Exam 2023 solution – Thermodynamique

PROBLÈME I ETHANOL AND WATER 18P

solution 1

1. $K_{H_1} = \frac{x_{EtOH}}{p_{EtOH}} = \frac{0.05}{0.0109} = 4.5872(atm^{-1})$ 2p

2. Using Clasius-Claperon equation:

   $\ln \frac{p_{vap1}}{p_{vap2}} = \frac{\Delta_{vap}H}{R}(\frac{1}{T_2} - \frac{1}{T_1})$ 2p

   at $T_1 = 373$ K, $p_{vap1} = 1$ atm, therefore at $T_2 = 293$ K, $p_{vap2} = 0.0279$ atm. 2p

   According to Raolt Law : $p = p_{vap} \times x_{\mathrm{H_2O}}$

   $p = 0.0279 \times 0.95 = 0.0265$ atm

   since there is no specificity on whether the calculation is for the mixture, or for pure water, using Raolt law here for further calculation gives partial points

3. at 60^oC: $K_{H_2} = \frac{x_{EtOH}}{p_{EtOH}} = \frac{0.05}{0.1424} = 0.3511(atm^{-1})$ 2p

   With the result from the previous part, we have 2 equations with 2 variables:

   $a + \frac{b}{293} = \ln 4.5872$ 1p

   $a + \frac{b}{333} = \ln 0.3511$ 1p

   solve these equations give: a = -19.8716 and b = 6268.7 2p

solution 2

1. $K_{H_1} = \frac{p_{EtOH}}{x_{EtOH}} = \frac{0.0109}{0.05} = 0.218$ 2p

2. Using Clasius-Claperon equation:

   $\ln \frac{p_{vap1}}{p_{vap2}} = \frac{\Delta_{vap}H}{R}(\frac{1}{T_2} - \frac{1}{T_1})$ 2p

   at $T_1 = 373$ K, $p_{vap1} = 1$ atm, therefore at $T_2 = 293$ K, $p_{vap2} = 0.0279$ atm. 2p

3. at 60^oC: $K_{H_2} = \frac{p_{EtOH}}{x_{EtOH}} = \frac{0.1424}{0.05} = 2.848(atm^{-1})$ 2p

   With the result from the previous part, we have 2 equations with 2 variables:

   $a + \frac{b}{293} = \ln 0.218$ 1p

   $a + \frac{b}{333} = \ln 2.848$ 1p

   solve these equations give: a = 19.8709 and b = -6268.5 2p calcualte follows either solution 1 or solution 2 get full mark.

inconsistent unit: -0.5p

calculation error: -1p

wrong starting equation: -1p

4. Azeotrope point: At this point, the mixture has the same composition in the gas phase and in the liquid phase. Another way of saying this is: the mixture has the same boiling temperature and curb temperature. 1p

   The boiling point at the azeotrope point will have a minimum boiling point or maximum vapor pressure. 1p

   It is not possible to separate them using distillation. 1p

   mixture diagram: 3p

   wrong name of line: -0.5p, azeotropic point: 1p, indicate correct axis 0.5p each

   plot T-x instead, but still correct: -1p, wrong azeotrope type: -2p

   misplace azeotrope point: -0.5p

   misdrawn curve: -1p

   wrong composition written: -1p

   badly indicated limit: -1p

   non indicated limit: -0.5p

   unfinished sides: -1p

   matching pure boiling points , other inaccurate indication: -0.5p

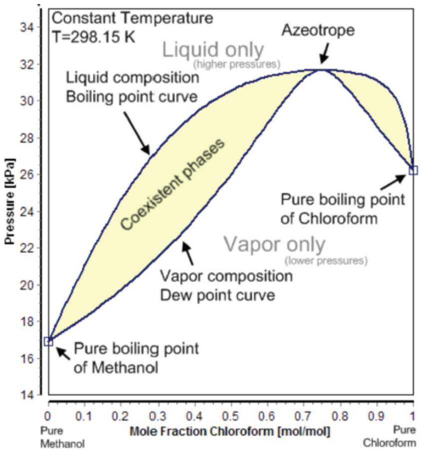

FIG. 1. Temperature dependence on the composition of mixture

Problème II Burning coal (20p)

1. At 298K:

   $\Delta H_{298K} = 2 \times \Delta_f H^{\ominus}_{298K}(CO) = -221.05(\mathrm{kJ/mol})$ (2p)

