Problems sheet for the 2nd exam [Equilibrium theory]
(12:00-14:00, November 24, 2018)
Physical Chemistry for Energy Engineering

*1: Please do not write answers in this problems sheet. What is written in the problems sheet is not evaluated. *2: Please return both the problems sheet and the answer sheet after the exam.

[Problem-I: 6pt for each (30 pt in total)]

(1) Please derive Maxwell relations for internal energy (U) and for enthalpy (H).

From the first law

$$dU = TdS - PdV$$

Here, we compare this with the total derivative of $U = U(S,V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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

Since the cross derivatives are equal, we have

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

Similarly

$$dH = d(U + PV) = TdS - PdV + PdV + VdP = TdS + VdP$$

Here, we compare this with the total derivative of $H = H(S,P)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since the cross derivatives are equal, we have

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

(2) Please derive the following two equations: $(\partial\bar{G}/\partial P)_T = \bar{V}$ and $(\partial\bar{G}/\partial T)_P = -\bar{S}$.

*Note that $\bar{G}$ means "molar" Gibbs energy: $\bar{G} = \frac{G}{n}$. The $\bar{V}$ and $\bar{S}$ hold the same notation.

Differential equation of Gibbs energy ($G = U - TS + PV$) is:

$$dG = dU - TdS - SdT + PdV + VdP$$

Considering a process along a reversible path, the first law is:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Hence,

$$dG = -SdT + VdP$$

Here, we can compare it with the total derivative of $G = G(T,P)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \;,\quad \text{then}$$

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

Dividing both sides with n,

$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$ and $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$

(3) Based on the 2nd law of thermodynamics (namely "*There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the system,* $dS \geq \frac{\delta q}{T}$*, where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.*"), please derive criteria to judge whether a given chemical reaction can spontaneously take place or not at a constant-T constant-V condition.

As the first law: $dU = \delta q + \delta w$*, and* $\delta w = -P_{external} dV$

As a const.-V system, $\delta w = 0$ *. Hence,* $dU + PdV = d(U) = \delta q$*.*

Here, we apply the equation above into the second law ($dS \geq \delta q/T$*),* $dU \leq TdS$ (for const.-V).

where the equal sign is for reversible process and the unequal sign for irreversible process.

In constant-T condition, the differential of Helmholtz energy is written as:

$dA = dU - TdS - SdT = dU - TdS$ *[quasi-static const.-T]*

If we introduce this relation into the equation to judge whether the process is reversible or irreversible:

$dU - TdS = dA \leq 0$ *[quasi-static const.-V const.-P]*

$dA = d(U - TS) = 0$ *[rev. const-V const.-P]*

In summary, dA is a good index to judge the reaction direction: $dA \leq 0$ where the equal sign is for equilibrium state (reversible process) and the unequal sign for spontaneous process (irreversible process).

(4) For the coexistence of two phases (e.g. liquid and gas phases of N_2) at an equilibrium under constant-T constant-P condition, the molar Gibbs energy of the two phases needed to be equal with each other. Please derive this. You can use the fact that the Gibbs energy of the system must be minimized at an equilibrium state.

The Gibbs energy of this system is given by

$$G = G^l + G^g$$

where G^l and G^g are the Gibbs energies of the liquid and the gas phase.

Now, suppose dn mole are transferred from the liquid to the solid phase, where T and P are kept constant. The infinitesimal change in Gibbs energy for this process is:

$$dG = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l$$

As $dn^l = -dn^g$, then

$$dG = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$$

Here, we define *chemical potentials,* $\mu^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T}$ and $\mu^l = \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}$, which corresponds to per-mole Gibbs energy, then

$dG = [\mu^g - \mu^l] dn^g$ (constant T and P)

For this, if the two phases are in equilibrium with each other, then $dG = 0$, because no change should occur in equilibrium. And because we suppose some amount of the liquid phase is transferred to the gas phase (dn^g) here, to make $dG = 0$ in this condition, $\mu^g = \mu^l$ is needed.

