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Examination, Thermodynamics B, 6 hp, 2021–01–11, at 9:00–13:00.

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!*

1 Miscellanous questions

(i). A main statement throughout the course is that work and heat are (1p) different things and that it is important to know the difference.
Explain the fundamental difference between these two kinds of energy transfer.

Solution: Heat flow is a spontaneous process whereas work is due to the action of some "agent". Heat flow is accompanied by an increase in entropy since it takes place when the system spontaneously moves *towards* equilibrium. Work can, in principle, be done quasistatically which means that the system is always *at* equilibrium.

- (ii). Which of the following statements are true and which are false? (2p) (Correct/wrong answers give $\pm \frac{1}{2}$ p, but a negative total is taken to zero.)
 - (a) A reversible change of volume is always quasistatic.
 - (b) A quasistatic compression is always reversible.
 - (c) As one approaches a critical point $L/\Delta V$ vanishes (where L is the latent heat).
 - (d) An adiabatic compression gives a lower final pressure than an isothermal compression between the same initial and final volume and with the same initial pressure.

Solution: True, false, false, false.

2 Energy conversion in a hair dryer

Anna is curious about the air flow (volume per unit of time) that comes out of her hair dryer but since it is difficult to measure the flow she sets out for an approximate calculation. She notes that the dryer has a power of 1 kW and measures the increase in temperature of the air through the hair dryer and finds it to be $\approx 30^{\circ}$ C. Calculate the flow in liters per second from the above information by (4p) only making use of the formulas on the formula sheet on the last pages of the exam, in your solution. Assume that the ingoing air has a temperature of 22° C.

Hint: First calculate the flow in terms of number of molecules per unit time and convert this to volume per unit time in a second step.

Solution: Since the heating takes place at constant pressure, the proper quantity to use is

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{d}{dT}[U + PV] = \frac{d}{dT}\left[\frac{f}{2}Nk_BT + Nk_BT\right] = \left(\frac{f}{2} + 1\right)Nk_B$$

We then calculate the flow in terms of number of particles per unit time from

$$E = C_P \Delta T = \left(\frac{f+2}{2}\right) N k_B \Delta T \quad \Rightarrow \quad \frac{dN}{dt} = \frac{1}{\left(\frac{f+2}{2}\right) k_B \Delta T} \frac{dE}{dt}.$$

Here dE/dt = 1 kW is the power of the hair dryer. Then make use of

$$PV = Nk_B T_{\text{out}} \quad \Rightarrow \quad V = \frac{k_B T_{\text{out}}}{P} N_F$$

(using $T_{\rm out} = T_{\rm in} + \Delta T = 273 + 22 + 30 = 325$ K) which together gives

$$\frac{dV}{dt} = \frac{k_B T_{\text{out}}}{P} \frac{dN}{dt} = \frac{k_B T_{\text{out}}}{P} \frac{1}{\left(\frac{f+2}{2}\right) k_B \Delta T} \frac{dE}{dt} = \frac{2}{f+2} \frac{T_{\text{out}}}{P \Delta T} \frac{dE}{dt}$$

With numbers this becomes

$$\frac{dV}{dt} = \frac{2}{7} \frac{325}{10^5 \cdot 30} \cdot 1000 = \frac{2 \cdot 325 \cdot 10^3}{7 \cdot 30 \cdot 10^5} \approx 0.031 \text{m}^3/\text{s} \approx 31\ell/\text{s}$$

3 The Sackur-Tetrode equation

The entropy of a monatomic ideal gas is

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

a) Write down the thermodynamic identity and show that it immediately leads to expressions for 1/T and p/T in terms of the entropy. (1p)

Solution: The thermodynamic identity is

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN.$$

which gives

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N},$$

and

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{UN}.$$

b) Derive the ideal gas law from the Sackur-Tetrode equation and (1p) the expression for p/T from part a).

Solution: Write $S = Nk_B \ln V$ + terms independent of V. We then get

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{UN} = \frac{Nk_B}{V},$$

which gives the ideal gas law, $pV = Nk_BT$.

c) Likewise, determine the temperature of the gas from the Sackur- (1p) Tetrode equation and show that it leads to a well-known relation between temperature and kinetic energy.

Solution: We have $S = Nk_B \frac{3}{2} \ln U + \text{terms independent}$ of U. We then find

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{3Nk_B}{2U},$$

and $U = \frac{3}{2}Nk_BT$.

4 Heat engine

Consider an engine cycle consisting of three steps: (1) adiabatic expansion from volume V_1 to V_2 (2) isothermal compression at temperature T_2 back to the V_1 , and (3) increase of pressure at constant volume back to the original state.

a) Make a reasonably correct sketch of this cycle in a P-V diagram (1p) that 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 (3). Heat leaves in the isothermal compression, step (2). The isotherm should be close to (well, not altogether different from) a 1/x curve. Step (3) should be a vertical line.

b) Determine Q_h and Q_c and find the efficiency of the engine in terms (2p) of V_1 , V_2 , and f and/or γ .

