cdot 9{,}648 \cdot 10^4}\ln\frac{0{,}01}{0{,}2}$$

$$= 1{,}10 - 0{,}0128 \ln 0{,}05 = 1{,}14\,V$$

b) Initieel: $C_{0,Cu^{2+}} = 0{,}200\,mol/L$ en $C_{0,Zn^{2+}} = 0{,}010\,mol/L$

$$\Delta C_{Zn^{2+}} = -\Delta C_{Cu^{2+}} \equiv +\Delta C$$

$$E = E^{\ominus} - \frac{RT}{2F}\ln\frac{C_{Zn^{2+}}}{C_{Cu^{2+}}} = E^{\ominus} - \frac{RT}{2F}\ln\frac{C_{0Zn^{2+}} + \Delta C}{C_{0Cu^{2+}} - \Delta C}$$

evenwicht: $E = 0 = 1{,}10 - 0{,}0128 \ln\frac{C_{0Zn^{2+}} + \Delta C}{C_{0Cu^{2+}} - \Delta C}$ (LQ-$...)

$$\Rightarrow \frac{C_{0Zn^{2+}} + \Delta C}{C_{0Cu^{2+}} - \Delta C} = \exp\frac{1{,}10}{0{,}0128} = 2{,}1 \cdot 10^{37}$$

$$\Rightarrow C_{0,Cu^{2+}} - \Delta C = \frac{C_{0Zn^{2+}} + \Delta C}{2{,}1 \cdot 10^{37}} \approx 0$$

$$\Rightarrow \begin{cases} C_{eq,Cu^{2+}} \approx 0\,mol/L \\ C_{eq,Zn^{2+}} \approx 0{,}210\,mol/L \end{cases}$$

c) $$\eta = \frac{W_L}{W_i + W_L} = \frac{R_L}{R_i + R_L} = \frac{100}{120} = 0{,}833 \text{ or } 83{,}3\%$$

d) freezing point depression:

$$\Delta T = \left(\frac{R T_{fus}^{*2}}{\Delta_{fus}H}\right)x_B = \frac{8{,}314 \cdot 273{,}15^2}{6{,}008 \cdot 10^3}x_B = 103{,}25\,x_B$$

@ t_0: $$x_B = \frac{n_B}{n_A + n_B} \approx \frac{0{,}01 \cdot 3}{0{,}01 \cdot 3 + \frac{1000}{18}} \approx \frac{0{,}03}{55{,}6} = 5{,}4 \cdot 10^{-4}$$ for Zn half cell

⇒ for Cu half cell x_B is larger!

$$\Rightarrow \Delta T = 103{,}25 \cdot 5{,}4 \cdot 10^{-4} = 0{,}056$$ ⇒ minimal temp. is $-0{,}056°C$

@ t_∞: Cu half cell has $n_B \approx 0$ ⇒ minimal temp. is $-0°C$