# Introduction to Statistical Physics Solution Manual

Kerson Huang

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## 1.1

Mass of water =10<sup>6</sup>g, temperature raised by 20<sup>°</sup>C. Heat needed  $Q = 2 \times 10^{7}$ cal =  $8.37 \times 10^{7}$ J.=23.2 kwh. Work needed =  $mgh = 14 \times 150 \times 29000 = 6.09 \times 10^7$  ft-lb = 22.9 kwh.

#### 1.2

Work done along various paths are as follows  $ab:$   $\int^b$ 

$$
\int_{a}^{b} PdV = Nk_B T_1 \int_{a}^{b} \frac{dV}{V} = Nk_B T_1 \ln \frac{V_b}{V_a}
$$

cd:

$$
P_d(V_d - V_b) = Nk_B T_3 \left(1 - \frac{V_b}{V_d}\right)
$$

de:

$$
N k_B T_3 \int_d^e \frac{dV}{V} = N k_B T_3 \ln \frac{V_a}{V_d}
$$

No work is done along bc and ea. The total work done is the sum of the above. Heat absorbed equals total work done, since internal energy is unchanged in a closed cycle.

$$
1.3\,
$$

(a)

$$
\alpha = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{bV_0 T^{b-1}}{T_0^b V}
$$

(b)

$$
\Delta V = \frac{bV_0T^{b-1}}{T_0^b} \Delta T
$$

$$
P = \frac{Nk_BT}{V} = \frac{Nk_BT_0^b}{V_0}T^{1-b}
$$
Work done =  $P\Delta V = bNk_B\Delta T$ 



### 1.4

Consider an element of the column of gas, of unit cross section, and height between z and  $z+dz$ . The weight of the element is  $-gdM$ , where  $dM$  is the mass of the element:  $dM = mndz$ , where m is the molecular mass, and  $n = P/k_BT$ is the local density, with  $P$  the pressure. For equilibrium, the weight must equal the pressure differential:  $dP = -gdM$ . Thus,  $dP/P = -(mg/k_BT)dz$ . At constant  $T$ , we have  $dp/P = dn/n$ . Therefore

$$
n(z) = n(0)e^{-mgz/k_B T}
$$

1.5

No change in internal energy, and no work is done. Therefore total heat absorbed  $\Delta Q = \Delta Q_1 + \Delta Q_2 = 0$ . That is, heat just pass from one body to the other. Suppose the final temperature is  $T$ . Then

 $\Delta Q_1 = C_1(T - T_1), \Delta Q_2 = C_2(T - T_2).$  Therefore

$$
T = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}
$$

1.6

Work done by the system is  $-\int H dM$ . Thus the work on the system is

$$
\int H dM = \frac{\kappa}{T} \int H dH = \frac{\kappa H^2}{2T}
$$

#### 1.7

Consider the hysteresis cycle in the sense indicated in Fig.1.6. Solve for the magnetic field:

$$
H = \pm H_0 + \tanh^{-1}(M/M_0)
$$

( + for lower branch, – for upper branch.). Using  $W = -\int H dM$ , we obtain

$$
W = -\int_{-M_0}^{M_0} dM[H_0 + \tanh^{-1}(M/M_0)] - \int_{M_0}^{-M_0} dM[-H_0 + \tanh^{-1}(M/M_0)]
$$
  
= -4M<sub>0</sub>H<sub>0</sub>

1.8

A log log plot of mass vs. A is shown in the following graph. The dashed line is a straightline for reference.



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CHAPTER 1.

2.1

Use the  $dQ$  equation with  $P, T$  as independent variables:  $dQ = C_P dT + [(\partial U/\partial P)_T + P(\partial V/\partial P)_T]dP$ For an ideal gas  $(\partial U/\partial P)_T = 0$ ,  $P(\partial V/\partial P)_T = -V$ . Thus  $dQ = C_P dT - V dP.$ The heat capacity is given by  $C = C_P - V(\partial P/\partial T)_{\text{path}}.$ The path is  $P = aV^b$ , or equivalently  $P^{b+1} = a(Nk_BT)^b$  by the equation of state. Hence

 $V(\partial P/\partial T)_{\text{path}} = [ab/(b+1)]V(Nk_BT)^bT^{-1} = bNk_B/(b+1)$ . Therefore

$$
C = C_P - \frac{b}{b+1} N k_B
$$

This correctly reduces to  $C_P$  for  $b = 0$ .

