

Thermodynamics tutorhour 8

January 13nd 2022

Preparation for the exam:
Tips and Tricks

Structure of the exam

In recent years the exam consisted of four exercises, each with four questions. For each question the maximum score was five points.

Exercise 1:

Formulas (four questions)

- Some definitions or descriptions of concepts
- Quantities: is it a state function or not?
- Explaining symbols and explaining when an equation is applicable.
- Application of a concept (example: reversible, irreversible)
- Simple calculation with a given equation

Exercise 2:

Electrochemical reactions and electrochemical cells (four questions)

- Expressing a reaction in terms of half-reactions
 - NB: half-reactions are frequently noted as reduction reactions (with the electrons on the left side of the chemical equation)
- Prediction of the direction of the electrochemical reaction, when producing current or during charging.
- Calculation of the standard potential (E^θ)
- Calculation of the standard electromotive force of a electrochemical cell (E_{cel}^θ)
- Calculations, using the Nernst equation.
- Calculations, using Ohm's law.
- Calculation of the potential E or Gibbs free energy: $\Delta_r G = - \nu F E$
- Calculation of equilibria: $\Delta_r G^\theta = - RT \ln K$
- Calculation of the relative yield

Simple introduction to EMF/Voltage:

<http://www.roelhendriks.eu/Natuurkunde/w2L%20elektronica/elektronica%20theorie.pdf>

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Subject IV: Carnot engine and relative yield

- $Q_1/Q_2 = -T_1/T_2$
- $\eta = 1 - T_c/T_h$

How to pass the thermodynamics exam?

Although the thermodynamics course is difficult, the exam is not impossible.

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These are all learning issues. Study hard and score all the points!

Don't let yourself down!

Glossary

Microscopic On an atomic or molecular scale.

Macroscopic Seen from a helicopter view, in such a way that we can forget about microscopic processes (averaging).

System That part of the universe in which we are interested; we only consider macroscopic systems with many particles. thermodynamics.

Surroundings The rest of the universe we need to allow exchange of matter or energy with the system; is also a system, but not *the* system.

Thermal bath A heat reservoir (usually as surroundings), from which you can extract heat or to which you can deliver heat, without changing the temperature of the reservoir.

State variables Macroscopic quantities (P, V, T, n, \dots) that describe the thermodynamic state of a system. For a complete description a minimal amount of (independent) state variables is required.

Equation of state Relation between state variables that determines the possible states of the system in thermodynamic equilibrium.

Thermodynamic equilibrium A system is in thermodynamic equilibrium if the state variables of the system do not change spontaneously.

State function A (thermodynamic) single valued function of the (independent) state variables; The value of a state function is independent of the way the system has reached a certain state.

Reversible process A process during which the system is in thermodynamic equilibrium at every moment; with that a reversible process is also reversible.

Formulae

Boundary conditions

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$dW = -P_{ext}.dV + dW' \quad \text{and} \quad dW'_{max} = (dG)_{P,T}$$

$$dQ|_P = C_P dT \quad \text{and} \quad dQ|_V = C_V dT$$

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$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

$$dS_{tot} = dS + dS_{env} \geq 0$$

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Put effort in this [checklist of key equations](#).

Do you know the realm of the equations?

Do you know what all the symbols stand for?

Do you know the boundary conditions of the equations?

Formulae

Boundary conditions

$$A = U - TS$$

$$dA = -PdV - SdT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta_r G^\ominus + RT \ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT \ln K = -\Delta_r G^\ominus$$

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad dW' = Edq \quad \text{furthermore} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^\ominus + RT \ln a_i = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j d\mu_j = 0$$

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G is an important function, when p and T are constant

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Q is analog to the chemical equilibrium quotient

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Formulae

Boundary conditions

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{trs}}H} \right) x_B$$

$$\Delta S = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Pi = [B]RT = \frac{n_B}{V}RT$$

$$S = k \ln W$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q} \quad \text{with} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad \langle X \rangle = N \langle x \rangle = N \sum_i x_i \frac{n_i}{N}$$

Formulae

Boundary conditions

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Depression of freezing point or elevation of boiling point relative to T^*
Only if: perfect mixture, low concentrations

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Your own checklist of key equations: Molar fraction

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Partial pressure

$$\Pi = \rho \cdot g \cdot h$$

Molality

$$dH = c_p dT$$

$$\Delta_r G = -vF \Delta E_{\text{cell}}$$

$$\Delta H = Q \text{ (at constant pressure)}$$

$$\eta = 1 - T_c/T_h$$

$$\eta = R_L/(R_L + R_i)$$

$$E_L = E_{EMF} \cdot R_L/(R_i + R_L)$$

$$E = hc/\lambda \quad \text{etcetera}$$

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Or leading to a function above:

$Q + W (= U)$

$S_{\text{tot}} - S_{\text{sur}} (= S_{\text{sys}})$

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When a complicated formula is involved:

- Which variables are kept constant (isothermic, isobaric, ...).
- Can you simplify integrals by putting independent variables in front of the integral sign?
- Can you simplify the equation by using some sensible approximations?

