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Examination, Thermodynamics B, 6 hp, 2025–01–13 at 8:00–14:00.

Allowed aids: Calculator, Beta, Physics Handbook, English dictionary.

Hand in each problem on a separate page.
The calculations and the reasoning should be easy to follow. *Good luck!*
Note that the given solutions are sometimes too short to give full points at an exam.

1 Hair dryer

Calculate the power required for a hair dryer with an outgoing air flow of (4p)
$\Phi = 25\ell/\text{s}$ to increase the temperature of the air by $\Delta T = 30°$C. You should
only make use of the equations in the formula sheet on the last pages of
the exam. For simplicity, take the temperature of the incoming air to be
$T_{\text{in}} = 27\,°$C. *Hint:* first calculate the relation between V and Q.

> **Solution:** Since the air is heated at constant pressure the proper
> quantity to use is C_P. The needed heat is
>
> $$Q = C_P \Delta T = \left(\frac{f}{2} + 1 \right) N k_B \Delta T.$$
>
> At temperature $T_{\text{out}} = T_{\text{in}} + \Delta T = 330$ K we can determine the
> number of particles for the volume V and the required power for
> the flow $\Phi = dV/dt$ becomes
>
> $$\frac{dQ}{dt} = \left(\frac{f}{2} + 1 \right) \frac{P}{T_{\text{out}}} \frac{dV}{dt} \Delta T = 795 \approx 800W.$$

2 The Sackur-Tetrode equation—consistency test

The entropy of a monatomic ideal gas is (4p)

$$S = N k_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$

In an adiabatic process the entropy should be unchanged and a consistency
test for the above expression is that S is indeed unchanged during an adia-
batic process. Show that by starting from

$$PV^\gamma = \text{const},$$

that holds for adiabatic processes.

Solution: The equation for the adiabatic process may be written

$$\text{const} = PV^{\gamma} = PVV^{\gamma-1} = Nk_BTV^{\gamma-1} \Rightarrow \text{const} = VT^{1/(\gamma-1)} = VT^{f/2}.$$

We also have $U = (f/2)Nk_BT$ which means that $U/N = \text{const} \times T$. When using that in the Sackur-Tetrode equation we find

$$S = Nk_B\left[\ln\left(\frac{V}{N}(CT)^{3/2}\right) + \frac{5}{2}\right], \quad C = \frac{4\pi m}{3h^2},$$

and since $VT^{3/2} = \text{const}$ this expression is a constant in an adiabatic process.

3 Heat capacity formula

Use the thermodynamic identity to derive the heat capacity formula (2p)

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V.$$

Then derive a similar formula for C_P, by first writing dH in terms of dS and dP.

Solution: Start from $dH = TdS + VdP$ to get

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

4 Heat engine

Consider an engine cycle for an ideal diatomic gas with the following three steps:

$1 \to 2$ adiabatic compression from V_1 to V_2,

$2 \to 3$ isothermal expansion to the original volume at temperature T_2,

$3 \to 1$ cooling from T_2 to T_1 at constant volume.

a) Make a reasonably correct sketch of this cycle in a *P-V* diagram that (1p) includes the volumes V_1 and V_2. Also show at which stages heat is entering and leaving the process by putting in arrows for Q_h and Q_c.

> **Solution:** Heat enters at step $2 \to 3$. Heat leaves in the cooling at step $3 \to 1$. The isotherm should be close to (well, not altogether different from) a $1/V$ curve. Step $3 \to 1$ should be a vertical line.

b) Calculate the amount of work and heat for each step of the cycle, (2p)