### 2.2

Use a Carnot engine to extracted energy from 1 gram of water between 300 K and 290 K.

Max efficiency  $\eta = 1 - (290/300) = 1/30$ .

$$
W = \eta C \Delta T = \frac{1}{30} (4.164 \text{ J g}^{-1} \text{K}^{-1} \times 1 \text{ g} \times 10 \text{ K}) = 1.39 \text{ J}
$$

Gravitational potential energy = 1 g × 9.8 kg s<sup>-2</sup> × 110 m = 1.08 J

### 2.3

The highest and lowest available temperatures are,  $600 \text{ F} = 588.7 \text{ K}$  and 70  $F = 294.3$  K.

The efficiency of the power plant is  $W/Q_1 = 0.6[1 - (294.3/588.7)] = 0.3$ . In one second:  $W = 10^6$  J.

So  $Q_2 = 2.33 \times 10^6$  J =  $C_V \Delta T$ . Use  $C_V = 4.184$  J g<sup>-1</sup>K<sup>-1</sup>,

### 5

Flow rate =  $6000 \times (0.305 \text{m})^3$ 

$$
\Delta T = \frac{2.33 \times 10^6 \text{ J}}{(4.184 \text{ J g}^{-1} \text{K}^{-2})6000(0.305 \text{ m})^3 \text{ 10}^6 \text{ cm}^2/\text{m}^3} = 3.27 \times 10^{-3} K
$$

2.4 (a)

Since water is incompressible, a unit mass input gives a unit mass output. The net heat supplied per unit mass is  $\Delta Q = C(T_1 - T) - C(T - T_2)$ ,

where C is the specific heat of water (per unit mass.) In steady state  $v^2/2 =$  $\Delta Q$ . This gives

$$
v = \sqrt{2\Delta Q} = \sqrt{2C(T_1 + T_2 - 2T)}
$$

(b)

The entropy depends on the temperature like  $\ln T$ . A unit volume of water from each of the input streams has total entropy  $\ln T_1 + \ln T_2$  This makes two unit volumes in the output stream, with entropy  $2 \ln T$ . Therefore the change in entropy is  $\ln (T^2/T_1T_2) \geq 0$ . Thus  $T \geq \sqrt{T_1T_2}$ , and

$$
v_{\text{max}} = \sqrt{2C} \left| \sqrt{T_1} - \sqrt{T_2} \right|
$$

2.5  
\n(a)  
\n
$$
PV_1^{\gamma} = 2P_0 V_0^{\gamma}, PV_2^{\gamma} = 2\langle P_0 V_0^{\gamma} \rangle
$$
  
\n $(V_1/V_2)^{\gamma} = 2.$   $[(\bar{L} + a)/(L - a)]^{\gamma} = 2.$   
\n $\frac{a}{L} = \frac{2^{1/\gamma} - 1}{2}$ 

$$
\frac{a}{L} = \frac{2^{1/\gamma} - 1}{2^{1/\gamma} + 1}
$$

(b)  
\n
$$
\Delta U = \Delta Q - W, \, \Delta Q = 0.
$$
  
\n
$$
C_V \Delta T = -W, \, \Delta T = -W/C_V.
$$
  
\n
$$
T_1 = 2T_0 + \Delta T = 2T_0 - (W/C_V), \, T_2 = T_0 - \Delta T = T_0 + (W/C_V).
$$

$$
P = \frac{RT_1}{V_1} = \frac{R\left[2T_0 - (W/C_V)\right]}{A\left(L + a\right)}
$$

