General Physics - Thermodynamics – PHYS-106(i)

Exam 2024 answer

PROBLÈME I AMMONIA DECOMPOSITION 22P

1. $\Delta H^{\ominus}$ of the reaction is: 1p

$$\Delta H^{\ominus} = \frac{3}{2}\Delta_f^{\ominus} H(\mathrm{H_2}) + \frac{1}{2}\Delta_f^{\ominus} H(\mathrm{N_2}) - \Delta_f^{\ominus} H(\mathrm{NH_3}) = 46.1\ \mathrm{kJ\,mol^{-1}}$$

$\Delta S^{\ominus}$ of the reaction is: 1p

$$\Delta S^{\ominus} = \frac{3}{2} S^{\ominus}(\mathrm{H_2}) + \frac{1}{2} S^{o}(\mathrm{N_2}) - S^{\ominus}(\mathrm{NH_3})$$

$$\Delta S^{\ominus} = \frac{3}{2}\cdot 130.68\ \mathrm{J\,mol^{-1}\,K^{-1}} + \frac{1}{2}\cdot 191.61\ \mathrm{J\,mol^{-1}\,K^{-1}} - 192.77\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

$$\Delta S^{\ominus} = 99.055\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

ΔG^{o} of the reaction is: 1p

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} = 46.1\ \mathrm{kJ\,mol^{-1}} - \frac{298\ \mathrm{K}\cdot 99.055\ \mathrm{J\,mol^{-1}\,K^{-1}}}{1000} = 16.5816\ \mathrm{kJ\,mol^{-1}}$$

formula: 0.5p, result 0.5p, no clear unit: -0.25p

Formula of $\Delta H^{\ominus}$ can ignore the enthalpy formation of elementary gases.

2. At 600 K, and since $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ is independent of temperature: 0.5p

$$\Delta G^{\ominus}(600\mathrm{K}) = \Delta H^{\ominus} - T\Delta S^{\ominus} = 46.1\ \mathrm{kJ\,mol^{-1}} - \frac{600\ \mathrm{K}\cdot 99.055\ \mathrm{J\,mol^{-1}\,K^{-1}}}{1000} = -13.333\ \mathrm{kJ\,mol^{-1}}$$

no more point given for formula since it is the same as the first part, incorrect final answer: -0.5p, no clear unit: -0.25pt

The equilibrium constant at this temperature is: 1.5p

$$K^{\ominus} = \exp\frac{-\Delta G^{\ominus}}{RT} = 14.48$$

formula: 1p, result 0.5p, incorrect final answer: -0.5p

Reaction	$NH_3(g)$	$\rightleftharpoons$	$\frac{1}{2}N_2(g)$	$+$	$\frac{3}{2}H_2(g)$
Initial	1				
React	x		$\frac{1}{2}x$		$\frac{3}{2}x$
Final	1-x		$\frac{1}{2}x$		$\frac{3}{2}x$

The equilibirium constant for the reaction is: 1p

$$K_p = \frac{p_{N_2}^{1/2} \cdot p_{H_2}^{3/2}}{p_{NH_3}} = \frac{(1/2x)^{1/2} \cdot (3/2x)^{3/2}}{1-x} \approx \frac{1.3x^2}{1-x}\ \text{bar}$$

still give full point if the final derivation is not given

Since $p^{\ominus} = 1$ bar we have: 1p

$$K_p \equiv K^{\ominus} \rightarrow \frac{1.3x^2}{1-x} = 14.48\ \text{bar} \rightarrow x = 0.923\ \text{bar}$$

The final pressure of NH_3 is 0.077 bar.

if the variable naming is different, but the final result is the same, still give fullpoint for this part, which is 1p

no clear unit: -0.25p

give point for formula even if the standard pressure is not clearly stated

3. For the reaction to be spontaneous: 2p

$$\Delta G^{\ominus} < 0 \rightarrow T > \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}} = 465.4\ \text{K or } 192.4^{\circ}\text{C}$$

0.5p for mentioning Gibbs free energy negative, 1p for mentioning the effect of positive sign of entropy on the temperature comparison

no clear unit: -0.25p

4. The combustion reaction of $C_3H_7OH_{(g)}$ at 298 K is: 1p

$$C_3H_7OH(g) + \frac{9}{2}O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

The heat combustion of the reaction at 298 K is: 1p

$$\Delta H^o = 3 \cdot \Delta_f H^o(CO_2(g)) + 4 \cdot \Delta_f H^o(H_2O(l)) - \Delta_f H^o(C_3H_7OH(g)) = -2005.63 \text{ kJ mol}^{-1}$$

incorrect final answer: -0.5p, no clear unit: -0.25p

Formula of ΔH^o can ignore the enthalpy formation of elementary gases.

