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 ($E_{\mathrm{cel}}{}^{\theta}$)
- Calculations, using the Nernst equation.
- Calculations, using Ohm’s law.
- Calculation of the potential *E* or Gibbs free energy: $\Delta_r G = - \nu \mathrm{F} E$
- Calculation of equilibria: $\Delta_r G^{\theta} = - \mathrm{RT} \ln \mathrm{K}$
- Calculation of the relative yield

Simple introduction to EMF/Voltage:

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

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- elevation of boiling point
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Subject III: Statistical thermodynamics

- partition function
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Subject IV: Carnot engine and relative yield

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

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Consists of a number of learning issues:

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- What do the symbols in the equation stand for?
- Explain the formula.

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These are all learning issues. Study hard and score all the points!
Don’t let yourself down!

Appendix B

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 $(P, V, T, n, \cdots)$ 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

$$PV = nRT = NkT$$

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

$$\Delta U = W + Q$$

$$\mathrm{d}W = -P_{ext.}\mathrm{d}V + \mathrm{d}W' \quad \text{and} \quad \mathrm{d}W'_{max} = (\mathrm{d}G)_{P,T}$$

$$\mathrm{d}Q|_P = C_P\mathrm{d}T \quad \text{and} \quad \mathrm{d}Q|_V = C_V\mathrm{d}T$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} \geq \frac{\mathrm{d}Q}{T}$$

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$$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + \sum_i \mu_i \mathrm{d}n_i$$

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Only if mono-atomic perfect gas (no vibration nor rotations).

Differentiation gives: $C_v = 3/2\,R$

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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

$$A = U - TS$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

$$G = H - TS$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$$

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

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

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad \mathrm{d}W' = E\mathrm{d}q \quad \text{furthermore} \quad E = IR \quad \text{and} \quad P = EI$$

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

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

$$\sum_j n_j \mathrm{d}\mu_j = 0$$

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

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

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

$$S = k \ln W$$

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

Formulae

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

Depression of freezing point or elevation of boiling point relative to T*

Only if: perfect mixture, low concentrations

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Molar fraction

Partial pressure

Л = $\rho \cdot g \cdot h$

Molality

$dH = c_p dT$

$\Delta_r G = -\nu F \Delta E_{cell}$

$\Delta H = Q$ (at constant pressure)

$\eta = 1 - T_c/T_h$

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

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

$E = hc/\lambda$

etcetera

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Or leading to a function above:

$Q + W \quad (= U)$

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

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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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Some questions start with: “*Estimate …* “
That means you can make some **sensible approximations**.

Answers

Question 1

a) $C_{12}H_{22}O_{11}$ + 13 H_2O → 12 CO_2 + 48 H^+ + 48 e^-

O_2 + 4 H^+ + 4 e^- → 2 H_2O (x12)

total: $C_{12}H_{22}O_{11}$ + 12 O_2 → 12 CO_2 +11 H_2O

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b) $\Delta E^{\theta}_{cell} = E^{\theta}_{+pole} - E^{\theta}_{-pole}$

$1.37 = 1.23 - E^{\theta}_{-pole}$

$E^{\theta}_{-pole} = -0.14$ V

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c) $\Delta E_{\text{cell}} = \Delta E^{\Theta}_{\text{cell}} - \dfrac{\text{R}T}{\nu\text{F}} \ln Q = 1.37 - \dfrac{\text{R}T}{\nu\text{F}} \ln \dfrac{a_{CO_2}^{12} \cdot a_{H_2O}^{11}}{a_{C_{12}H_{22}O_{11}} \cdot a_{O_2}^{12}}$

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$$a_{gas} = \frac{p_{gas}}{p^{\Theta}} \quad \text{and} \quad a_{H_2O} = a_{C_{12}H_{22}O_{11}} = 1$$

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

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$1.37 = 1.23 - E^{\theta}_{-pole}$

$E^{\theta}_{-pole} = -\ 0.14$ V

c) $$\Delta E_{\text{cell}} = \Delta E^{\Theta}_{\text{cell}} - \frac{\text{R}T}{\nu \text{F}} \ln Q = 1.37 - \frac{\text{R}T}{\nu \text{F}} \ln \frac{a^{12}_{CO_2} \cdot a^{11}_{H_2O}}{a_{C_{12}H_{22}O_{11}} \cdot a^{12}_{O_2}}$$

$a_{gas} = \frac{p_{gas}}{p^{\Theta}}$ and $a_{H_2O} = a_{C_{12}H_{22}O_{11}} = 1$