This is the condition of coexistence as follows:

✓ If $\mu^g < \mu^l$, $[\mu^g - \mu^l] < 0$. Thus, the process of $dn^g > 0$ (transfer from the liquid phase to the gas phase). Because μ^g and μ^l are considered to be independent of n^g and n^l. This reaction continues until all liquid phase changed to the gas phase. This means the liquid phase disappears, which violates the assumption "coexistence".

✓ If $\mu^g > \mu^l$, $dn^g < 0$. By the same discussion, we can say that the gas phase disappears in this case, which again violates the assumption "coexistence".

✓ Only the case of $\mu^g = \mu^l$, the Gibbs energy of the system is independent of n^g and n^l as $\mathrm{G} = n^g\,\mu^g + n^l\,\mu^l = \left(n^g + n^l\right)\mu^g$, where $n^g + n^l$ is constant due to the mass conservation of the system. In this case, with the same constant Gibbs energy of the system, all N2 can exist as liquid, all N2 can exist as gas, or liquid N2 and gas N2 can coexist.

(5) Using the fact stated in (4), derive the Clapeyron equation, which is given as $\dfrac{dP_{trs}}{dT_{trs}} = \dfrac{\Delta_{trs}\bar{H}}{T_{trs}\Delta_{trs}\bar{V}}$ where P_{trs}, T_{trs}, and $\bar{V}$ are the pressure, temperature and molar volume at the transition condition (the condition when the two phases coexist), and $\Delta_{trs}\bar{V}$ and $\Delta_{trs}\bar{H}$ is the molar volume and enthalpy changes by the phase transition, respectively.

As they are in equilibrium,

$$\mu^\alpha(T,P) = \mu^\beta(T,P)$$

where α and β indicate different phases. Now take the differentials of both sides

$$d\mu^\alpha(T,P) = d\mu^\beta(T,P)$$

$$\left(\frac{\partial\mu^\alpha}{\partial P}\right)_T dP + \left(\frac{\partial\mu^\alpha}{\partial T}\right)_P dT = \left(\frac{\partial\mu^\beta}{\partial P}\right)_T dP + \left(\frac{\partial\mu^\beta}{\partial T}\right)_P dT$$

Since μ is simply the molar Gibbs energy for a single substance, utilizing $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ (*these were previously derived along Maxwell relations)

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \left(\frac{\partial\bar{G}}{\partial P}\right)_T = \bar{V} \text{ and } \left(\frac{\partial\mu}{\partial T}\right)_P = \left(\frac{\partial\bar{G}}{\partial T}\right)_P = -\bar{S}$$

where $\bar{V}$ and $\bar{S}$ are the molar volume and the molar entropy. Then,

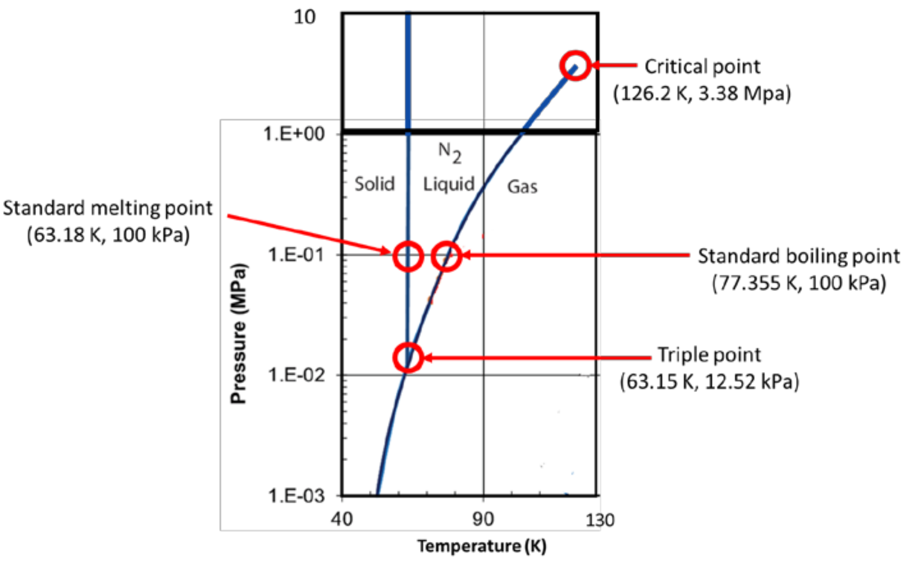
$$\bar{V}^\alpha dP - \bar{S}^\alpha dT = \bar{V}^\beta dP - \bar{S}^\beta dT$$