(c)  
\n
$$
W = A \int_0^a dx (P_1 - P_2)
$$
\n
$$
P_1 = 2P_0 V_0^{\gamma} / [A(L+x)]^{\gamma}, P_2 = P_0 V_0^{\gamma} / [A(L-x)]^{\gamma}.
$$
\n
$$
W = \frac{P_0 V_0}{\gamma - 1} \left( 1 - \frac{a}{L^{-\gamma}} \right) \left( 1 - \frac{2a}{L} \right)
$$

2.6 (a)  $PV = U/3$ ,  $U = \sigma VT^4$ .  $P = \sigma T^4/3$ .  $dS = dQ/T = (dU + PdV)/T.$ Integrate along paths with  $T = \text{const}$ ,  $V = \text{const}$ .

$$
S = \frac{4}{3}\sigma VT^3
$$

(b)  $S =$ Constant. ∴  $T^3 \sim V^{-1}$ . Thus

$$
T \sim R^{-1}
$$

2.7

The heat absorbed by an ideal gas in an isothermal process is

$$
\Delta Q = NkT \ln(V_f/V_i)
$$

where  $V_f$  and  $V_i$  are respectively the final and initial volume. The temperature T in this formula is the ideal-gas temperature.

Draw a Carnot cycle on the  $PV$  diagram, and label the corners 1234 clockwise from the upper left.

The heat absorbed at the upper temperature  $T_2$ , and the heat rejected at the lower temperature  $T_1$ , are

 $Q_2 = NkT_2 \ln(V_2/V_1)$  $Q_1 = NkT_1 \ln(V_3/V_4)$ Because 23 and 12 lie on adiabatic lines, we have  $V_2 T_2^{\gamma - 1} = V_3 T_1^{\gamma - 1}$ <br> $V_1 T_2^{\gamma - 1} = V_4 T_1^{\gamma - 1}$ Dividing one equation by the other yields  $V_2/V_1 = V_3/V_4$ .

The efficiency of the cycle is therefore

$$
\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}
$$

2.8 Diesel cycle:  $Q_2 = C_P (T_3 - T_2)$  $Q_1 = C_V (T_4 - T_1)$  $\eta = 1 - (Q_1/Q_2) = 1 - \gamma^{-1}[(T_4 - T_1)/(T_3 - T_2)]$ We have  $P_3 = P_2$ , hence  $T_3/T_2 = V_3/V_2 = r_c$ The processes 12 and 34 are adiabatic, with  $TV^{\gamma-1} = \text{constant}$ .  $V_4 = V_1$ . Thus

 $T_3 V_3^{\gamma -1} = T_4 V_1^{\gamma -1}$ <br>  $T_2 V_2^{\gamma -1} = T_1 V_1^{\gamma -1}$ Using the three relations derived, we obtain

$$
\eta = 1 - \frac{1}{\gamma} \frac{r_c^{\gamma} - 1}{r^{\gamma - 1}(r_c - 1)}
$$

2.9 Otto cycle:  $Q_2 = C_V (T_3 - T_2)$  $Q_1 = C_V (T_4 - T_1)$  $\eta = 1 - (Q_1/Q_2) = 1 - [(T_4 - T_1)/(T_3 - T_2)]$ The processes 12 and 34 are adiabatic, with  $TV^{\gamma-1} = \text{constant}$ . We have  $V_4 = V_1, V_3 = V_2$  Thus  $T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}.$  $T_3V_2^{\gamma-1} = T_4V_1^{\gamma-1}.$ Taking the ratio of these equations, we have  $T_2/T_1 = T_3/T_4 = r^{\gamma - 1}.$ Thus  $,1-\gamma$ 

$$
\eta = 1 - r^{1-}
$$

2.10 First note  $T_b/T_a = V_b/V_a = 2$ .



W (Net work done) =  $NkT_a(1 - \ln 2)$  $Q_2$  (Heat absorbed) =  $C_P T_a = \frac{5}{2} N k T_a$ 

$$
\eta = \frac{W}{Q_2} = \frac{2}{5}(1 - \ln 2) = 0.12
$$

In comparison,  $\eta_{\text{Carnot}} = 1 - (T_b/T_a) = 0.5$ .