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Which equations are relevant for this subject?

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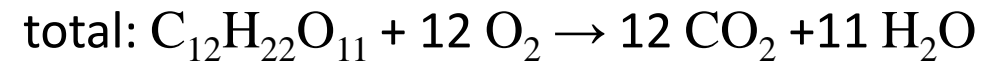
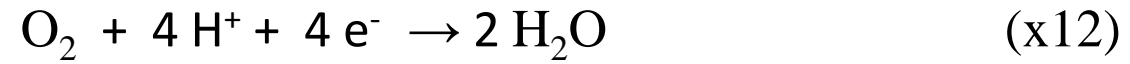
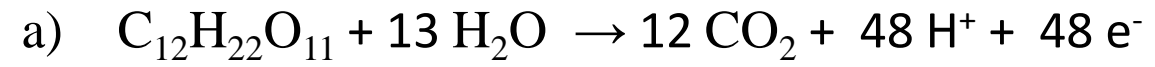
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Some questions start with: “*Estimate ...*”

That means you can make some sensible approximations.

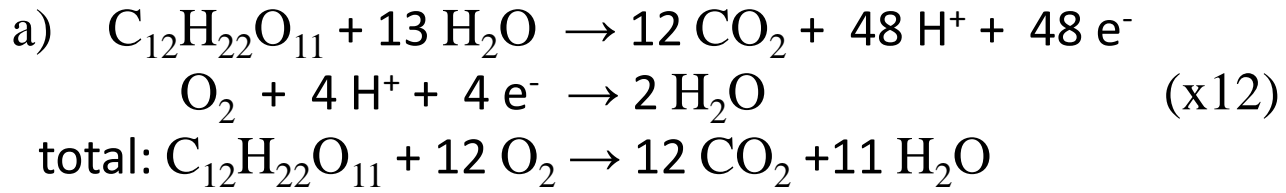
Answers

Question 1



Answers

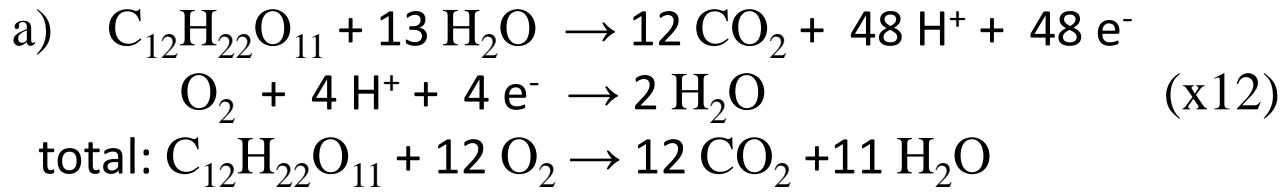
Question 1



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$$\Delta E_{cell}^{\theta} = E_{+pole}^{\theta} - E_{-pole}^{\theta}$$
$$1.37 = 1.23 - E_{-pole}^{\theta}$$
$$E_{-pole}^{\theta} = -0.14 \text{ V}$$

Answers

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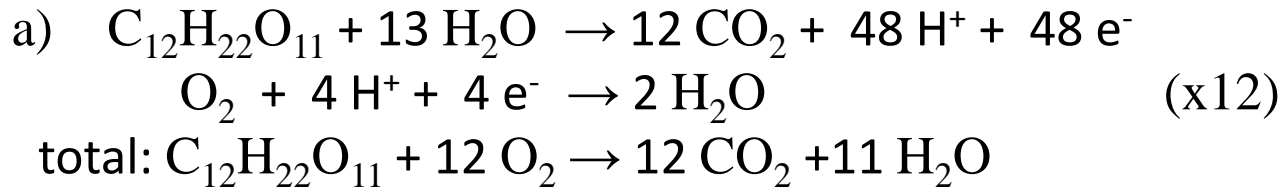
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c)
$$\Delta E_{cell} = \Delta E_{cell}^{\ominus} - \frac{RT}{\nu F} \ln Q = 1.37 - \frac{RT}{\nu F} \ln \frac{a_{\text{CO}_2}^{12} \cdot a_{\text{H}_2\text{O}}^{11}}{a_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} \cdot a_{\text{O}_2}^{12}}$$

$$a_{gas} = \frac{p_{gas}}{p^{\ominus}} \quad \text{and} \quad a_{\text{H}_2\text{O}} = a_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 1$$