Since we consider the two phases are in equilibrium each other

$$\frac{dP}{dT} = \frac{\bar{S}^\beta - \bar{S}^\alpha}{\bar{V}^\beta - \bar{V}^\alpha} = \frac{\Delta_{trs}\bar{S}}{\Delta_{trs}\bar{V}} = \frac{\Delta_{trs}\bar{H}/T}{\Delta_{trs}\bar{V}} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}}$$

[Problem-II:8 pt for (1), 6 pt for (2), 6 pt for (3), 6 pt for (4), 6 pt for (5) (32 pt in total)]

(1) Sketch the phase diagram of nitrogen (N_2) as accurate as possible using the following data: triple point at 63.15 K, 12.52 kPa; critical point at 126.2 K and 3.39 MPa; standard melting point at 63.18 K; and standard boiling point at 77.355 K. The x-axis should be temperature over 50-130 K, the y-axis should be pressure over 1k-10M Pa with common logarithms. Please do not forget to specify some key values in the figure. In addition, please explain some key features, if there, by text.



The key feature is that the temperature-pressure graph of liquid-solid coexistence has a negative slope, which can be seen the difference between standard melting point

(2) Using the data given in (1), answer whether the molar volume of nitrogen increase or decrease by melting. Give a scientific reason for it clearly.

The molar volume increases by melting as follows.

Clapeyron equation gives the pressure dependence on temperature in the phase transition as follows:

$$\frac{dP_{trs}}{dT_{trs}} = \frac{\Delta_{trs}\overline{H}}{T_{trs}\Delta_{trs}\overline{V}}.$$

For melting, $\Delta_{trs}\overline{H}$ >0 is always achieved because the enthalpy is mainly related to the interaction strength and the interaction strength in solid is larger than that in liquid, namely $H_{sol} < H_{liq}$. In the phase diagram, comparison between the standard melting point and triple point indicates the positive slope in the solid-liquid coexistence curve, namely $dP_{trs}/dT_{trs} > 0$. To satisfy this, $\Delta_{trs}\overline{V}$ >0 is needed, which means the molar volume increases by melting.

(3) Using the figure given in (1), roughly estimate the saturated vapor pressure of N_2 gas at 100 K. Give a scientific justification for it clearly.

0.6 MPa

The phase diagram indicates, at 100 K, liquid and gas phases coexist if the pressure is 0.6 MPa. This means the molar Gibbs energy (=chemical potential) of liquid and that of gas become the same at 100 K and 0.6 MPa, namely $\mu_l\left(100K, 0.6MPa\right) = \mu_g\left(100K, 0.6MPa\right)$. For condensed phases, namely liquid and solid, the pressure dependence of enthalpy and entropy, and thus Gibbs energy, is small compared with gas. Thus, we can consider, $\mu_g\left(100K, 0.6MPa\right) = \mu_l\left(100K, 0.6MPa\right) \sim \mu_l\left(100K, 1atm\right)$. Thus, the saturated vapor pressure can be considered to be 0.6 MPa.

*Sorry this problem was inappropriate. The temperature should be less than the standard/normal boiling point (77 K). The coexistence of [0.6 MPa gas N2] and [0.1 MPa liquid N2] is quite difficult to be achieved. (If the temperature was lower than 77 K, the coexisting gas pressure with "0.1 MPa liquid N2" becomes lower than 0.1 MPa. This is quite possible if some other gasses coexist in the system, as the liquid pressure is of the total pressure while the gas pressure is of the partial pressure.)