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

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

Answers

Question 1

a) $C_{12}H_{22}O_{11} + 13\ H_2O \rightarrow 12\ CO_2 + 48\ H^+ + 48\ e^-$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ (x12)

total: $C_{12}H_{22}O_{11} + 12\ O_2 \rightarrow 12\ CO_2 + 11\ H_2O$

b) $\Delta E^{\theta}_{cell} = E^{\theta}_{+pole} - E^{\theta}_{-pole}$

$1.37 = 1.23 - E^{\theta}_{-pole}$

$E^{\theta}_{-pole} = -0.14\ \mathrm{V}$

c) $\Delta E_{\mathrm{cell}} = \Delta E^{\Theta}_{\mathrm{cell}} - \dfrac{\mathrm{R}T}{\nu\mathrm{F}} \ln Q = 1.37 - \dfrac{\mathrm{R}T}{\nu\mathrm{F}} \ln \dfrac{a^{12}_{CO_2} \cdot a^{11}_{H_2O}}{a_{C_{12}H_{22}O_{11}} \cdot a^{12}_{O_2}}$

$a_{gas} = \dfrac{p_{gas}}{p^{\Theta}}$ and $a_{H_2O} = a_{C_{12}H_{22}O_{11}} = 1$

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

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

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

Question 2

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

$$\mathrm{NH_3\ (l)}_{\mathrm{T\ =\ 185.4\ K}} \xrightarrow{\text{irreversible}} \mathrm{NH_3\ (s)}_{\mathrm{T\ =\ 185.4\ K}}$$

Question 2

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

$$\begin{tikzcd}
NH_3\,(l)_{\,T\,=\,195.4\ K} & \\
NH_3\,(l)_{\,T\,=\,185.4\ K} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & NH_3\,(s)_{\,T\,=\,185.4\ K}
\end{tikzcd}$$

Question 2

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

$$\begin{tikzcd}
\mathrm{NH_3\,(l)}_{\,T\,=\,195.4\ \mathrm{K}} \arrow[r, "2"] & \mathrm{NH_3\,(s)}_{\,T\,=\,195.4\ \mathrm{K}} \\
\mathrm{NH_3\,(l)}_{\,T\,=\,185.4\ \mathrm{K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\,(s)}_{\,T\,=\,185.4\ \mathrm{K}}
\end{tikzcd}$$

Question 2

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

$$\begin{tikzcd}
NH_3\,(l)_{\ T\,=\,195.4\ K} \arrow[r, "2"] & NH_3\,(s)_{\ T\,=\,195.4\ K} \arrow[d, "3"'] \\
NH_3\,(l)_{\ T\,=\,185.4\ K} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & NH_3\,(s)_{\ T\,=\,185.4\ K}
\end{tikzcd}$$

Question 2

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

$$\begin{tikzcd}
\mathrm{NH_3\ (l)}\ _{\mathrm{T\,=\,195.4\ K}} \arrow[r, "2"] & \mathrm{NH_3\ (s)}\ _{\mathrm{T\,=\,195.4\ K}} \arrow[d, "3"'] \\
\mathrm{NH_3\ (l)}\ _{\mathrm{T\,=\,185.4\ K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\ (s)}\ _{\mathrm{T\,=\,185.4\ K}}
\end{tikzcd}$$

b) $\mathrm{d}H = \int \mathrm{C_p}\, \mathrm{d}T$ $\mathrm{C_p}$ not dependent on T, so $\mathrm{d}H = \mathrm{C_p} \int \mathrm{d}T$

and $\Delta H = \mathrm{C_p}\, \Delta T$

Question 2

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

$$\begin{tikzcd}
NH_3\,(l)_{\,T = 195.4\ K} \arrow[r, "2"] & NH_3\,(s)_{\,T = 195.4\ K} \arrow[d, "3"] \\
NH_3\,(l)_{\,T = 185.4\ K} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & NH_3\,(s)_{\,T = 185.4\ K}
\end{tikzcd}$$

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

and $\Delta H = C_p\, \Delta T$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Question 2

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

$$\begin{tikzcd}
\mathrm{NH_3\,(l)}_{\mathrm{T\,=\,195.4\,K}} \arrow[r, "2"] & \mathrm{NH_3\,(s)}_{\mathrm{T\,=\,195.4\,K}} \arrow[d, "3"] \\
\mathrm{NH_3\,(l)}_{\mathrm{T\,=\,185.4\,K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\,(s)}_{\mathrm{T\,=\,185.4\,K}}
\end{tikzcd}$$

b) $\mathrm{d}H = \int \mathrm{C_p}\,\mathrm{d}T$ $\quad$ $\mathrm{C_p}$ not dependent on T, so $\mathrm{d}H = \mathrm{C_p} \int \mathrm{d}T$

and $\Delta H = \mathrm{C_p}\,\Delta T$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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

Question 2

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

$$\begin{tikzcd}
NH_3\,(l)_{\;T\,=\,195.4\,K} \arrow[r, "2"] & NH_3\,(s)_{\;T\,=\,195.4\,K} \arrow[d, "3"] \\
NH_3\,(l)_{\;T\,=\,185.4\,K} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & NH_3\,(s)_{\;T\,=\,185.4\,K}
\end{tikzcd}$$

b) $\mathrm{d}H = \int C_p\, \mathrm{d}T$ $\quad$ C_p not dependent on T, so $\mathrm{d}H = C_p \int \mathrm{d}T$

and $\Delta H = C_p\, \Delta T$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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

