

**PHY3750**  
**DEVOIR 4**

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**Problem 1.** (9.4) The Gibbs energy of a system is  $G = nRT \ln \frac{P}{P_0} - AP$ , where  $P_0$  and  $A$  are constants.

a) The expression for  $G$  is a fundamental equation because it is a thermodynamic potential and is a function  $G = G(T, P)$

b) Find  $P(V, T)$

We know

$$\begin{aligned} V &= \left( \frac{\partial G}{\partial P} \right)_T = \frac{nRT P_0}{P P_0} - A \\ &= \frac{nRT}{P} - A \end{aligned}$$

So we have

$$P(V, T) = \frac{nRT}{V + A}$$

c) Find  $S(V, T)$

We know

$$\begin{aligned} S &= - \left( \frac{\partial G}{\partial T} \right)_P \\ &= -nR \ln \frac{P}{P_0} \\ S(V, T) &= -nR \ln \frac{nRT}{P_0(V + A)} \end{aligned}$$

d) Find  $F(V, T)$

We know that  $S = - \left( \frac{\partial F}{\partial T} \right)_V$ , so

$$F = - \int S dT + g(V)$$

where  $g(V)$  is some function of  $V$ . Now

$$\begin{aligned} - \int S dT &= - \int -nR \ln \frac{nRT}{P_0(V + A)} dT \\ &= nR \int \ln \frac{nRT}{P_0(V + A)} dT \\ &= nR \left( \int \ln \frac{nR}{P_0(V + A)} dT + \int \ln T dT \right) \\ &= nRT \ln \frac{nR}{P_0(V + A)} + nRT \ln T - nRT \\ &= nRT \left( \ln \frac{nRT}{P_0(V + A)} - 1 \right) + \text{constant} \end{aligned}$$

So we have

$$F = nRT \left( \ln \frac{nRT}{P_0(V+A)} - 1 \right) + g(V) + F'_0$$

For some constant  $F'_0$ . Now,

$$\begin{aligned} -P &= \left( \frac{\partial F}{\partial V} \right)_T \\ \frac{-nRT}{V+A} &= nRT \left( \frac{P_0(V+A)}{nRT} \frac{nRT}{P_0} \left( -\frac{1}{(V+A)^2} \right) \right) + \frac{\partial g}{\partial V} \\ \frac{-nRT}{V+A} &= \frac{-nRT}{V+A} + \frac{\partial g}{\partial V} \\ \frac{\partial g}{\partial V} &= 0 \implies g = \text{constant} \end{aligned}$$

Now that we know  $g(V)$  is constant, we can write

$$F(V, T) = nRT \left( \ln \frac{nRT}{P_0(V+A)} - 1 \right) + F_0 \quad \square$$

**Problem 2.** (9.8)

Since  $c_p = \frac{T}{n} \left( \frac{\partial S}{\partial T} \right)_P$  and  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  and  $\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ , for the reversible adiabatic expansion we have

$$\begin{aligned} \left( \frac{\partial T}{\partial P} \right)_S &= - \left( \frac{\partial S}{\partial P} \right)_T \left( \frac{\partial T}{\partial S} \right)_P = \frac{- \left( \frac{\partial S}{\partial P} \right)_T}{\left( \frac{\partial S}{\partial T} \right)_P} = \frac{\left( \frac{\partial V}{\partial T} \right)_P T}{nc_p} \\ \left( \frac{\partial T}{\partial P} \right)_S &= \frac{\beta VT}{nc_p} \end{aligned}$$

For the adiabatic throttling, we note that the Joule-Thomson coefficient is  $\mu \equiv \left( \frac{\partial T}{\partial P} \right)_H$  and  $\mu > 0$  when the gas is cooling. Since the process happens at constant enthalpy we have

$$\begin{aligned} 0 &= dH = TdS + VdP \\ 0 &= TdS + VdP \end{aligned}$$

Using  $TdS = nc_p dT - T \left( \frac{\partial V}{\partial T} \right)_P dP = nc_p dT - TV\beta dP$  we get

$$\begin{aligned} 0 &= nc_p dT - TV\beta dP + VdP \\ &= nc_p dT + V(1 - \beta T) dP \\ \left( \frac{\partial T}{\partial P} \right)_H &= \frac{V}{nc_p} (\beta T - 1) = \frac{\beta VT}{nc_p} - \frac{V}{nc_p} \end{aligned}$$