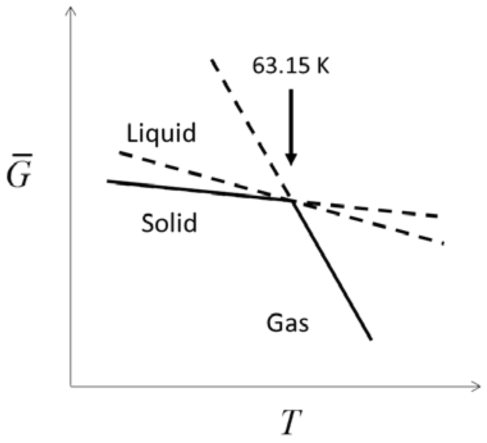
*Since this problem was inappropriate, I gave all 6pt.

(4) Please draw a T-$\bar{G}$ diagram of nitrogen at temperatures around the triple point under constant pressure condition (12.52 kPa). Please show 3 lines corresponding to $\bar{G}$ for gas, liquid and solid. Use x-axis for T and y-axis for $\bar{G}$.

*Just draw it in a qualitatively correct manner. The same for (5).

In $\bar{G} - T$ graph:

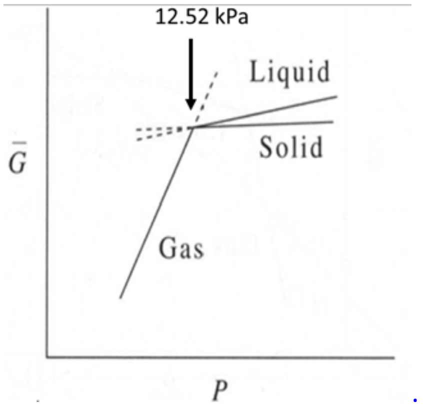
- $(\partial \bar{G}/\partial T)_P = \overline{-S} < 0$. Thus the slope in this graph must be positive.
- $\overline{S^g} \gg \overline{S^l} > \overline{S^s}$ is confirmed in (2).



(5) Please draw a P-$\bar{G}$ diagram of nitrogen at pressures around the triple point under constant temperature condition (63.15 K). Please show 3 lines corresponding to $\bar{G}$ for gas, liquid and solid. Use x-axis for P and y-axis for $\bar{G}$.

In $\bar{G} - P$ graph:

- $(\partial \bar{G}/\partial P)_T = \bar{V} > 0$. Thus the slope in this graph must be positive.
- $\overline{V^g} \gg \overline{V^l} > \overline{V^s}$ is confirmed in (2).



[Problem-III: 7pt, 10pt: 17 pt in total]

(1) Derive the equation to show the temperature dependence of (molar) entropy at a constant pressure condition.

If we treat H and S as functions of T and P thus H(T, P) and S(T, P), their total derivatives are:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad \text{and} \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

As the first and second laws for a reversible process:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV, \quad dH = d(U + PV) = TdS + VdP$$

By substituting this equation to the first left one:

$$dS = \frac{1}{T}(dH - VdP) = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left[-V + \left(\frac{\partial H}{\partial P}\right)_T\right] dP = \frac{C_P}{T} dT + \frac{1}{T}\left[-V + \left(\frac{\partial H}{\partial P}\right)_T\right] dP$$

Here we used the definition of constant-pressure heat capacity: $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$

In comparison with the total derivative of S given above:

$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ and $\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[-V + \left(\frac{\partial H}{\partial P}\right)_T\right]$

By making an integral with respect to T (with keeping P constant):

$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)dT}{T}$ *(constant P)*

Hence, we can calculate S of an arbitrary temperature, S(T), if we know S(0 K):

$S(T) = S(0\ K) + \int_0^T \frac{C_P(T')dT'}{T'}$ *(constant P)*

(2) Calculate the standard molar entropy of $N_2(g)$ at 298.15 K using the following data. Please assume the entropy at 10 K is nearly 0.

