

Exercise Problems - Week 2

# Statistical Mechanics and Thermodynamics

SoSe 2018

Due: 5 Nov 2018

JGU Mainz - Institut für Physik

---

**Choose 4 of the 6 problems below. Each problem is worth 12 points.**

**Problem 1**

---

Find the change of temperature of a quantity of water carried by a downward current to a depth of 1km in a lake at  $27^{\circ}C$ . For water at this temperature

$$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = 0.00013 \text{deg}^{-1}$$

and you may assume: "no heat exchange" ( $\Delta Q = 0$ ).

Given:  $g = 980 \text{ cm/s}^2$ , and  $\rho = 1 \text{ gm/cm}^3$ ,  $c_P \sim 1 \text{ cal/g} \cdot \text{deg}$  for water, and  $1 \text{ cal} = 4.18 \times 10^7 \text{ erg}$ .

**Problem 2**

---

1. Define the thermodynamic energy function  $H$  (enthalpy),  $G$  (Gibbs free energy), and  $F$  (Helmholtz free energy) for a homogeneous system in term of  $U$  (internal energy) and the thermodynamic variables ( $S, T, P, V$ ). What are the natural variables for each function?
2. Derive the Maxwell relations between the partial derivatives of the thermodynamic variables. Justify each step in words.

**Problem 3**

---

1. Write down differential equations for the internal energy  $U$ , the enthalpy  $H$ , the Helmholtz free energy  $F$ , and the Gibbs function  $G$ .
2. Derive, showing your reasoning the four Maxwell's Relations.

3. Show that

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P.$$

4. For a van der Waals gas, show that the internal energy increases as the volume increases. The van der Waals equation of state is

$$P = \frac{RT}{V - b} - \frac{a}{V^2}.$$

**Problem 4**

---

Heat is added to 0.5kg of ice at  $0^{\circ}C$  until it is all melted. The latent heat of melting for water is  $334 \text{ J/g}$ .

1. What is the change in entropy of the water?
2. If the source of heat is a very massive body at a temperature of  $20^{\circ}C$ , what is the change in entropy of this body?
3. What is the total change in entropy of the water and the heat source?

---

## Problem 5

---

1. Assuming that water is incompressible, estimate the change in Gibbs energy  $\Delta G$  in joules of  $100 \text{ cm}^3$  of water at  $25^\circ$  when the pressure is changed from 1 atm. to 100 atm. (Note that  $1 \text{ atm.} = 1.013 \times 10^5 \text{ N/m}^2$ .)
2. In fact the volume of a sample does change when it is subjected to pressure, and so we ought to see how to take the effect into account, and then judge whether it is significant. The volume varies in a way that can be determined by specifying the isothermal compressibility  $\kappa = -V^{-1}(\partial V/\partial P)_T$ , and we may assume that this is virtually constant over a pressure range of interest. Deduce an expression for the Gibbs energy  $G_f$  at the pressure  $p_f$  in terms of its value  $G_i$  at the initial pressure  $p_i$ , the original volume of the sample  $V_i$ , and the compressibility  $\kappa$ . Take the limit of  $\kappa \rightarrow 0$  in your expression for  $\Delta G \equiv G_f - G_i$ , and show that it reduces to the expression used in the first part.

---

## Problem 6

---

A particular system obeys the following relations: For internal energy;

$$U = PV$$

and for the pressure,

$$P = BT^2$$

where  $V$  is volume,  $T$  absolute temperature, and  $B$  is a constant.

1. Find the fundamental equation of this system, that is how the entropy  $S$  depends on  $U$  and  $T$  and an arbitrary constant  $S_c$ .
2. Discuss and show whether  $S$  obeys the Third Law of Thermodynamics.
3. Calculate how much heat is transferred into the system when the volume changes from  $V_0$  to  $2V_0$  during an isobaric process ( $P = P_0$ ).
4. Calculate the amount of work done by the system when  $V$  changes from  $V_0$  to  $2V_0$  under isobaric condition ( $P = P_0$ ).
5. Show that your results from the previous two parts obey the First Law of Thermodynamics.