Since  $\frac{V}{nc_p}$  is always positive we have:

$$\left( \frac{\partial T}{\partial P} \right)_S > \left( \frac{\partial T}{\partial P} \right)_S - \frac{V}{nc_p} = \left( \frac{\partial T}{\partial P} \right)_H = \mu > 0$$

The temperature difference for the first method and for the second method is given by

$$\Delta T_1 = \int_{P_i}^{P_f} \left( \frac{\partial T}{\partial P} \right)_H dP \quad \Delta T_2 = \int_{P_i}^{P_f} \left( \frac{\partial T}{\partial P} \right)_S dP$$

How do you have a reversible adiabatic expansion at constant pressure? Assuming the initial and final pressures are different and since  $\left(\frac{\partial T}{\partial P}\right)_S > \left(\frac{\partial T}{\partial P}\right)_H$ , we have

$$\Delta T_2 > \Delta T_1$$

**Problem 3.** (9.12) The state equation of an electromagnetic ray in thermal equilibrium with a box of volume  $V$  and temperature  $T$  is  $P = aT^4/3$  where  $a$  is a constant. The internal energy is given by  $U = aT^4V$ . It was shown that the entropy is  $S = 4aT^3V/3$ .

a) Find  $S(U, V)$ .

Let's eliminate  $T$ :

$$\begin{aligned} U &= aT^4V \implies T = \left(\frac{U}{aV}\right)^{\frac{1}{4}} \text{ so} \\ S &= \frac{4aT^3V}{3} = \frac{4a\left(\frac{U}{aV}\right)^{\frac{3}{4}}V}{3} \\ S(U, V) &= \frac{4(aVU^3)^{1/4}}{3} \end{aligned}$$

b) Find the internal energy  $U$  in variables that yield a fundamental equation.

We want  $U(S, V)$

$$\begin{aligned} S &= \frac{4(aVU^3)^{1/4}}{3} \\ aVU^3 &= \left(\frac{3S}{4}\right)^4 \\ U^3 &= \frac{81}{256} \frac{S^4}{aV} \\ U(S, V) &= \left(\frac{81}{256}\right)^{\frac{1}{3}} \left(\frac{S^4}{aV}\right)^{\frac{1}{3}} \end{aligned}$$

c) Find the Helmholtz energy.

We want  $F(T, V)$  where  $F = U - TS$ :

$$\begin{aligned} F &= U - TS \\ &= aT^4V - T \frac{4aT^3V}{3} \\ &= aT^4V - \frac{4}{3}aT^4V \\ F(T, V) &= -\frac{1}{3}aT^4V \end{aligned}$$

d) Find the Gibbs energy and the chemical potential of the photon in blackbody radiation.

We want  $G(T, P)$  where  $G = U - TS + PV = F + PV$

$$\begin{aligned} G &= F + PV \\ &= -\frac{1}{3}aT^4V + PV \\ &= -PV + PV = 0 \end{aligned}$$

Since  $G = \mu n$ , where  $\mu$  is the chemical potential, we have that  $0 = G = \mu n$ . Since  $n \neq 0$ , we must have that  $\mu = 0$ . This can also be seen by looking at the differential of  $G$

$$dG = -SdT + PdV + \mu dn$$

In thermal equilibrium we would expect  $dT = dV = dG = 0 = \mu dn$ . But with photons, the number of photons is not conserved, since a photon can collide with an electron and be absorbed, and then the electron can fall to lower energy states releasing more than one photon. This means that  $dn \neq 0$  and therefore we'd need  $\mu = 0$  to satisfy the condition.