> **Solution:** We have an adiabatic compression which should leave $PV^\gamma = PVV^{\gamma-1} \propto TV^{\gamma-1}$ constant. Therefore
>
> $$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \quad \Rightarrow \quad T_1 = T_2(V_2/V_1)^{\gamma-1}.$$
>
> $1 \to 2$ The adiabatic process gives
>
> $$Q_{12} = 0.$$
>
> Using $\Delta U = W + Q$ and $Q = 0$ we get
>
> $$W_{12} = \Delta U = U_2 - U_1 = \frac{f}{2} N k_B (T_2 - T_1).$$
>
> $2 \to 3$
>
> $$W_{23} = -\int_{V_2}^{V_1} P(V)dV - N k_B T_2 \ln(V_1/V_2),$$
>
> and $Q_{23} = -W_{23} = N k_B T_2 \ln(V_1/V_2)$.
>
> $3 \to 1$ Constant volume:
>
> $$W_{31} = 0.$$
>
> $$Q_{31} = \Delta U = \frac{f}{2} N k_B (T_1 - T_2) = -\frac{f}{2} N k_B T_2 \left(1 - \frac{T_1}{T_2}\right).$$

c) Calculate the efficiency of the engine and express it in terms of $X \equiv$ (2p) $(V_1/V_2)^{\gamma-1}$, only.

> **Solution:** We now have $Q_h = Q_{23}$, $Q_c = -Q_{31}$, and $W_e = Q_h - Q_c$. The efficiency becomes
>
> $$\epsilon = \frac{W_e}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{1}{X}\frac{X-1}{\ln X}$$

5 Leaking refrigerator

Suppose that heat leaks into your kitchen refrigerator at an average rate of (3p) 300 W. Assuming ideal operations, how much electric power does it need? Do the calculations by starting from the second law of thermodynamics. Take the room temperature to be 20°C, and 4°C for the temperature in the refrigerator.

> **Solution:** Take $T_c = 273+4 = 277$ K and $T_h = 273+20 = 293$ K. During one second we have $Q_c = 300$ J, $Q_h = Q_c+W$ and entropy flows
>
> $$S_h = \frac{Q_h}{T_h}, \quad S_c = \frac{Q_c}{T_c}.$$
>
> Ideal operations means that $S_h = S_c$ and
>
> $$Q_h = Q_c\frac{T_h}{T_c} \quad \Rightarrow \quad W = Q_h - Q_c = \left(\frac{T_h}{T_c} - 1\right) Q_c = 17 \text{ J},$$
>
> for one second. This implies that the power ≈ 17W.

6 Chemical potential of an ideal gas

By starting from some formulas on the attached formula sheet show the (3p) following expression for the pressure dependence of the chemical potential for an ideal gas:

$$\mu(T, P) = \mu(T, P^\circ) + k_B T \ln(P/P^\circ).$$

(The pressure P° can be any reference pressure, but it is usually taken to be equal to the atmospheric pressure.)

Solution: We note that we have

$$\mu(T, P) = \mu(T, P^\circ) + \int_{P^\circ}^{P} \frac{\partial \mu}{\partial P'} dP'$$

The starting point is $\mu = G/N$ and $dG = -SdT + VdP + \mu dN$, which gives

$$V = \left(\frac{\partial G}{\partial P}\right)_{TN} \quad \Rightarrow \quad \frac{\partial \mu}{\partial P} = \frac{V}{N} = \frac{k_B T}{P},$$

and plugging this into the integral above gives the desired equation.

7 Derivation of the Clausius Clapeyron relation

The Clausius Clapeyron relation applies to the phase boundary e.g. between gas and liquid,

$$\frac{dP}{dT} = \frac{L}{T\Delta V}.$$

Along the phase boundary the Gibbs free energy for the different phases (gas and liquid) is equal, $G_g = G_\ell$. Use this fact together with the thermodynamic identity for Gibbs free energy, (3p)

$$dG = -SdT + VdP,$$

to derive the Clausius Clapeyron relation.

Solution: We have

$$dG_\ell = -S_\ell dT + V_\ell dP, \quad dG_g = -S_g dT + V_g dP.$$

Along the phase boundary we have $dG_g = dG_\ell$ and we may therefore write

$$-S_\ell dT + V_\ell dP = -S_g dT + V_g dP.$$

After rearranging we get

$$(S_g - S_\ell)dT = (V_g - V_\ell)dP \quad \Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V},$$

since the latent heat is $L = T\Delta S$.