The heat required to bring 1 kg of NH_3 from 298 K to 600 K, accounting for the heat efficiency, is:: 2p

$$Q = nC_p\Delta T \cdot \eta^{-1} = \frac{1000 \text{ g}}{17 \text{ g mol}^{-1}} \cdot 45.26 \text{ J mol}^{-1}\text{ K}^{-1} \cdot (600 \text{ K} - 298 \text{ K}) \cdot 0.8^{-1}$$

$$Q = 1005038 \text{ J or } 1005.038 \text{ kJ}$$

Correct formula for Q without efficiency: 1p, accounting for efficiency: 0.5p, result: 0.5p

incorrect final answer: -0.5p, no clear unit: -0.25p

The amount of isopropanol required is: 0.5p

$$m_{C_3H_7OH} = \frac{1005.038 \text{ kJ}}{2005.63 \text{ kJ mol}^{-1}} \cdot 60 \text{ g mol}^{-1} = 30.07 \text{ g}$$

incorrect final answer: -0.5p, no clear unit: -0.25p, allow for different mass unit, but if the answer is in other unit, -0.5p

If the heat combustion calculated wrong, and is used here, give point if the calculation here is correct, provided that the value is stated clearly.

The approximation is not valid because 2p

- At combustion temperature, water will be at gas state, therefore the calculation have to use the enthalpy value of gas water instead of liquid water.
- Combustion temperature of isopropanol has to be higher than 600 K, in order to transfer the heat from the combustion system to ammonia.
- Heat required to bring the reactants to combustion temperature.

one good reason to why the approximation is valid, or not valid, give full points: 2p

5. Based on Le Chatelier principle, when the pressure is increased, the equilibrium will shift toward decreasing the pressure, which in this case less NH_3 will decompose. 1p

   The reaction quotient at new pressure condition is: 0.5p

   $$Q_p = \frac{p_{\mathrm{N_2}}^{1/2} \cdot p_{\mathrm{H_2}}^{3/2}}{p_{\mathrm{NH_3}}} = \frac{2.3075^{1/2} \cdot 6.9225^{3/2}}{0.3850} = 71.86 \text{ bar}$$

   Because $Q_p > K_p$ the reaction will evolve to the left, confirming the prediction. 0.5p

   if a different calculation is used, but can still conclude that the prediction is correct, give full point for this part, which is 1p

   If the wrong value of pressure is used, but the calculation of Q is still correct, still give full point, which is 0.5p, provided the pressure value is mentioned

   if Qp can be proven to be 5 times the original equilibrium because the pressure increases 5 times, still give 0.5p

6. Change in enthalpy is calculated as: 1p

   $$\Delta H(T) = \Delta H^o + \sum_i \nu_i C_p \Delta T$$

   Ploting numerical value, we have: 0.5p

   $$\Delta H(T) = 46.1 + \left(\frac{1}{2} \cdot 30.1 + \frac{3}{2} \cdot 29.32 - 45.26\right) \frac{1}{1000}(T - 298)$$

   $$\Delta H(T) = 41.9965 \text{ kJ mol}^{-1} + 0.01377 \cdot T \text{ kJ mol}^{-1}$$

   Change in entropy of the reaction is calculated as: 1p

   $$\Delta S(T) = \Delta S^o + \sum_i \nu_i C_p \ln \frac{T}{T_o}$$

   Ploting numerical value we have: 0.5p

   $$\Delta S(T) = \left(\frac{1}{2} \cdot 191.61 + \frac{3}{2} \cdot 130.68 - 192.77\right) + \left(\frac{1}{2} \cdot 30.1 + \frac{3}{2} \cdot 29.32 - 45.26\right) \cdot \ln \frac{T}{298}$$

   $$\Delta S(T) = 20.6060 \text{ J mol}^{-1}\,\text{K}^{-1} + 13.77 \cdot \ln T \text{ J mol}^{-1}\,\text{K}^{-1}$$

Change in Gibbs free energy at temperature T is: 0.5p

$$\Delta G^o = 41.9965 \text{ kJ mol}^{-1} + 0.01377T \text{ kJ mol}^{-1} - \frac{T}{1000}(20.6060 + 13.77 \ln T) \text{ kJ mol}^{-1}$$

$$\Delta G^o = 41.9965 \text{ kJ mol}^{-1} - 0.006836T \text{ kJ mol}^{-1} - 0.01377T \ln T \text{ kJ mol}^{-1}$$