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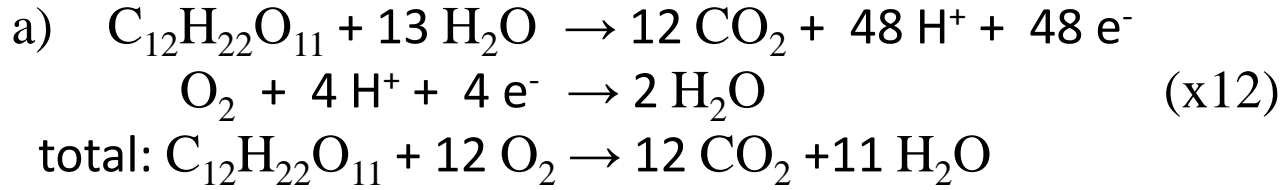
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$$\Delta E_{cell} = 1.37 - \frac{8.3145 \cdot 298}{48 \cdot 9.648 \cdot 10^4} \ln \frac{1^{12} \cdot 1^{11}}{1 \cdot 0,212^{12}} = 1,36 \text{ V}$$

Answers

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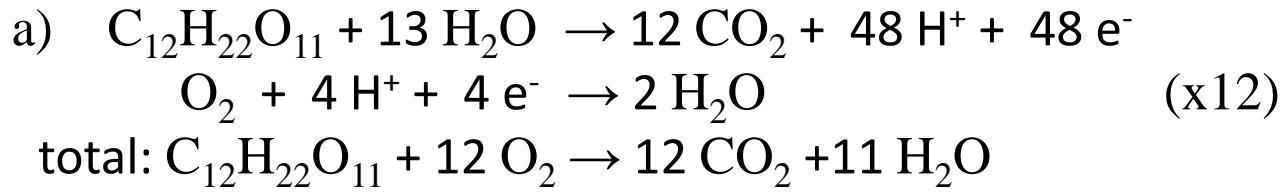
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d) $E = I \cdot R \quad I = \frac{E}{R} = \frac{1.28 V}{2 \cdot 10^3 \Omega} = 6.4 \cdot 10^{-4} A$, this means $6.4 \cdot 10^{-4} C$ per second

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c)
$$E_{-pole}^{\theta} = -0.14 \text{ V}$$
$$\Delta E_{cell} = \Delta E_{cell}^{\theta} - \frac{RT}{\nu F} \ln Q = 1.37 - \frac{RT}{\nu F} \ln \frac{a_{\text{CO}_2}^{12} \cdot a_{\text{H}_2\text{O}}^{11}}{a_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} \cdot a_{\text{O}_2}^{12}} \quad a_{gas} = \frac{p_{gas}}{p^{\ominus}} \quad \text{and} \quad a_{\text{H}_2\text{O}} = a_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 1$$

$$\Delta E_{cell} = 1.37 - \frac{8.3145 \cdot 298}{48 \cdot 9.648 \cdot 10^4} \ln \frac{1^{12} \cdot 1^{11}}{1 \cdot 0,212^{12}} = 1,36 \text{ V}$$

d)
$$E = I \cdot R \quad I = \frac{E}{R} = \frac{1.28 \text{ V}}{2 \cdot 10^3 \Omega} = 6.4 \cdot 10^{-4} \text{ A, this means } 6.4 \cdot 10^{-4} \text{ C per second}$$

$$\# \text{ e}^- = \frac{6.4 \cdot 10^{-4} \text{ C}}{1.602 \cdot 10^{-19} \text{ C/electron}} = 4 \cdot 10^{15} = \# \text{ protons}$$

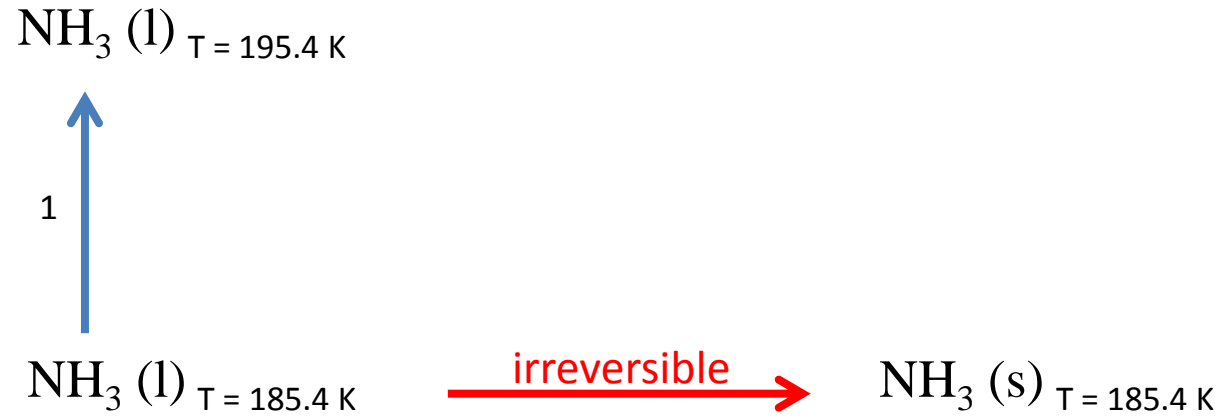
Question 2

a) A reversible path as an alternative for the process:



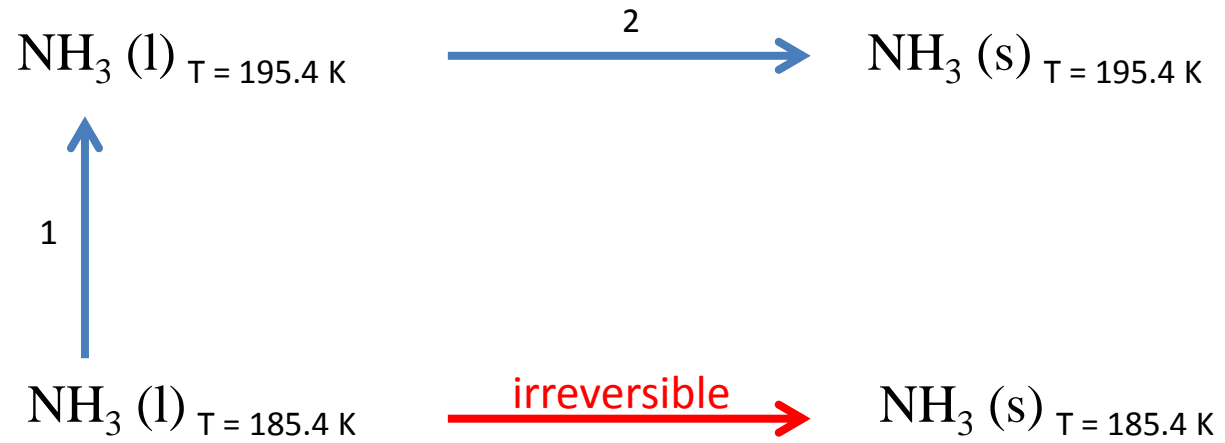
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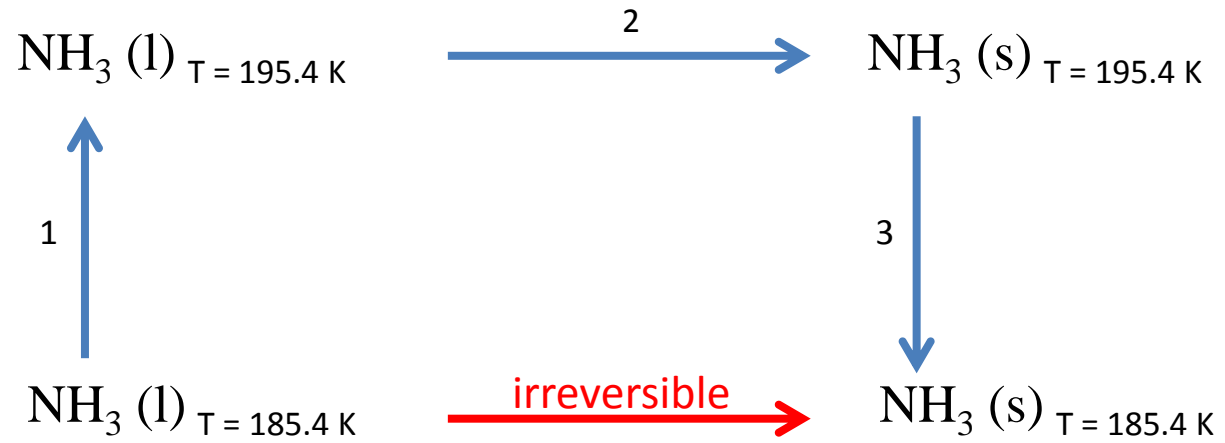
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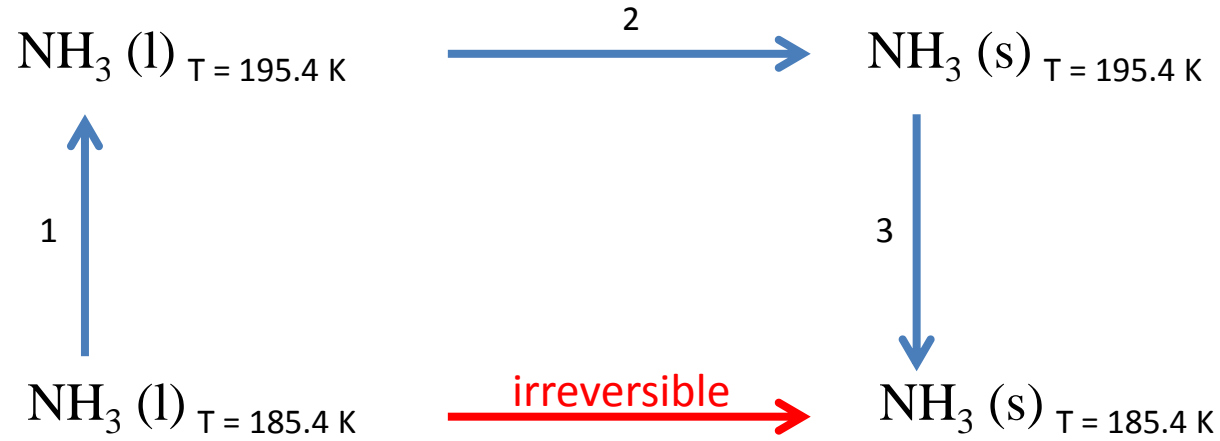
Question 2

