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Examination, Thermodynamics B, 5hp, 2016–01–11, at 9:00–15:00.

Allowed aids: Calculator, Beta, Physics Handbook, one A4-sized paper with notes and equations.

Hand in each problem on a separate page. The calculations and the reasoning should be easy to follow. *Good luck!*

1 General questions

- a) We have written the ideal gas law in two different ways: pV = (1p) Nk_BT and pV = nRT. Explain the relation between N and n and the relation between k_B and R.
- b) Under what circumstances is "entalpy" a useful quantity? Why? (1p)

2 Multiplicity and entropy

- a) Explain the concepts *microstate*, *macrostate* and *multiplicity*. To (2p) be specific, consider a paramagnet with three dipoles that can point either up or down.
- b) What is the relation between entropy and multiplicity? (1p)
- c) Formulate the second law of thermodynamics. (1p)

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)
- b) Derive the ideal gas law from the expression for p/T. (1p)
- c) Likewise, determine the temperature for the gas and show that this (1p) leads to a well-known relation between temperature and kinetic energy.
- d) Based on the result from "c)", suggest a generalization of the (1p) Sackur-Tetrode equation for general f. (This should not be a full derivation.)

4 Sharpness of the multiplicity function

In the lectures we have used combinatorics and Stirling's equation to analyze the multiplicity function. We will now do the same thing using the Central limit theorem from statistics (explained below). We are especially interested in determining the width of the multiplicity function.

If $S = \sum_{i}^{N} s_{i}$ where the s_{i} are random numbers from some distribution, and N is not too small (N = 10 is usually sufficient), it follows from the Central limit theorem that S will be normally distributed,

$$P(S) \propto e^{-S^2/\sigma^2}$$

With the variance of s_i given by σ_1^2 it follows from elementary statistics that $\sigma^2 = N \sigma_1^2$.

Consider a system that consists of N two-state variables, with possible values $\uparrow = 1$ and $\downarrow = -1$ with equal probability.

- a) Determine S_{max} such that the range of possible S values is (1p) $-S_{\text{max}} \leq S \leq S_{\text{max}}$.
- b) Introduce a convenient measure for the width of the distribution, (1p) δS and determine how $\delta S/S_{\text{max}}$ depends on N.
- c) What is the physical relevance of the above result when N is a (1p) macroscopic value, say $N = 10^{20}$.

5 Heat engine

The figure shows the cycle traversed in the direction $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$, for a reversible heat engine. Note the variables on the axes! Take $T_1 = 200^{\circ}$ C, $T_2 = T_3 = 320^{\circ}$ C, $S_1 = S_2 = 1.2 \text{ kJ/K}, S_3 = 2.4 \text{ kJ/K}.$



(2p)

Hint: Use

a) Calculate the work per cycle.

$$W = -\oint p \ dV$$

for the work done on the system, together with the thermodynamic identity, " $dU = \dots$ ".

b) Calculate the efficiency of this heat engine. (2p)

6 Outdoor refrigerator

Some people put the freezer in an outhouse with outdoor temperature (4p) to save energy. Estimate the saving (in percent) by moving the freezer outdoors if we assume optimal efficiency, indoor temperature $T_{\rm in} = 20^{\circ}$ C, outdoor temperature $T_{\rm out} = 0^{\circ}$ C, and the desired temperature in the freezer, $T_c = -20^{\circ}$ C.

(It might well be that some freezers don't work well at such conditions, but that need not concern us here.)

7 The fuel cell

Consider the fuel cell that combines hydrogen and oxygen gas to produce water and at the same time delivers electical work. Assume ideal conditions. The values in the table are for one mole of the various substances at 25°C.

Substance	$\Delta H \ \mathrm{kJ}$	$\Delta G \ \mathrm{kJ}$	$S \mathrm{J/K}$
H_2 (g)	0	0	130.68
O_2 (g)	0	0	205.14
$H_2O(l)$	-285.83	-237.13	69.91

c) How much work can be extracted for each mole of hydrogen? (1p)

d) How much heat is involved? Is the heat generated as waste heat (2p) or is it necessary to supply heat to run the process? Show that the same result may be obtained from the values in the table in two different ways.

Topics in Thermodynamics, 1.5 hp

8 Mixtures of two types of molecules

Consider a mixture where x is the fraction of B molecules and 1 - x is the fraction of A molecules. If they are not mixed, the total free energy is just the sum of the separate free energies,

$$G = (1 - x)G_A^0 + xG_B^0.$$

We now consider so-called nonideal mixtures in which the mixing increases the energy, denoted by ΔU_{mixing} . There is also an entropy term,

$$\Delta S_{\text{mixing}} = -R[x \ln x + (1-x)\ln(1-x)].$$

- a) Sketch typical curves of G(x) a different temperatures from T = 0 (2p) to higher T.
- b) Under certain (rather common) conditions the homogenous mix- (2p) ture is not the stable state but the system splits up into an A-rich phase and a B-rich phase, since this gives a lower free energy. Make a sketch that illustrates this phenomenon and identify x_a of the A-rich composition and x_b of the B-rich composition in the figure.
- c) ΔS_{mixing} has infinite slopes both at x = 0 and at x = 1. Why is (1p) that significant?

9 Thermodynamics of radiation

The energy density for radiation is given by

$$u = \beta T^4,$$

where $\beta = 7.56 \times 10^{-16} \text{Jm}^{-3} \text{K}^{-4}$.

a) Use the above plus the equations

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{VN}, \quad C_v = T\left(\frac{\partial S}{\partial T}\right)_{VN}$$

to derive an expression for the entropy.

b) Consider blackbody radiation originally at a temperature of 4000 K that expands adiabatically from 10 to 5120 cm³. What is the (2p) final temperature?

(2p)