At 600 K, using the new formula, we have: 0.5p

$$\Delta G^o = -14.9565 \text{ kJ mol}^{-1}$$

The new value is more negative than the previous value without the approximation, meaning the equilibrium will shift to the right. 0.5p

no clear unit: -0.25p each, if each formula does not give the correct value at 298 K, consider all numerical derivation wrong and -0.5p each

completely wrong formula but correct conclusion, no point given for conclusion alone

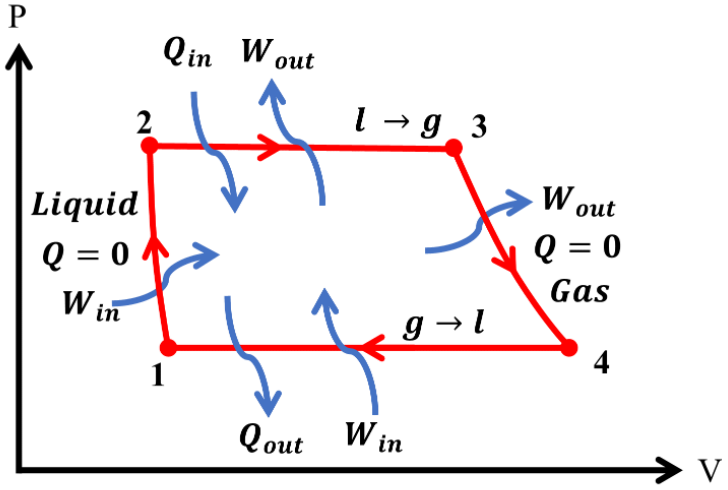
Not give points for result of ΔH and ΔS at 600 K since the question does not ask about these values.

Formula alone without any calculation is 2.5p total, 1p for ΔH, 1p for ΔS, 0.5p for ΔG

Key calculation: Cp: 0,5p, ΔS at 298 K: 0.5p

PROBLÈME II STEAM POWER CYCLE 16.5P

1. The new p-V diagram: 5.5p



correct axis: 0.5p, correct state names: 0.5p, correct direction: 0.5p, correct shape: 1p, correct phase indication: 1p, each work and heat direction: 0.25p

shape requirement: 2-3 and 1-4 has to be paralel with each other and have constant pressure; 1-2 and 3-4 does not bend backward; each mistake is -0.25p.

direction can be indicated by both arrow on the transformation or a circular arrow inside or outside the process, providing the direction is consistent

accept negative and positive indication of work and heat, since it is equivalent to the direction of work and heat

for transformation including phase transition, mention that it is a mixture without direction, or the name of the phase transition, give full points

2. Since 3 → 4 process is adiabatic: 1p

$$p_3^{1-\gamma} T_3^{\gamma} = p_4^{1-\gamma} T_4^{\gamma}$$

Since the degree of freedom of vapor water is 8, $\gamma = \dfrac{f+2}{f} = 1.25$ 1p

Ploting numerical value, we have: 1p

$$150^{1-1.25} T_3^{1.25} = 0.1^{1-1.25} (44 + 273)^{1.25} \to T_3 = 1368.6 \text{ K or } 1095.6^{\circ}\text{C}$$

incorrect final answer: -0.5p, no clear unit: -0.25p

To calculate vaporization temperature of water at 150 bar, Claperon-Calusius equation is used: 1p

$$\ln\frac{p}{p_0} = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

Ploting numerical value, we have: 1p

$$\ln\frac{150}{1} = \frac{\Delta H}{R}\left(\frac{1}{373\ \mathrm{K}} - \frac{1}{T_\mathrm{evap}}\right) \rightarrow T_\mathrm{evap} = 602.76\ \mathrm{K}\ \text{or}\ 329.76^\mathrm{o}\mathrm{C}$$

incorrect final answer: -0.5p, no clear unit: -0.25p

consider numerical error

3. The heat required to bring 1kg of water from T_2 to T_3 is calculated as: 1p

$$Q_\mathrm{in} = C_p(\text{liquid})(T_\mathrm{evap} - T_2) + \Delta H_\mathrm{evap} + C_p(\text{steam})(T_3 - T_\mathrm{evap})$$

