Prof. Dr. Hans Peter Büchler WS 2013/14, 12. November 2013

1. How to open a freezer (Oral)

Consider a freezer of volume $V_F = 0.1m^3$ and depth D = 40cm. The room temperature is $T_H = 20^{\circ}C$, the temperature of the freezer working liquid is $T_C = -20^{\circ}C$. The air pressure at ground level $P_{air} = 1.01 \times 10^5 \left[\frac{kg}{ms^2}\right]$. Assume that the room is much bigger than the freezer and full of an ideal diatomic gas. The ideal gas undergoing adiabatic process satisfies $pV^{\gamma} = constant$, where for diatomic molecules the adiabatic constant $\gamma = 1.4$.

- (a) Describe what happens while the freezer door is open. What happens with the air inside the freezer after the door is closed?
- (b) Calculate the force that keeps the door closed. Please give both an analytic expression and a numeric result.

Assume that the freezer door is a piston (see Figure 1), which travels the distance d = 2cm before the outside and inside air get into contact and the door opens. The



Figure 1: Freezer door as a piston.

work W_p done by a person opening the door depends on the way of doing it.

- (a) First, consider opening the door very slowly. Show that in this case, the work W_p is equal to the change of the free energy $\Delta F(T, V)$ of the gas inside the freezer. Calculate W_p .
- (b) Second, consider opening the door very quickly. Change of which thermodynamical potential is equal to the work W_p in this case? Calculate W_p .
- (c) The work W_p depends on the speed of opening the door. Why? Where does the work come from? No equations required.

2. Legendre Transformation (Oral)

The Legendre transform of the function f(x) is defined by

$$f^*(p) := \mathcal{L}f(p) = \sup_x [xp - f(x)] \tag{1}$$

Here, we will show that the Legendre transformation of the strictly convex functions is involutive, i.e. $f^{**} := (f^*)^* = f$.

The function f is convex if it satisfies the following inequality,

$$f(\lambda x_1 + (1 - \lambda)x_2) \le \lambda f(x_1) + (1 - \lambda)f(x_2) \qquad \forall \lambda \in [0, 1],$$
(2)

and strictly convex if inequality is saturated only for $\lambda = 0, 1$ or $x_1 = x_2$.

- (a) How can we understand the Legendre transformation geometrically? How to reconstruct (geometrically) the original function f(x) from the Legendre transform $f^*(p)$?
- (b) Show, that $f^*(p)$ is convex. For that purpose consider $f^*(\lambda p_1 + (1 \lambda)p_2)$.
- (c) Assuming that f(x) is continuously differentiable and strictly convex, show that

$$f^*(p) = \tilde{x}p - f(\tilde{x}),\tag{3}$$

where \tilde{x} is defined by the relation $p = f'(\tilde{x})$. The Legendre transformation changes the independent variable from x to p.

- (d) Assuming that f(x) is continuously differentiable and strictly convex, show that $f^*(p)$ is strictly convex.
- (e) If f(x) is continuously differentiable and strictly convex, show that

$$f^{**}(x) = f(x).$$
 (4)

In order to do this apply the Legendre transformation to $f^*(p)$.

(f) Calculate the Legendre transform $f^*(p)$ of the function

$$f(x) = \begin{cases} x^2/2 & x \le 1\\ x - 1/2 & 1 \le x \le 2\\ x^2 - 3x + 7/2 & 2 \le x \end{cases}$$

(g) Calculate the Legendre transform $f^*(p)$ of the function

$$f(x) = \begin{cases} x^2/2 & x \le 1\\ -x^2 + 4x - 5/2 & 1 \le x \le 2\\ x^2 - 3x + 7/2 & 2 \le x \end{cases}$$

which is not convex. How does the backwards transformed function $f^{**}(x)$ look like?

3. Joule-Thomson Effect (Written)

A gas (not necessarily ideal) is forced to slowly flow adiabatically (no heat exchange with the environment) and irreversibly through a porous plug from volume 1 to 2 (see Figure 2), in such a way that during the process p_1, p_2 are constant.

(a) Show, that during the process the enthalpy H = U + pV is conserved.



Figure 2: Cylinder with porous plug between two pistons.

(b) The temperature of the gas changes when it is forced through the porous plug. Depending on the sign of $(\partial T/\partial p)_H$ it warms up or a cools down (Joule-Thomson effect). The curve, which separates two regimes in the p-T diagram, is called the inversion curve. Show that it satisfies

$$T\left(\frac{\partial V}{\partial T}\right)_p - V = 0.$$
(5)

Under which circumstances does the cooling take place?

Hint

Calculate $(\partial T/\partial p)_H$ with the help of Sheet 1. Ex. 1. Use the Maxwell relation for the Gibbs free energy.

(c) Show that the temperature of the ideal gas cannot be changed using the Joule-Thomson effect.

Remark. The Joule-Thomson expansion is one of the steps in the cycle of conventional refrigerators.