2. The reaction will use 1 mole C(graphite) to react completely with 0.5 mole $\mathrm{O_2}$ and produce 1 mole CO

   $Q_{carbon} = nC_p^{\ominus}(carbon)\Delta T = 1 \times 8.527 \times (298 - 1000) = -5986(\mathrm{J})$ (2p)

   $Q_{\mathrm{O_2}} = nC_p^{\ominus}(\mathrm{O_2})\Delta T = 0.5 \times 29.355 \times (298 - 1000) = -10304(\mathrm{J})$ (2p)

   $Q_{\mathrm{CO}} = nC_p^{\ominus}(\mathrm{CO})\Delta T = 1 \times 29.142 \times (1000 - 298) = 20458(\mathrm{J})$ (2p)

   The heat released by the reaction is calculated as:

   $Q = \Delta_f H^{\ominus}_{298}(CO) + Q_{carbon} + Q_{\mathrm{O_2}} + Q_{\mathrm{CO}} = -106.357(\mathrm{kJ})$ (2p)

3. The reaction will use 1 mole of C(graphite) to react completely with 1 mole $\mathrm{O_2}$ and produce 1 mole $\mathrm{CO_2}$

   $Q_{carbon} = nC_p^{\ominus}(carbon)\Delta T = 1 \times 8.527 \times (298 - 1000) = -5986(\mathrm{J})$ (2p)

   $Q_{\mathrm{O_2}} = nC_p^{\ominus}(\mathrm{O_2})\Delta T = 1 \times 29.355 \times (298 - 1000) = -20608(\mathrm{J})$ (2p)

   $Q_{\mathrm{CO_2}} = nC_p^{\ominus}(\mathrm{CO})\Delta T = 1 \times 37.110 \times (1000 - 298) = 26051(\mathrm{J})$ (2p)

   The heat released by the reaction is calculated as:

   $Q = \Delta_f H^{\ominus}_{298}(\mathrm{CO_2}) + Q_{carbon} + Q_{\mathrm{O_2}} + Q_{\mathrm{CO}} = -394.0520(\mathrm{kJ})$ (2p)

4. Since the heat released by the first reaction is less than the second reaction, (1p)

   Burn C(graphite) in excess oxygen will generate more energy. (1p)

   correct formula but wrong result, 1p

   Wrong unit, -0.5p, wrong sign, -0.5p

   wrong temperature: 1p each

PROBLÈME III ICE 30P

1. For the transition from liquid to ice I:

   $\Delta V = V_{iceI} - V_{liquid} = 2.42ml = 2.42 \times 10^{-6}(m^3)$ 1p

   From the Clausius equation:

   $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$ 1p

   calculate the left side at 1800 bar:

   $\frac{dT}{dp} = b + \frac{c}{p} - \frac{d}{p^2} + \frac{e}{2\sqrt{p}} = -0.0115(\mathrm{K\,bar}^{-1})$ 2p

   differetiated form: 1p, result: 1p

   $\Delta H = T\Delta V \times \frac{dp}{dT} = 254.5 \times 2.42 \times 10^{-6} \times \frac{-1}{0.0115} = -5355.1(\mathrm{J\,mol}^{-1})$ 2p

   formula: 1p, result: 1p

2. At 3000 bar:

   $\frac{dT}{dp} = b + \frac{c}{p} - \frac{d}{p^2} + \frac{e}{2\sqrt{p}} = 0.0037 > 0$ 3p

   $\frac{\Delta H}{T\Delta V} > 0$ 1p

   The process from water to ice is exothermic, therefore $\Delta H < 0$. 2p

   we have:

   $V_{iceIII} < V_{liquid}$ 2p

   the density of ice III is higher than liquid, therefore higher than ice I. 2p

   alternative answer

   Since increasing the pressure shifts the equilibrium to a state with lower pressure, according to Le Chatelier's Principle, ice III has a lower pressure 6p

   fail to correlate external pressure with the density of the phase: -6p

   $V_{iceIII} < V_{liquid}$ 2p

   the density of ice III is higher than liquid, therefore higher than ice I. 2p

3. At 2100 bar, ice I transform into ice III:

   From the Clausius equation:

   $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$ 1p

   $\frac{dT}{dp} = b + \frac{c}{p} - \frac{d}{p^2} + \frac{e}{2\sqrt{p}} = -0.2854(\mathrm{K\,bar}^{-1})$ 2p

   differetiated form: 1p, result: 1p

   $\frac{\Delta H}{T\Delta V} < 0$ 1p

   Since the density of ice I is smaller than that of ice III, $V_{iceIII} - V_{iceI} < 0$ 1p

   Therefore $\Delta H > 0$, the transformation from ice I to ice III is endothermic. 2p

4. Phase diagram of ice I, ice III, and liquid water. 7p

   each correct phase: 1p

   Indicate triple point: 1p

   indicate the wrong relative angle of each line: -1p.