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

Question 2

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

$$\begin{tikzcd}
\mathrm{NH_3\ (l)}_{\ T\,=\,195.4\ \mathrm{K}} \arrow[r, "2"] & \mathrm{NH_3\ (s)}_{\ T\,=\,195.4\ \mathrm{K}} \arrow[d, "3"'] \\
\mathrm{NH_3\ (l)}_{\ T\,=\,185.4\ \mathrm{K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\ (s)}_{\ T\,=\,185.4\ \mathrm{K}}
\end{tikzcd}$$

b) $\mathrm{d}H = \int \mathrm{C_p}\, \mathrm{d}T$ $\mathrm{C_p}$ not dependent on T, so $\mathrm{d}H = \mathrm{C_p} \int \mathrm{d}T$

and $\Delta H = \mathrm{C_p}\, \Delta T$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

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

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

$$\Delta H_{fus} = +\,5\,199 \text{ J/mol}$$

c) The alternative path:

$$\begin{tikzcd}
\mathrm{NH_3\ (l)}\ _{T\,=\,195.4\text{ K}} \arrow[r, "2"] & \mathrm{NH_3\ (s)}\ _{T\,=\,195.4\text{ K}} \arrow[d, "3"'] \\
\mathrm{NH_3\ (l)}\ _{T\,=\,185.4\text{ K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\ (s)}\ _{T\,=\,185.4\text{ K}}
\end{tikzcd}$$

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

c) The alternative path:

$$\begin{tikzcd}
\mathrm{NH_3\,(l)}_{\ T\,=\,195.4\ \mathrm{K}} \arrow[r, "2"] & \mathrm{NH_3\,(s)}_{\ T\,=\,195.4\ \mathrm{K}} \arrow[d, "3"'] \\
\mathrm{NH_3\,(l)}_{\ T\,=\,185.4\ \mathrm{K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\,(s)}_{\ T\,=\,185.4\ \mathrm{K}}
\end{tikzcd}$$

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

$$\mathrm{d}S = \int \frac{C_{p\,(l)}}{T}\,\mathrm{d}T + \frac{\Delta H_{\mathrm{trans}}}{T_{\mathrm{trans}}} + \int \frac{C_{p\,(s)}}{T}\,\mathrm{d}T$$

c) The alternative path:

$$\begin{tikzcd}
\mathrm{NH_3\,(l)}_{\text{T = 195.4 K}} \arrow[r, "2"] & \mathrm{NH_3\,(s)}_{\text{T = 195.4 K}} \arrow[d, "3"] \\
\mathrm{NH_3\,(l)}_{\text{T = 185.4 K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\,(s)}_{\text{T = 185.4 K}}
\end{tikzcd}$$

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

$$\mathrm{d}S = \int \frac{C_{p\,(l)}}{T}\mathrm{d}T + \frac{\Delta H_{trans}}{T_{trans}} + \int \frac{C_{p\,(s)}}{T}\mathrm{d}T$$

$$\Delta S = 75.3 \ln \frac{195.4}{185.4} + \frac{-5\,652}{195.4} + 30.0 \ln \frac{185.4}{195.4}$$

$$\Delta S = -26.55 \text{ J/mol·K}$$

c) The alternative path:

$$\begin{tikzcd}
\mathrm{NH_3\ (l)}_{\ \mathrm{T = 195.4\ K}} \arrow[r, "2"] & \mathrm{NH_3\ (s)}_{\ \mathrm{T = 195.4\ K}} \arrow[d, "3"'] \\
\mathrm{NH_3\ (l)}_{\ \mathrm{T = 185.4\ K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\ (s)}_{\ \mathrm{T = 185.4\ K}}
\end{tikzcd}$$

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

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

$$\Delta S = 75.3 \ln \frac{195.4}{185.4} + \frac{-5\,652}{195.4} + 30.0 \ln \frac{185.4}{195.4}$$

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

d) $$\frac{Q}{T} = \frac{-5\,199}{185.4} = -28.04\ \mathrm{J/mol{\cdot}K}$$

c) The alternative path:

$$\begin{tikzcd}
\mathrm{NH_3\ (l)}\ {}_{T\,=\,195.4\ \mathrm{K}} \arrow[r, "2"] & \mathrm{NH_3\ (s)}\ {}_{T\,=\,195.4\ \mathrm{K}} \arrow[d, "3"] \\
\mathrm{NH_3\ (l)}\ {}_{T\,=\,185.4\ \mathrm{K}} \arrow[u, "1"] \arrow[r, "\text{irreversible}"] & \mathrm{NH_3\ (s)}\ {}_{T\,=\,185.4\ \mathrm{K}}
\end{tikzcd}$$

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

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

$$\Delta S = 75.3 \ln \frac{195.4}{185.4} + \frac{-5\,652}{195.4} + 30.0 \ln \frac{185.4}{195.4}$$

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

d) $\dfrac{Q}{T} = \dfrac{-5\,199}{185.4} = -28.04\ \mathrm{J/mol{\cdot}K} \quad \Rightarrow \quad \Delta S > \dfrac{Q}{T}$ as the Clausius inequality predicts