**Problem 4.** (9.14) Let a spring obey Hooke's law where the tension  $f$  is given by  $f = -k(l - l_0)$  where  $k$  is the spring constant,  $l$  is the length, and  $l_0$  is the (constant) length when  $f = 0$ . The spring constant is a function of the temperature:  $k(T)$ . Find the **Helmholtz energy**, the **internal energy**, and the **entropy** as a function of  $l$ .

The Helmholtz energy is  $F = U - TS$  and  $dF = -SdT - fdl$ . We know that

$$\left(\frac{\partial F}{\partial l}\right)_T = -f = k(l - l_0)$$

Treating  $k$  as a constant since it only depends on  $T$ ,

$$F = \frac{1}{2}kl^2 + g(T)$$

where  $g$  is some unknown function of  $T$ .

$$S = -\left(\frac{\partial F}{\partial T}\right)_l = -\frac{1}{2}l^2 \frac{dk}{dT} - \frac{dg}{dT}$$

Let's use  $\left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial f}{\partial T}\right)_l$ :

$$\begin{aligned} \left(\frac{\partial S}{\partial l}\right)_T &= \left(\frac{\partial f}{\partial T}\right)_l \\ -\frac{dk}{dT}l &= -(l - l_0)\frac{dk}{dT} = -\frac{dk}{dT}l + \frac{dk}{dT}l_0 \\ \frac{dk}{dT}l_0 &= 0 \end{aligned}$$

Since  $l_0$  is not zero (because then the spring wouldn't exist at zero tension!), we conclude that  $\frac{dk}{dT} = 0$ , so  $k = \text{constant}$ . This means  $S = -\frac{dg}{dT}$  and that  $S$  doesn't depend on  $l$ .

Now we want to find how the internal energy  $U$  depends on  $l$ . Since  $F = U - TS$  and since  $S$  doesn't depend on  $l$ ,

$$kl = \left(\frac{\partial F}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T$$

This means

$$U = \frac{1}{2}kl^2 + h(T)$$

for some function  $h(T)$ . Similarly,

$$\begin{aligned} \left(\frac{\partial F}{\partial T}\right)_l &= \left(\frac{\partial U}{\partial T}\right)_l - S - T\frac{dS}{dT} \\ \frac{dg}{dT} &= \frac{dh}{dT} + \frac{dg}{dT} + T\frac{d^2g}{dT^2} \\ \frac{dh}{dT} &= -T\frac{d^2g}{dT^2} \\ -\frac{1}{T}\frac{dh}{dT} &= \frac{d^2g}{dT^2} \end{aligned}$$

How to evaluate this?

**Problem 5.** (10.3) Find the change of the chemical potential with pressure for adiabatic compression. The change of chemical potential is given by

$$\Delta\mu = \int_{P_i}^{P_f} \left( \frac{\partial\mu}{\partial P} \right)_{S,n} dP$$

Start from the Gibbs-Duhem relation  $SdT - VdP + nd\mu = 0$ :

$$\begin{aligned} nd\mu &= VdP - SdT \\ \left( \frac{\partial\mu}{\partial P} \right)_{S,n} &= \frac{V}{n} - \frac{S}{n} \left( \frac{\partial T}{\partial P} \right)_{S,n} \\ &= \frac{V}{n} - \frac{S}{n} \frac{1}{\left( \frac{\partial P}{\partial T} \right)_S} \\ &= \frac{V}{n} - \frac{S}{n} \frac{1}{-\left( \frac{\partial P}{\partial S} \right)_T \left( \frac{\partial S}{\partial T} \right)_P} \\ &= \frac{V}{n} - \frac{S}{n} \frac{T}{nc_p \left( \frac{\partial T}{\partial V} \right)_P} \\ \left( \frac{\partial\mu}{\partial P} \right)_{S,n} &= \frac{V}{n} - \frac{S}{n} \frac{T}{nc_p V \beta} = \frac{V}{n} - \frac{ST}{n^2 c_p V \beta} \end{aligned}$$