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Question 2

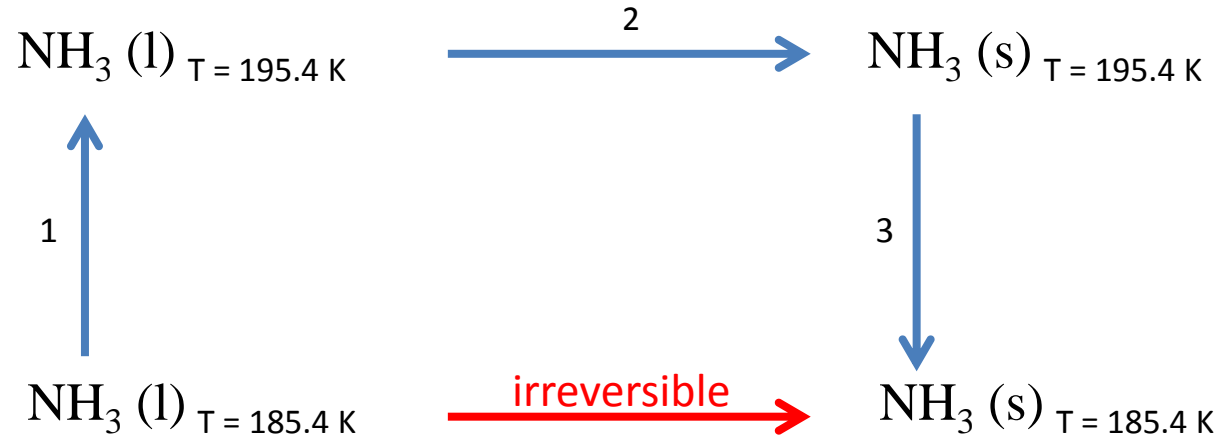
a) A reversible path as an alternative for the process:



b) $dH = \int C_p dT$ C_p not dependent on T , so $dH = C_p \int dT$
and $\Delta H = C_p \Delta T$

Question 2

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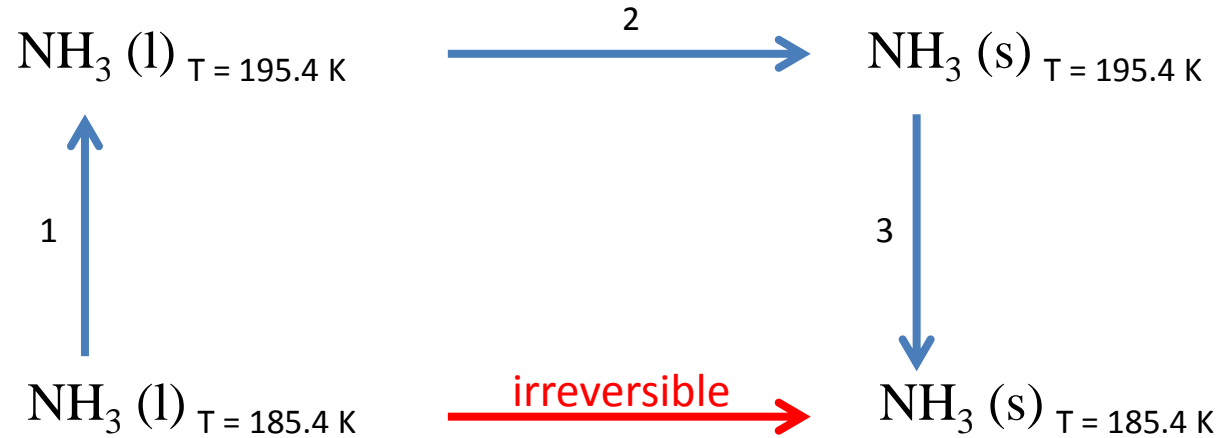


b) $dH = \int C_p dT$ C_p not dependent on T , so $dH = C_p \int dT$
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$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Question 2