Ploting numerical value, we have: 1p

$$Q_\mathrm{in} = 4.1816(329.76 - 50)\ \mathrm{kJ\,kg^{-1}} + 2264.7\ \mathrm{kJ\,kg^{-1}} + 1.996(1095.6 - 329.76)\ \mathrm{kJ\,kg^{-1}}$$

$$Q_\mathrm{in} = 4963.2\ \mathrm{kJ\,kg^{-1}}\ \text{or}\ \mathrm{kJ}$$

incorrect final answer: -0.5p, no clear unit: -0.25p

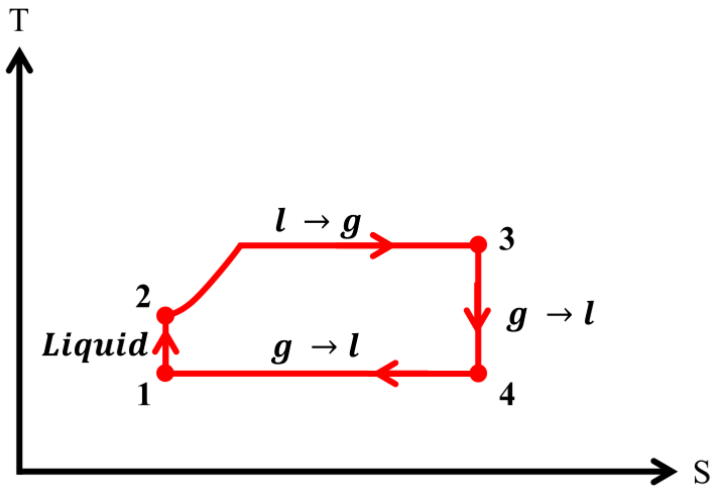
if wrong temperature value in the previous part is used here, still give points if the calculation is correct and that temperature value is stated clearly

if the degree of freedom is used to calculate Cp and that Cp value is used in the calculation, considered as wrong calculation and -1p per one related calculation

4. The new diagram: 3.5p

correct axis: 0.5p, correct states name: 0.5p, correct direction: 0.5p, correct shape: 1p, correct phase indication: 1p

shape requirement: 1-2 and 3-4 has to be vertical. 2-3 has to show the transition, 1-4 has to be horizontal. Any shape requirement not met is -0.25p



direction can be indicated by both arrow on the transformation or a circular arrow inside or outside the process, providing the direction is consistent.

for transformationincluding phase transition, mention that it is a mixture give full points, direction is not necessary

The new heat in is: 0.5p

$$Q_{\text{in}} = 4.1816(329.76 - 50)\ \text{kJ}\,\text{kg}^{-1} + 2264.7\ \text{kJ}\,\text{kg}^{-1} = 3434.5\ \text{kJ}\,\text{kg}^{-1}\ \text{or kJ}$$

PROBLÈME III NON-LINEAR BEHAVIOUR OF HENRY'S LAW 12P

1. The concentration calculated per 1 L of solution is: 1.5p

$$C_A(\text{M}) = \frac{n_A}{V_{H_2O}(\ell)} = \frac{n_A}{\frac{18\ \text{g mol}^{-1}}{1000\ \text{g}\,\ell^{-1}} \cdot n_{H_2O}} \approx \frac{55.56 n_A}{n_{\text{total}}} = 55.56 \cdot x_A$$

   Because $n_{\text{total}} = n_A + n_{H_2O} \approx n_{H_2O}$ in the extreme diluted limit.

   formula: 0.5p, mention assumption: 0.5p, final result 0.5p

   The Henry constant is: 0.5p

$$K_H = \frac{p_A}{x_A} = \frac{55.56 \cdot p_A}{C_A} = 55.56 \cdot K_{\text{eq}}$$

   if the derivation is compounded, give full point if the pressure is presented and the approximation is presented

   At the given condition: 2p

$$K_{\text{eq}} = \frac{2 \cdot 10^{-8}}{57.6 \cdot 10^{-6}} = 3.472 \cdot 10^{-4}\ \text{atm M}^{-1} \text{ and } K_H = 55.56 \cdot K_{\text{eq}} = 1.93 \cdot 10^{-2}\ \text{atm}$$

   each result 0.5p

   no clear unit for eq constant: -0.25p

2. The relationship between the equilibrium constant and ΔG^o is: 2.5p

$$\Delta G^o = -RT \ln K_{\text{eq}} = -RT \ln \frac{K_H}{55.56} \equiv \Delta H^o - T\Delta S^o$$

   relation between Gibbs free energy and Keq is 1p, mentioning enthalpy and entropy is 1p

$$\ln K_H = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} + \ln 55.56$$

   final formula is 0.5p

   accept final answer without calculating the coefficient, as long as the formula writen is consistent with how the coefficient is calculatetd