So

$$\begin{aligned} \Delta\mu &= \int_{P_i}^{P_f} \left( \frac{\partial\mu}{\partial P} \right)_{S,n} dP \\ &= \int_{P_i}^{P_f} \frac{V}{n} - \frac{ST}{n^2 c_p V \beta} dP \\ &= \int_{P_i}^{P_f} \frac{V}{n} dP - \int_{P_i}^{P_f} \frac{ST}{n^2 c_p V \beta} dP \end{aligned}$$

Since it is an adiabatic compression,  $PV^\gamma = P_i V_i^\gamma \implies V = \left( \frac{P_i}{P} \right)^{1/\gamma} V_i$ .

$$\begin{aligned} \Delta\mu &= \int_{P_i}^{P_f} \frac{V}{n} dP - \int_{P_i}^{P_f} \frac{ST}{n^2 c_p V \beta} dP \\ &= \frac{P_i^{1/\gamma} V_i}{n} \int_{P_i}^{P_f} \frac{1}{P^{1/\gamma}} dP - \frac{1}{n^2 c_p \beta V_i P_i^{1/\gamma}} \int_{P_i}^{P_f} \frac{ST}{P^{1/\gamma}} dP \\ &= \frac{P_i^{1/\gamma} V_i}{n} \frac{1}{-\frac{1}{\gamma} + 1} (P_f^{\frac{\gamma-1}{\gamma}} - P_i^{\frac{\gamma-1}{\gamma}}) - \frac{1}{n^2 c_p \beta V_i P_i^{1/\gamma}} \int_{P_i}^{P_f} \frac{ST}{P^{1/\gamma}} dP \\ \Delta\mu &= \frac{P_i^{1/\gamma} V_i}{n} \left( \frac{\gamma-1}{\gamma} \right) (P_f^{\frac{\gamma-1}{\gamma}} - P_i^{\frac{\gamma-1}{\gamma}}) - \frac{1}{n^2 c_p \beta V_i P_i^{1/\gamma}} \int_{P_i}^{P_f} \frac{ST}{P^{1/\gamma}} dP \end{aligned}$$

**Problem 6.** (11.3) Analyze the behaviour of entropy at low temperatures

a) Of an ideal gas. ( $PV = nRT$ )

For an ideal gas,  $S = S_0 + nc_V \ln \frac{T}{T_0} + nR \ln \frac{V}{V_0}$ . According to the third law, for two systems in thermal equilibrium ( $T_1 = T_2 \equiv T$ ) we'd expect

$$\lim_{T \rightarrow 0} (S_2 - S_1) = 0$$

Instead we have

$$\begin{aligned}
 \Delta S = S_2 - S_1 &= nc_V \ln \frac{T}{T_0} + nR \ln \frac{V_2}{V_0} - nc_V \ln \frac{T}{T_0} - nR \ln \frac{V_1}{V_0} \\
 &= nc_V \ln 1 + nR \ln \frac{V_2}{V_1} = nR \ln \frac{V_2}{V_1} \\
 &= nR \ln \frac{P_1}{P_2}
 \end{aligned}$$

We see that for an ideal gas, the difference in entropy between two states in thermal equilibrium does not depend on the temperature  $T$ , and that  $\Delta S$  is non-zero independent of  $T$ .

**b)** Of a Van der Waals gas.  $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

For a Van der Waals gas, we derive the entropy from the  $TdS$  equation

$$\begin{aligned}
 TdS &= nc_V dT + T \left( \frac{\partial P}{\partial T} \right)_V dV \\
 dS &= \frac{nc_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV \\
 &= \frac{nc_V}{T} dT + \frac{nR}{V - nb} dV \\
 S &= nc_V \ln \frac{T}{T_0} + nR \ln(V - nb)
 \end{aligned}$$

The Van der Waals equation does not satisfy the third law similar to the ideal gas law.