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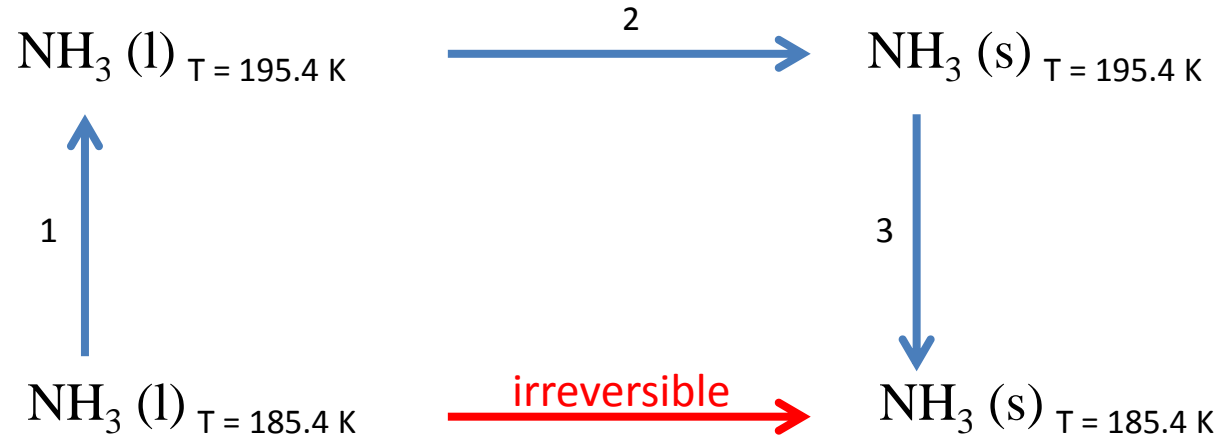


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$$\Delta H = C_{p(\text{liquid})}\Delta T + \Delta H_2 + C_{p(\text{solid})}\Delta T$$

Question 2

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b) $dH = \int C_p dT$ C_p not dependent on T , so $dH = C_p \int dT$
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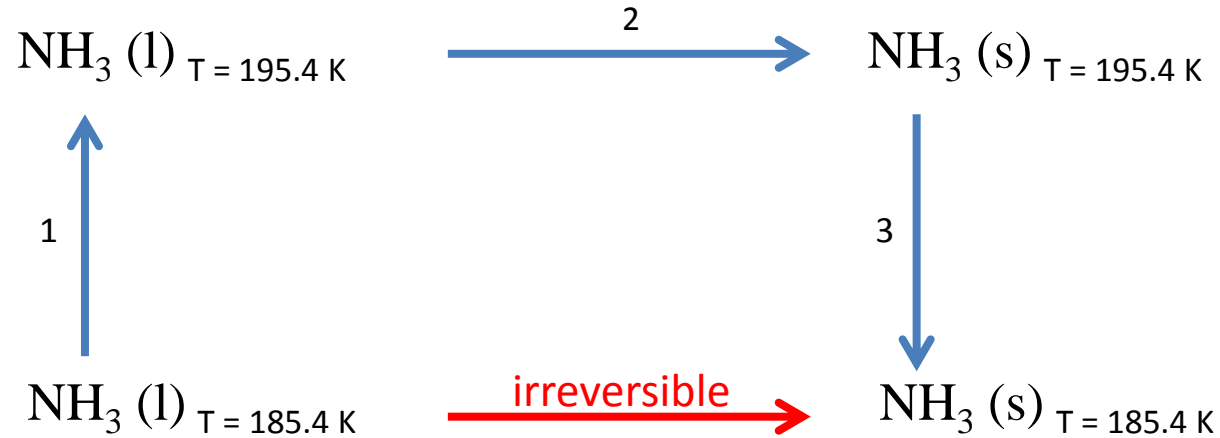
$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H = C_{p(\text{liquid})}\Delta T + \Delta H_2 + C_{p(\text{solid})}\Delta T$$

$$\Delta H = 75.3 \times 10 - 5\,652 + 30.0 \times (-10) = -5\,199 \text{ J/mol}$$