   Axis label wrong: -1p.

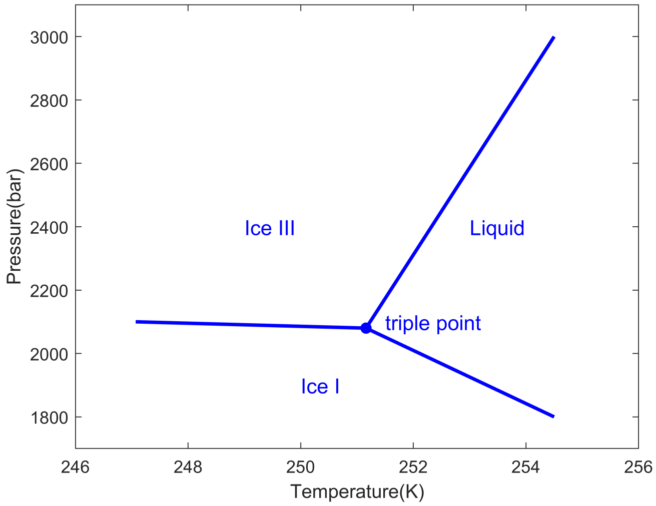

FIG. 2. phase transition between ice I and ice III

PROBLÈME IV ADVANCE CARNOT CYCLE 30P

1. The T-S diagram of the carnot cycle: 2.5p

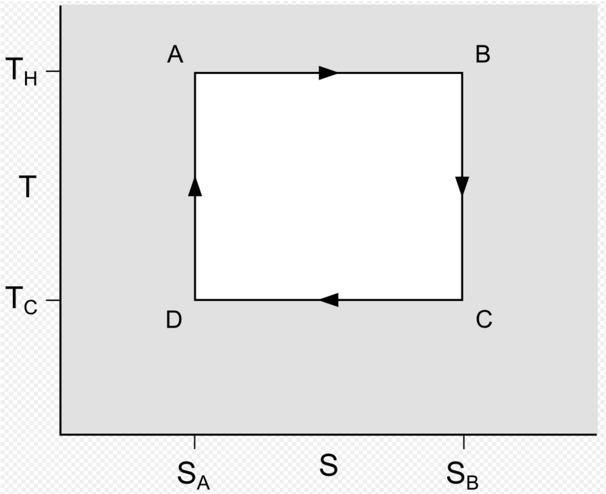

FIG. 3.

correct axis: 0.5p each, correct phase: 0.25p each, correct arrow direction 0.5p

points are given fully it the arrow direction is indicated in different ways, but still indicates the correct direction.

flip graph: -0.5p

2. during n_e cycle, 2 -> 3 is adiabatic transformation:

$T^+V_2^{\gamma-1} = T^-(n)V_3^{\gamma-1}(n) -> \frac{T^+}{T^-(n)} = (\frac{V_3(n)}{V_2})^{\gamma-1}$ 1p

4 -> 1 is also an adiabatic transformation, similarly, we have:

$\frac{T^+}{T^-(n)} = (\frac{V_4(n)}{V_1})^{\gamma-1}$ 1p

We then have:

$\frac{V_3(n)}{V_4(n)} = \frac{V_2}{V_1}$ 1p

solve differently but get the same result: fullpoint

3. 3 -> 4 is isothermal transformation, $\Delta U = 0$, we have:

$Q^-(n) = -W = NRT^-(n) \ln \frac{V_4(n)}{V_3(n)}$ 1p

from the previous part, we have:

$Q^-(n) = -NRT^-(n) \ln \frac{V_2}{V_1}$ 1p

4. Work of the system is calculated as:

   $W_{tot} = W_{1->2} + W_{3->4}$ 1p

   write down total work differently: fullpoint

   $W_{tot} = -NRT^{+} \ln \frac{V_2}{V_1} - NRT^{-}(n) \ln \frac{V_4(n)}{V_3(n)}$ 2p

   write down formula for work of 1->2 and 3->4, 1p each

   Based on the previous part, $\frac{V_3(n)}{V_4(n)} = \frac{V_2}{V_1}$

   $W_{tot} = -NRT^{+} \ln \frac{V_2}{V_1} + NRT^{-}(n) \ln \frac{V_2}{V_1} = NR(T^{-}(n) - T^{+}) \ln \frac{V_2}{V_1}$ 1p

