

Thermal Physics: Problem Set #5

Refrigerators, Chemical Thermodynamics, Boltzmann Factor

$$\text{COP} = \frac{Q_c}{W}; \text{COP} \leq \frac{T_c}{T_h - T_c}; F = U - TS; H = U + PV; G = H - TS; P_s(T) = \frac{1}{Z(T)} e^{-E_s/kT}; Z(T) = \sum_s e^{-E_s/kT}$$

Due: Friday Feb. 13 by 6 pm

Note: We will have class on **Saturday Feb. 21, 10:00-2:00** to make up for the week of March 2-6.

Reading Assignment: for Mon, 4.4, 5.1 (18 pgs) (Liquefaction of gases & Chemical thermodynamics)
for Wed, 5.2, 6.1 (15 pgs) (Free energies and Boltzmann factor)
for Fri, 6.2 (9 pgs) (Canonical partition function)

Overview: While heat engines extract useful work from the spontaneous flow of energy from hot to cold reservoirs, refrigerators are devices that reverse this energy flow due to the input of work. The efficiency of a refrigerator is measured by a coefficient of performance (COP) defined above such that a larger COP is better. As with heat engines, the second law puts a restriction on the maximum COP possible for any device. The analysis of actual refrigerators is complicated by the fact that the working fluid in such devices undergoes a liquid-gas phase transition. Thus we must resort to looking up tabulated enthalpy and entropy values of the refrigerant used (analogous to using steam tables to analyze a steam engine). Different types of thermodynamic processes are most naturally described using particular sets of thermodynamic variables. This leads us to define a set of free energies that provide different representations of our original energy function $U(S, V, N)$. Enthalpy $H(S, P, N)$ is one such a free energy where we switch variables from V to P . We have three pairs of so-called conjugate variables $[(S, T), (V, P), \text{ and } (N, \mu)]$ that can be exchanged using a Legendre transformation. We will use the Gibbs free energy $G(T, P, N)$ to analyze energy production by batteries and fuel cells. Underlying all of this thermodynamics is the theory of statistical mechanics. For each set of thermodynamic variables we will define a different statistical mechanical ensemble characterized by a probability distribution function. We begin our formal study of this elegant theory by first considering the canonical ensemble defined in terms of the variables NVT and characterized by the Boltzmann probability function given above.

Problem Assignment: (10 problems total)

4.10 (Power consumption of a kitchen refrigerator)

4.30 (Operational details of a kitchen refrigerator)

*4.33 (Making liquid nitrogen) [Christian]

5.1 (Free energies for a mole of argon gas)

5.3 (Thermodynamics of the lead-acid battery)

5.5 (Thermodynamics of a natural gas fuel cell)

*6.3 (Two state system) [Andrew]

6.5 (Three state system)

*A1. Legendre Transforms of the Energy [Richard] present results for F , H , and G

There are six possible Legendre transforms of the internal energy $U(S, V, N)$ given by changing one or more of the extensive variables S , V , or N to their conjugate partner intensive variables T , $-P$, or μ , respectively. (There is a seventh transform but it is trivially zero). These transforms are constructed by simply subtracting the product of the conjugate pair from U . For example, to switch from the S to T representation, we construct $F = U - TS$. The differential form for F is

*denotes a problem to be presented in class

given by $dF = dU - d(TS) = dU - TdS - SdT$. Construct all six transforms and write out the differential form, the "equation of state" relating P and V , and the "Maxwell relation" (see problem 5.12) relating T and V in each case.

[Example ... for the (T, V, N) representation:

transform: $F(T, V, N) = U - TS$

differential form: $dF = -SdT - PdV + \mu dN$

PV -equation of state: $P = -(\partial F / \partial V)_{T, N}$

TV -Maxwell relation: $(\partial P / \partial T)_{V, N} = (\partial S / \partial V)_{T, N}$



A2. Joule-Thomson Throttling

In the Joule-Thomson throttling process a gas undergoes an adiabatic expansion from a region of constant pressure P_i to a region with constant pressure P_f with $P_f < P_i$. The two regions are separated by a porous plug such as a wad of cotton wool or a glass frit. As shown in the text, this process occurs at constant enthalpy $H(S, P, N) = U + PV$ and can be used to cool a gas.

a) The temperature change of the gas in this constant enthalpy process is given by the Joule-Thomson coefficient $c_{JT} = (\partial T / \partial P)_H$. Show that

$$c_{JT} = \frac{V}{C_p} (T\alpha - 1) \quad \text{where } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad C_p = T \left(\frac{\partial S}{\partial T} \right)_P$$

Hint: combine $dH = TdS + VdP$ with the exact differential for $S(T, P)$ and note that $dH=0$ here.

Use a Maxwell relation to convert $(\partial S / \partial P)_T$ into the derivative needed for α .

b) Can this process be used to cool an ideal gas?

c) Under what conditions can this process be used to cool/heat a gas described by a second virial equation of state

$$P = \frac{NkT}{V} \left(1 + B(T) \frac{N}{V} \right) \approx \frac{N}{V} (kT + PB(T)).$$

(Note that since $B(T)$ is a small correction we are justified in replacing the N/V factor with P/kT).