Question 2

a) A reversible path as an alternative for the process:



b) $dH = \int C_p dT$ C_p not dependent on T , so $dH = C_p \int dT$
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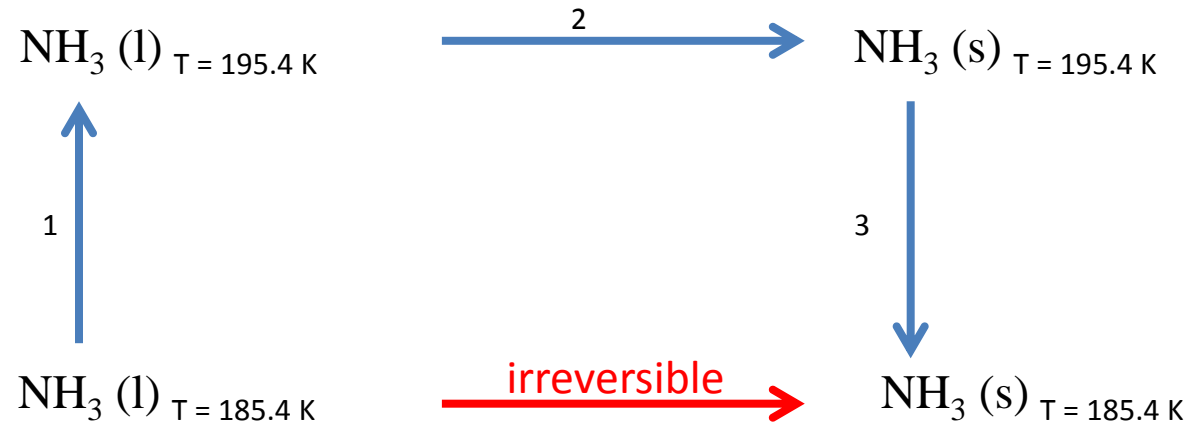
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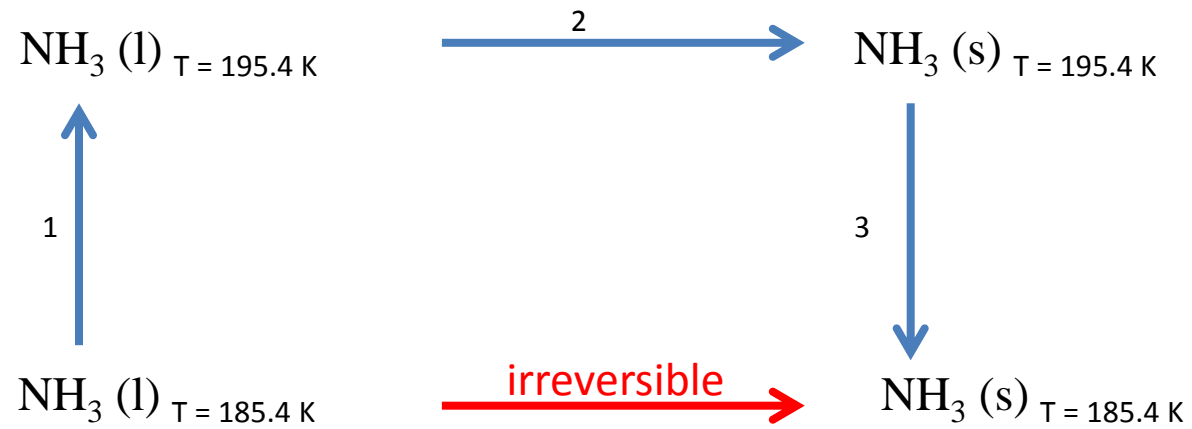
$$\Delta H_{fus} = +5\,199 \text{ J/mol}$$

c) The alternative path:



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

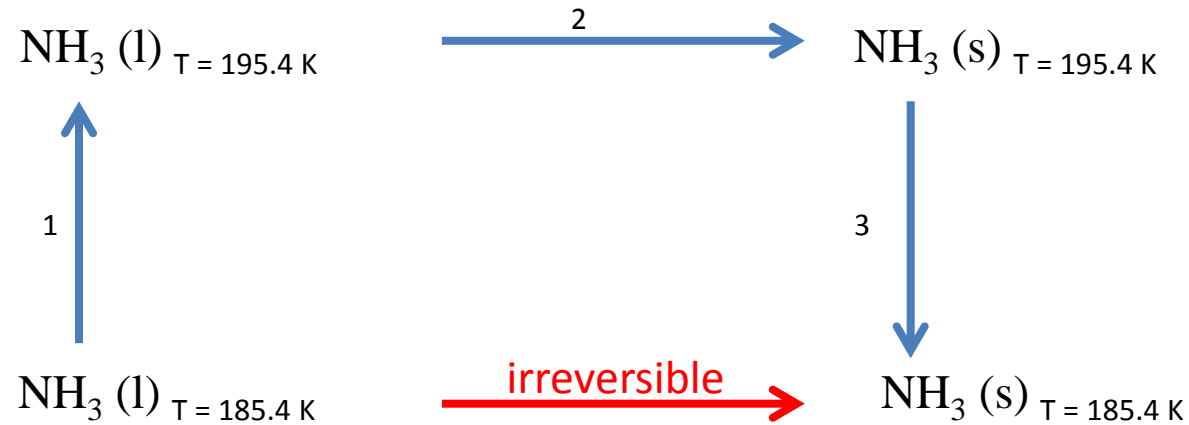
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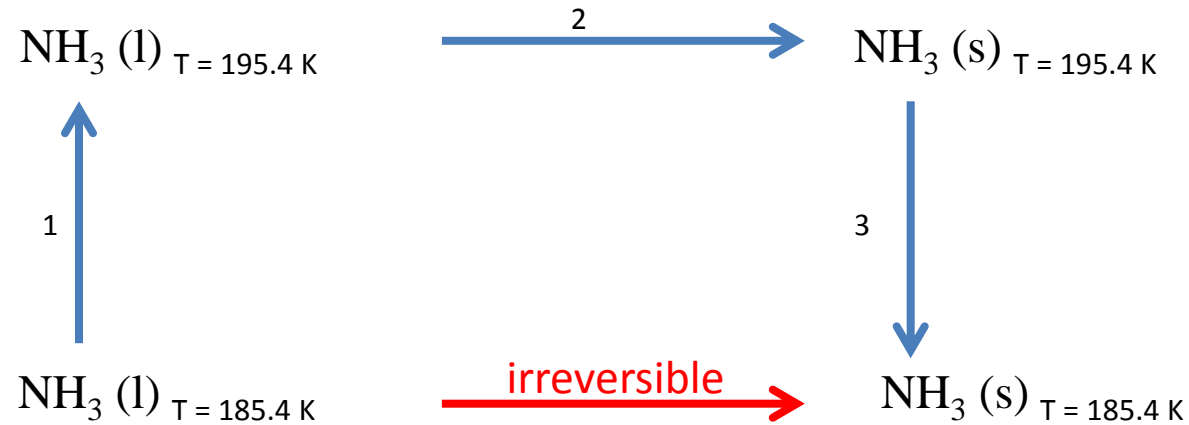
$$dS = \int \frac{C_{p(\text{l})}}{T} dT + \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} + \int \frac{C_{p(\text{s})}}{T} dT$$

c) The alternative path:



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$
$$dS = \int \frac{C_{p(\text{l})}}{T} dT + \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} + \int \frac{C_{p(\text{s})}}{T} dT$$
$$\Delta S = 75.3 \ln \frac{195.4}{185.4} + \frac{-5652}{195.4} + 30.0 \ln \frac{185.4}{195.4}$$
$$\Delta S = -26.55 \text{ J/mol}\cdot\text{K}$$

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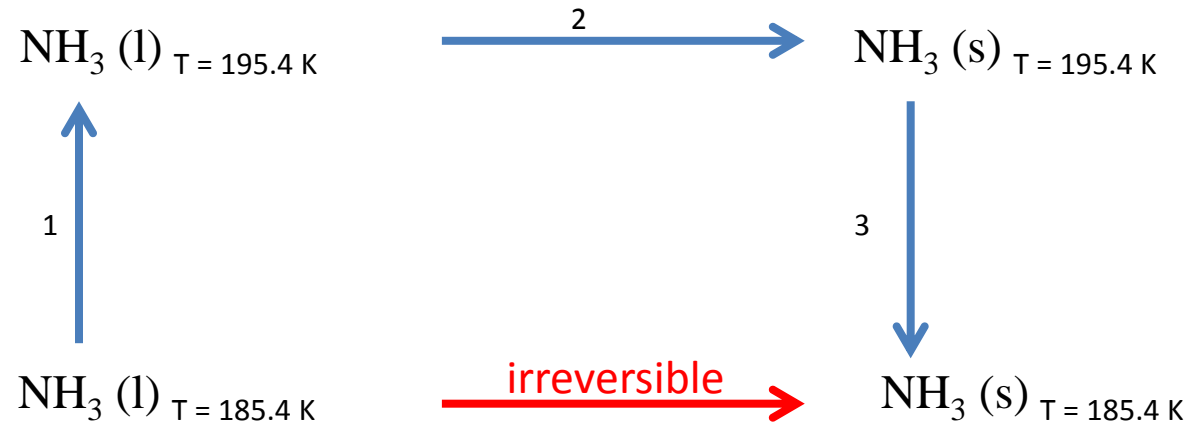
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d) $\frac{Q}{T} = \frac{-5199}{185.4} = -28.04 \text{ J/mol}\cdot\text{K}$

c) The alternative path:



$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

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$$\Delta S = -26.55 \text{ J/mol}\cdot\text{K}$$

d) $\frac{Q}{T} = \frac{-5199}{185.4} = -28.04 \text{ J/mol}\cdot\text{K} \Rightarrow \Delta S > \frac{Q}{T}$ as the Clausius inequality predicts