Number of points = 24

Formula sheet for Thermodynamics

Physical constants

k_B 1.381×10^{-23} J/K,
N_A 6.022×10^{23},
R 8.315 J/mol·K,
e 1.602×10^{-19} C.

1 General

- The ideal gas law: $PV = Nk_BT$, $PV = nRT$.
- Equipartition: $U_{\text{thermal}} = \frac{f}{2}Nk_BT$.
- First law of thermodynamics: $dU = W + Q$.
- Work: $W = -\int_{V_i}^{V_f} P(V)dV$, (quasistatic).
- Adiabatic process: $PV^\gamma = \text{const}$, $\gamma = \frac{f+2}{f}$.
- Heat capacity:

$$C = \frac{Q}{\Delta T}, \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

- Latent heat: $L = Q/m$.
- Thermal conductivity: $\frac{Q}{\Delta t} = -\kappa_t A \frac{dT}{dx}$.

2 The second law

- Multiplicity of a two-state paramagnet: $\Omega(N, N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$.
- Stirling's approximation: $\ln N! \approx N \ln N - N$.
- Entropy from multiplicity: $S = k_B \ln \Omega$.
- The Sackeur-Tetrode formula:

$$S = Nk_B \left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right]$$

3 Interactions and implications

- Definition of temperature: $T = \left(\frac{\partial S}{\partial U}\right)^{-1}$.
- The thermodynamic identity: $dU = TdS - PdV + \mu dN$.
- Entropy and heat: $S = Q/T$.

4 Engines and refrigerators

- Heat engine: $Q_h = Q_c + W_e$.
  In the context of heat engines we let W_e be positive when energy is leaving the system. This is thus an exception from the ordinary sign convention.
- Efficiency: $\eta = \text{benefit}/\text{cost} = W_e/Q_h$.
- Carnot efficiency: $\eta = 1 - T_c/T_h$.

5 Free energy and chemical thermodynamics

- Enthalpy: $H = U + PV$ and $dH = TdS + VdP + \mu dN$.
- Helmholtz free energy: $F = U - TS$ and $dF = -SdT - PdV + \mu dN$.
- Gibbs free energy: $G = U + PV - TS$ and $dG = -SdT + VdP + \mu dN$.
- Chemical potential: $\mu = G/N$.
- $\Delta G \leq W_{\text{other}}$ (at constant T and P).
- The Clausius-Clapeyron relation

$$\frac{dP}{dT} = \frac{L}{T\Delta V}.$$

Topics in Thermodynamics, 1.5hp

8 Chemical equilibrium

(a) Explain what relation between the chemical potentials μ_{H_2}, μ_{N_2}, and (2p) μ_{NH_3} which is implied by an equilibrium in the reaction

$$N_2 + 3H_2 \leftrightarrow 2NH_3.$$
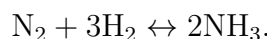
(b) Make use of the relation between the chemical potentials from part (a) (2p) and

$$\mu(T, P) = \mu^\circ(T) + k_B T \ln(P/P^\circ)$$

to derive

$$\frac{P_{NH_3}^2 (P^\circ)^2}{P_{N_2} P_{H_2}^3} = e^{-\Delta G^\circ / RT}.$$

In the above equations μ° represents the chemical potential of a species in its "standard state", i.e. when its partial pressure is P°. Each P_X is the partial pressure of species X. ΔG° is the "standard" Gibbs free energy of the reaction for one mole of N_2.

Solution: *The solution should follow rather directly from the text book.*

9 Liquefaction of air

The figures on the next page show the Gibbs free energy versus composition at a few different temperatures, T_1 through T_6. In these figures x is the fraction of oxygen; $x = 1$ is thus pure oxygen whereas $x = 0$ is pure nitrogen, Pure oxygen liquefies at 90.2 K and pure nitrogen liquefies at 77.4 K.

(a) Which of the figures is for 90.2 K (the boiling point of liquid oxygen) (1p) and which is for 77.4 K (the boiling point of nitrogen)?

Solution: Fig for T_5 is for 90.2 K and figure for T_1 is for 77.4 K. At these temperatures the free energies for liquid and gas are the same for pure oxygen and pure nitrogen, respectively.