$C_P^\circ[N_2(s)]/R = -0.03165 + (0.05460 K^{-1})T + (3.520 \times 10^{-3} K^{-2})T^2 - \left(2.064 \times 10^{-5} K^{-3}\right)T^3$ for 10 K < T < 63.15 K

$C_P^\circ[N_2(l)]/R = -18.44 + (1.053 K^{-1})T - (0.0148 K^{-2})T^2 + \left(7.064 \times 10^{-5} K^{-3}\right)T^3$ for 63.15 K < T < 77.36 K

$C_P^\circ[N_2(g)]/R = 3.500$ for T >77.36 K

$T_{fus} = 63.15K, \Delta\bar{H}_{fus} = 0.71 kJ/mol, T_{vap} = 77.36K, \Delta\bar{H}_{vap} = 5.57 kJ/mol$

$$\bar{S}^\circ(298.15K) = \bar{S}^\circ(10K) + \int_{10}^{63.15} \frac{C_{P,s}}{T} dT + \Delta\bar{S}^\circ_{s\to l} + \int_{63.15}^{77.36} \frac{C_{P,l}}{T} dT + \Delta\bar{S}^\circ_{l\to g} + \int_{77.36}^{298.15} \frac{C_{P,g}}{T} dT$$

$$\sim \int_{10}^{63.15} \frac{C_{P,s}}{T} dT + \Delta\bar{S}^\circ_{s\to l} + \int_{63.15}^{77.36} \frac{C_{P,l}}{T} dT + \Delta\bar{S}^\circ_{l\to g} + \int_{77.36}^{298.15} \frac{C_{P,g}}{T} dT$$

$$\int_{10}^{63.15} \frac{C_{P,s}}{T} dT = 66.15, \int_{63.15}^{77.36} \frac{C_{P,l}}{T} dT = 11.77, \int_{77.36}^{298.15} \frac{C_{P,g}}{T} dT = 39.24$$

Phase transition can be reversed by changing the temperature ever so slightly.

Considering it takes place at a fixed temperature (T_{trs}) and under a constant pressure

$$\Delta H = \Delta(U + PV) = \Delta U + P\Delta V = (q_P - P\Delta V) + P\Delta V = q_p$$

$$\Delta\bar{S}^\circ_{trs} = \frac{q_{trs,rev}}{T_{trs,rev}} = \frac{\Delta\bar{H}^\circ_{trs}}{T_{trs}}$$

$$\Delta\bar{S}^\circ_{s\to l} = \frac{710}{63.15} = 11.24, \Delta\bar{S}^\circ_{s\to l} = \frac{5570}{77.36} = 72.00$$

Note that the unit of entropy is all [J/K/mol].

$$\bar{S}^\circ(298.15K) = 66.15 + 11.24 + 11.77 + 72.00 + 39.24 = 200.4 \text{ [J/K/mol]}$$

[Problem-IV: (1) 7 pt (2) 7pt, (4) 7pt (21 pt in total)]

(1) It is know that “the maximum non-PV work that can be taken from a reaction under a constant-T constant-P condition” or “the minimum non-PV work that can be needed to proceed a reaction under a constant-T and constant-P condition” is equal to the Gibbs energy change by the reaction. Please derive this.

We first consider a reversible constant-Tprocess. For this, the following equation is satisfied:

$$\Delta G = \Delta(H - TS) = \Delta H - T\Delta S - S\Delta T = \Delta H - T\Delta S$$

Because the process is reversible,

$\Delta S = \int dS = \int \frac{\delta q_{rev}}{T} = \frac{q_{rev}}{T}$

Thus, $\Delta G = \Delta H - T\Delta S = \Delta H - q_{rev}$

According to the first law, we obtain

$\Delta G = \Delta H - q_{rev} = \Delta U + \Delta(PV) - q_{rev} = \Delta(PV) + w_{rev}$