3. The Henry constant at the new temperature is calculated as: 1p

$$K'_{\mathrm{H}} = \frac{55.56 \cdot p'_{\mathrm{A}}}{C_{\mathrm{A}}} = \frac{55.56 \cdot 1.1 \cdot 10^{-8}}{57.6 \cdot 10^{-6}} = 1.06 \cdot 10^{-2}\ \mathrm{atm}$$

   incorrect final answer: -0.5p

   With the relationship between Henry constant and tempeprature, it is possible to derive the formula to calculate ΔH^o: 1.5p

$$\ln \frac{K_{\mathrm{H}}}{K'_{\mathrm{H}}} = \frac{\Delta H^o}{R}\left(\frac{1}{T'} - \frac{1}{T}\right) \rightarrow \Delta H^o = 53.82\ \mathrm{kJ\,mol^{-1}}$$

   formula: 1p, final result 0.5p

   no clear unit: -0.25p, wrong sign: -0.25p

   if the formula to calculate ΔH^o is given using eq constant instead, still give full mark, which is 1p.

   From here we canculate ΔS^o: 1p

$$\Delta S^o = R \ln\left(\frac{K_{\mathrm{H}}}{55.56}\right) + \frac{\Delta H^o}{T} = 114.38\ \mathrm{J\,mol^{-1}\,K^{-1}}$$

   no clear unit: -0.25p, wrong sign: -0.25p

   If wrong calculation ΔS^o is from different unit of equilibrium constant, -0.5p for wrong result

   if the students establish two linear equation for solving ΔH and ΔS correctly, counts as correct formular for both ΔH and ΔS and give 1.5p.

4. The new equilibrium decrease the amount of unreacted HCHO in the solution. 1p

   According the Le Chatelier principle, this will shift the dilution equilrium to the left, meaning that more HCHO is produced in aqueous state. 1p

   not mentioning Le Chatelier principle: -0.5p

   maximum deduction for final result is 0.5p

Problème IV osmotic pressure 15p

1. Osmotic pressure across the semipermeable membrane is calculated as: 1p

$$\Pi = RTiM$$

Ploting numerical value, we have: 1/2p

$$\begin{aligned}\Pi = 8.314\frac{\mathrm{J}}{\mathrm{mol\ K}} \cdot 298\ \mathrm{K} \cdot 2 \cdot 0.6\ \mathrm{mM} &= 2973.09\ \mathrm{kPa} \\ &= 2973.09\ \mathrm{J/L} \\ &= 29.73\ \mathrm{bar}\end{aligned}$$

The resulting force points downward (sweet water -> salt water) 1/2p

no units: -0.25p; wrong units (Pa instead of kPa): -0.25

accept pressure value in all unit, as long as it is specified

2. At the membrane, there are three forces applied: gravity forces and osmotic pressure applied downward, and a force from the water applied upward: 0.5p

$$F_A = F_g + \Pi \cdot Area$$

Where $Area$ is the area of the membrane surface.

Solving this equation, we will have:

$$\rho_{\text{salt water}} g V_{\text{displaced volume}} = \rho_{\text{sweet water}} g V_{\text{sweet water}} + RTiM \cdot Area$$

$$\rho_{\text{salt water}} g h_o = \rho_{\text{sweet water}} g h_i + RTiM$$

$$h_i = \frac{\rho_{\text{salt water}}}{\rho_{\text{sweet water}}} h_o - \frac{RTiM}{\rho_{\text{sweet water}} g}$$

1.5p

3. Using the aboved formula, we have:

For $h_o = 1$ m, $h_i = -302.35$ m. 1p

For $h_o = 500$ m, $h_i = 209.12$ m. 1p

incorrect final answer: -0.5p, no unit: -0.25p, wrong sign: -0.25p

Wrong numerical values bc. of mistake in question 1: full points

4. A negative h_i value means water does not yet enter the tube. 1p

   A positive h_i value means water start to enter the tube. 1p

   explanation is not needed, only the physical observation is needed, and have to be stated clearly.

   0.5p each if there are explanation, but does not yet arrive at the physical observation.

5. h_i can increase linearly with h_o without any limit. 1p

   When $h_i = h_o$, we have: 1p

$$h_o \left(\frac{\rho_{\text{salt water}}}{\rho_{\text{sweet water}}} - 1 \right) = \frac{RTiM}{\rho_{\text{sweet water}} g}$$

$$h_o = 12135.05 \text{ m}$$

   incorrect final answer: -0.5p, no clear unit: -0.25p

   Correct calculation but incorrect numerical value bc of mistake in 1: full points

6. 5p

   It is not possible to construct such a machine.

   The implicit assumption here is that the salt concentration around the membrane does not change over time, thereby keeping the osmosis pressure constant.

   Mention of:

   - Perpetual motion (viol. of 2nd principle) 2p
   - violation of a TD principle 1p
   - technical difficulties 1p
   - depth of ocean 1p