(b) From the answer to the first part: explain how these temperatures are (1p) ordered, i.e. do we have $T_1 > T_2 > \ldots > T_6$ or is it the other way around? Also tell which of solid and dashed lines that corresponds to gas and which corresponds to liquid.

Solution: T_1 is the lowest temperature which follows from part (a). Dashed line corresponds to liquid, which is clear from the figure at the lowest temperature where the liquid should have the lowest free energy.

(c) Which of the figures is for the temperature where air, with 21% oxygen, first starts to liquefy? Draw a straight line in the figure that shows the lowest possible free energy. Also try to read off the composition of the liquid that is then produced, from the figure. (2p)
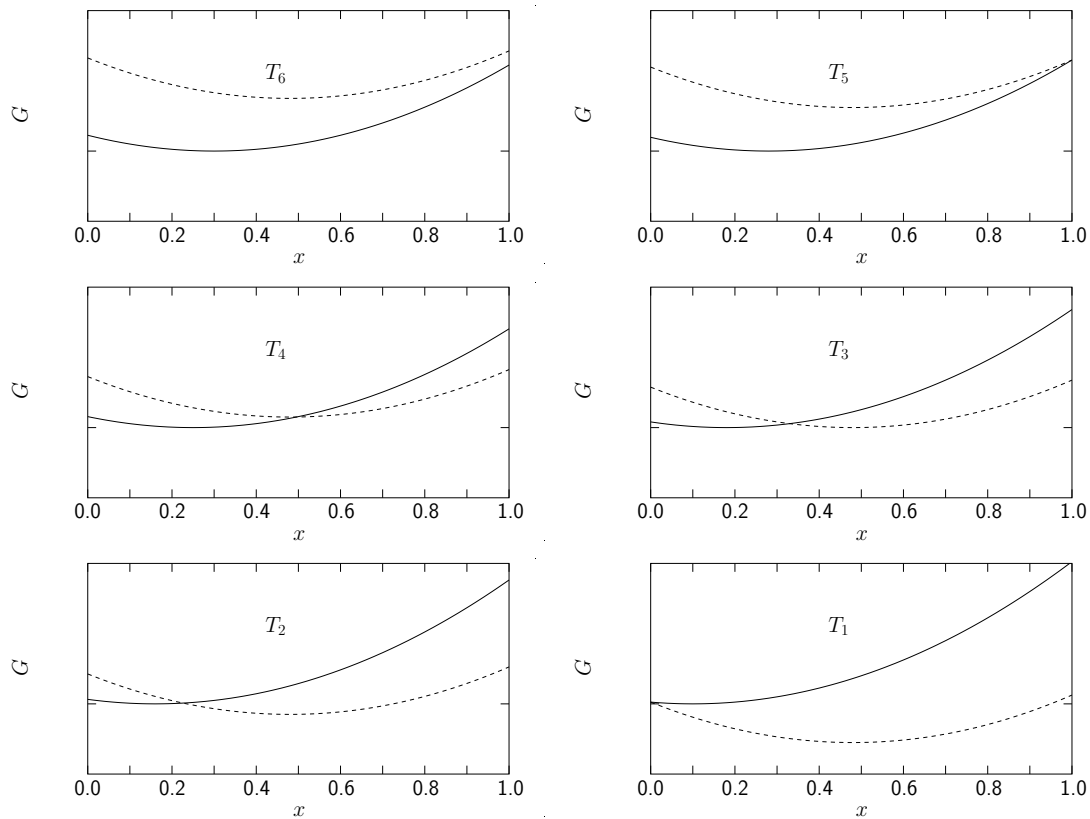
Solution: It is the figure with temperature T_3. Zooming in and making a dashed vertical line for 21% oxygen one sees that the free energy along the blue line between $x \approx 0.18$ and $x \approx 0.48$ gives a lower free energy than from the solid line for gas only. The liquid that forms will have about 50% oxygen. (I do of course not expect you to "zoom in", but this is only to try to explain better.)