5. $\Delta H_{23} = \Delta U_{23} + NR(T^{-}(n) - T^{+})$ 2p

   $\Delta U_{23} = NC_v(T^{-}(n) - T^{+}) = \frac{3}{2}NR(T^{-}(n) - T^{+})$ 2p

   calculate directly from Cp, fullpoint

   wrong prove: no point

   Based on this, we have:

   $\Delta H_{23} = \frac{5}{2}NR(T^{-}(n) - T^{+})$ 1p

   able to write down this formula but does not give the exact numerical result: -0.5p

   write down $\Delta H = C_p \Delta T$ or differential form: 2p

   Write down $C_p = C_v + NR$: 1p

   H = U + pV: 1p

6. Since the heat released to the cold source increases its temperature, we have:

   $Q = C_v^{-}(n)\Delta T^{-}(n) = NRT^{-}(n) \ln \frac{V_2}{V_1}$ 3p

   able to write separate formulas for the heat transferred, 1p each

   able to show the heat received from the cold source is equal to heat generated from the motor: 1p

   The change in temperature after a cycle is then calculated as:

   $\Delta T^{-}(n) = T^{-}(n) \frac{N}{N^{-}} \frac{1}{c^{-}(n)} \ln \frac{V_2}{V_1} = \lambda T^{-}(n)$

   In which: $\lambda(n) = \frac{N}{N^{-}} \frac{1}{c^{-}(n)} \ln \frac{V_2}{V_1}$ 2p

   since $V_2 > V_1$, therefore $\lambda(n) > 0$ 1p

   prove the inequality independently: 1p

7. To calculate the temperature for the current cycle compared to the previous cycle

   $T^-(n) = T^-(n-1)(1+\lambda(n-1))$ 0.5p

   Before cycle n_0, we have: $c^- = \frac{5}{2}$. 0.5p

   With that, we can calculate the temperature for cycle n_0 based on the temperature of the first cycle as follows:

   $T^-(n_0) = T^-(1)\prod_{n=1}^{n_0-1}(1+\lambda(n)) = T^-(1)(1+\frac{N}{N^-}\frac{2}{5}\ln\frac{V_2}{V_1})^{n_0-1}$ 1p

   At cycle $n_1 > n_0$, the coefficient for the heat capacity becomes $c^- = \frac{7}{2}$: 0.5p

   Because of that, the temperature at cycle n_1 is calculated as:

   $T^-(n_1) = T^-(1)(1+\frac{N}{N^-}\frac{2}{7}\ln\frac{V_2}{V_1})^{n_1-n_0}(1+\frac{N}{N^-}\frac{2}{5}\ln\frac{V_2}{V_1})^{n_0-1}$ 1p

   if not write down formula form lambda, but still separate different lambda, still get full-point

8. In the 5^{th} cycle, the efficiency of the cycle is reduced by 20% compared to the 1^{st} cycle, we have:

   $\eta(5) = 0.8\times\eta(1)$ 0.5p

   The efficiency is calculated as:

   $\eta(n) = \frac{T^+ - T^-(n)}{T^+}$ 0.5p

   Based on this, we have:

   $1 - \frac{T^-(5)}{T^+} = 0.8 - 0.8\times\frac{T^-(1)}{T^+}$ 0.5p

   Because $n_0 > 5$, the temperature of the 5th cycle is calculated as:

   $T^-(5) = T^-(1)(1+\lambda(n_0))^4$ in which: $\lambda = \frac{2}{5}\ln\frac{V_2}{V_1}$ 0.5p

   Therefore, we have: $\lambda(n_0) = \frac{2}{5}\ln\frac{V_2}{V_1} = (\frac{T^+}{5T^-(1)} + 0.8)^{1/4} - 1$ 1p

   $\frac{V_2}{V_1} = \exp\left(\frac{5N^-}{2N}[(\frac{T^+}{5T^-(1)} + 0.8)^{1/4} - 1]\right)$ 1p

   wrong sign: -0.5p

   wrong math expression: -0.5p