Then, if we consider P-V work and non-P-V with further assuming constant-P,

$\Delta G = \Delta(PV) + w_{rev} = P\Delta V + w_{rev-PV} + w_{rev-non-PV} = w_{rev-non-PV}$

This equation indicates:

- If $\Delta G < 0$ of a const.-T and const.-P process, the process will occur spontaneously and $w_{rev-non-PV}$ represents the work that can be done by the system if this change is carried out reversibly. Because the reversible process is the most efficient, this corresponds to the maximum non-PV work that this process can make.
- If $\Delta G > 0$ of a const.-T and const.-P process, the process will not occur spontaneously and $w_{rev-non-PV}$ represents the work that must be done on the system to make this process occur in a reversible manner. As the reversible process is the most efficient, this corresponds to the minimum non-PV work that needed to make this process occur.

(2) Consider the following reaction that occurs at constant-P constant-T condition (1 bar, 298.15 K):

$$\mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{H_2O}\ (l)\ .$$

It is know by experiments that the maximum non-PV work that can be taken from this reaction is 237.1 kJ/mol. Using the following data of the standard molar entropies at 298.15 K, calculate the standard molar enthalpy of formation ($\Delta_f H^\circ$) of H_2O (l) at 298.15 K.

*Note that "237.1 kJ/mol" means the maximum non-PV work of this reaction with 1 mol H2 and 0.5 mol O_2 is 237.1 kJ.

Substance	$\bar{S}^\circ$ (J/K/mol)
H_2 (g)	130.7
O_2 (g)	205.2
H_2O (l)	70.0

The standard Gibbs energy of reaction $\Delta_r G^\circ$ is $\Delta_r G^\circ = -237.1\ \mathrm{kJ/mol}$. The Gibbs energy of reaction is basically related to changes in enthalpy and entropy by reaction as $\Delta_r G = \Delta_r H - T\Delta_r S$.

From the data, $T\Delta_r S^\circ$=298.15x(70.0-(130.7+0.5x205.2))=298.15x(-163.3)=-48.7 kJ/mol

For the enthalpy, $\Delta_r H = \Delta_f H^\circ(H2O) - \Delta_f H^\circ(H2) - 0.5 \times \Delta_f H^\circ(O2)$, where $\Delta_f H^\circ(H2)$ and $\Delta_f H^\circ(O2)$ are 0 because they are the elementary substance of equilibrium phase. Thus, $\Delta_f H^\circ(H2O) = -237.1 + (-48.7) = -285.8\ \mathrm{kJ/mol}$

(3) Now we want to decompose liquid water electrically, namely electrolysis, as

$$\mathrm{H_2O}\ (l) \rightarrow \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g)$$

Determine how much voltage is at least needed to advance the water decomposition. If needed, please use the information given in (1) and/or (2) above.

*Hint: the electrical work, which is expressed as qV, where q is the charge and V is the voltage (difference between the anode and cathode), is the non-PV work here.

In the electrical decomposition of water, for example, the following reactions occur:

$$2\mathrm{H_2O}\ (l) + 2e^- \rightarrow \mathrm{H_2}(g) + 2\mathrm{OH}^-(aq)$$

$$2\mathrm{H_2O}\ (l) \rightarrow \mathrm{O_2}(g) + 4\mathrm{H}^+(aq) + 4e^-$$

This means to form 1 H_2, 2 electros are transferred between electrodes. The minimum non-PV work needed to make this reaction occur is 237.1 kJ/mol, which is used to transfer electrons. By the decomposition of 1 mol H2O, 1 mol H2 is formed and thus 2 mol electros need to be transferred. Therefore, the voltage (Vol) needed is expressed as follows:

$$\mathrm{Vol} \times \left(2 \times 6.02 \times 10^{23}\right) \times \left(1.6 \times 10^{-19}\right) = 237100$$

where the unit of energy is J/mol. Accordingly the voltage is determined to be

Vol = 1.23 V.