Solution: (The numbers refer to the three steps discussed above.)

- (1) $V^{\gamma}P = \text{const}$ and $PV \propto T$ gives $V^{\gamma-1}T = \text{const}$. Since the adiabatic process is between (V_1, T_1) and (V_2, T_2) we have $V_2^{\gamma-1}T_2 = V_1^{\gamma-1}T_1$ which gives $T_1/T_2 = (V_2/V_1)^{\gamma-1}$.
- (3) Increase of pressure at constant volume implies W = 0 which together with $\Delta U = W + Q$ gives $Q = \Delta U$:

$$Q_h = Q = \Delta U = Nk_B \frac{f}{2} (T_1 - T_2) = Nk_B \frac{f}{2} T_2 \left[(V_2/V_1)^{\gamma - 1} - 1 \right]$$

(2) Isothermal $\Rightarrow \Delta U = 0 \Rightarrow Q = -W$:

$$Q_c = -Q = W = -\int_{V_2}^{V_1} P(V)dV = Nk_B T_2 \int \frac{dV}{V} \\ = Nk_B T_2 \ln(V_2/V_1).$$

The efficiency becomes

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} = 1 - \frac{2}{f} \frac{\ln(V_2/V_1)}{(V_2/V_1)^{\gamma - 1} - 1}$$

c) Assume that the working substance is a two-atomic gas with (1p) "frozen" vibrational degrees of freedom and determine the optimal efficiency when $V_2 = 2V_1$.

Solution: Two-atomic gas, f = 5, gives $\gamma = (f+2)/f = 1.4$. We have

$$\eta = 1 - \frac{2}{f} \frac{\ln(V_2/V_1)}{(V_2/V_1)^{\gamma - 1} - 1} = 1 - 0.4 \frac{\ln 2}{2^{0.4} - 1} \approx 0.13.$$

5 Lead battery

For lead batteries, common in cars, the chemical reaction can be written

 $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O.$

Use the data in the table below to determine the amount of heat that (2p) is involved in the reaction. Is the heat generated as waste heat or is it necessary to supply heat to get current out of the battery?

Solution: In the reaction we have $\Delta S = 2 \times 148.5 + 2 \times 69.91 - (64.81 + 68.6 + 4 \times 0 + 2 \times 20.1) = 263.21 \text{ J/K}$ and find $Q = T\Delta S = 78.4$ kJ. Positive sign means a flow of heat into the system; heat has to be supplied to the system. (The numbers may be compared to $Q = \Delta H - \Delta G = -315.72 + 393.87 = 78.15$ kJ which can be calculated from tables with ΔH and ΔG in the textbook.)

Substance	$S \mathrm{J/K}$
Pb (s)	64.81
PbO_2 (s)	68.6
H^+ (aq)	0
SO_4^{2-} (l)	20.1
$PbSO_4$ (s)	148.5
$H_2O(l)$	69.91

Thermodynamic properties: Values for one mole of material at 298 K and 1 bar.

Number of points = 16

Topics in Thermodynamics, 1.5hp

6 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 (1p) oxygen) 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 (1p) are 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% (2p) 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.





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.)



7 Chemical equilibrium

a) According to the textbook, water at equilibrium contains about (2p) 500 million water molecules for every par of H⁺ and OH⁻ ions. On the other hand pH equal to 7 (neutral) means that the molality is $m_{\rm H^+} = 10^{-7}$. Reconcile these rather different numbers!

Solution: Recall that molality is number of moles per kilogram of the solvent. Since one mole of water weighs 18 g (from $2 \times 1 + 16$), one kilogram of water is $1000/18 \approx 56$ moles. This means that there are 55 moles of water per 10^{-7} moles of H⁺ ions which is a factor of $55 \times 10^7 \approx 500$ million.

$$H_2O \leftrightarrow H^+ + OH^-$$

implies that the chemical potentials at equilibrium satisfy

$$\mu_{\rm H_2O} = \mu_{\rm H^+} + \mu_{\rm OH^-}.$$

Solution: Chemical reactions typically take place at constant pressure and constant temperature and under these conditions the systems minimizes the Gibbs free energy. If the reaction goes to the right the change in Gibbs free energy per molecule is

$$\mu_{\rm H^+} + \mu_{\rm OH^-} - \mu_{\rm H_2O},$$

and the condition for equilibrium is that this quantity is equal to zero, since otherwise the Gibbs free energy could be lowered by moving the reaction to the right or to the left.

Formula sheet for Thermodynamics

Physical constants

- $k_B \quad 1.381 \times 10^{-23} \text{ J/K},$
- $N_A = 6.022 \times 10^{23},$
- R = 8.315 J/mol·K,
- $e \quad 1.602 \times 10^{-19} \text{ C.}$

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: $\Omega(N, N_{\uparrow}) = {N \choose N_{\uparrow}} = \frac{N!}{N_{\uparrow}!N_{\downarrow}!}$.
- 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

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