2.11

First note  $T_2 = 4T_1$ . The P, V, T for the points A, B, C, D are as follows:

	г		
		$V_1 = NkT_1/P_1$	$T_{1}$
B	$2P_1$	$2V_1$	$4T_1$
C	$2P_1$		$2T_1$
		$2V_1$	$2T_1$

(a) Heat supplied along  $ACB: C_V T_1 + C_P (2T_1) = \left(\frac{3}{2} + 5\right) N k_B T_1 = \frac{13}{2} N k_B T_1.$  $ADB: C_P T_1 + C_V (2T_1) = (\frac{5}{2} + 3) N k_B T_1 = \frac{11}{2} N k_B T_1.$  $AB$  :  $\Delta U + \Delta W = \frac{3}{2} N k_B (2T_1) + \frac{3}{2} P_1 V_1 = 6N k_B T_1.$ (b) Heat capacity =  $\Delta Q/\Delta T = 6Nk_BT_1/3T_1 = 2Nk_B$ . (c)

Work done =  $P_1V_1 = Nk_BT_1$ . Heat absorbed = Heat absorbed along ACB  $=(13/2)Nk_BT_1.$ 

$$
\eta = \frac{2}{13}
$$

2.12 (a)

Since no work is being done, and the temperatures diverge, heat must be transferred from the colder body to the hotter body, with no other effect, and this violates the Clausius statement of the second law.

(b)

The assertion is not true for physical black bodies, because they cannot be point-like but have finite size. Even if the two bodies have identical shapes, their optical images are not reciprocal. That is, the radiation from one body may form an image that is larger than the other body, and thus not completely absorbed by the other body.

 $\begin{tabular}{ll} \bf 10 & \bf CHAPTER \ 2. \end{tabular}$ 

3.1

(a) For a adiabatic process  $dS = 0$ , and the TdS equations give  $C_V dT = -(\alpha T / \kappa_T) dV$  $C_P dT = \alpha TV dP$ Dividing one by the other, we obtain  $C_P/C_V = \kappa_T[-V(\partial P/\partial V)_S] = \kappa_T/\kappa_S$ (b)  $C_V dT + (\alpha T / \kappa_T) dV = C_P dT - \alpha T V dPT$ . Put  $dT = (\partial T/\partial P)_V dP + (\partial T/\partial V)_P dV.$ Equate the coefficients of  $dP$  and  $dV$  on both sides. One of them gives  $C_P - C_V = (\alpha T V / \kappa_T)(\partial V / \partial T)_P = \alpha^2 T V / \kappa_T.$ (c) Using  $U = A + TS$ ,  $H = G + TS$  (enthalpy), we have

$$
C_V = (\partial U/\partial T)_V = (\partial A/\partial T)_V + S + T(\partial S/\partial T)_V = T(\partial S/\partial T)_V
$$
  
= 
$$
-T(\partial^2 A/\partial T^2)_V
$$

$$
C_P = (\partial H/\partial T)_P = (\partial G/\partial T)_P + S + T(\partial S/\partial T)_P = T(\partial S/\partial T)_P
$$
  
= 
$$
-T(\partial^2 G/\partial T^2)_P
$$

3.2

The Sacker-Tetrode equation is

 $S = Nk_B[(5/2) - \ln(n\lambda^3)]$ , where  $n = N/V$ , and  $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$ . (a)  $A = U - TS = (3/2)k_B T - TS = Nk_B T \ln(n\lambda^3) - Nk_B T.$  $G = A + PV = N k_B T \ln(n\lambda^3).$ (b) Write  $\ln(n\lambda^3) = \ln n + \ln \lambda^3$ . The second term is a function of T only.  $\mu = (\partial A/\partial N)_{V,T} = k_B T \ln(n\lambda^3) + N k_B T (\partial \ln n/\partial N)_{V,T} - k_B T = k_B T \ln(n\lambda^3).$  $\mu = (\partial G/\partial N)_{P,T} = k_B T \ln(n\lambda^3) + N k_B T (\partial \ln n/\partial N)_{P,T} = k_B T \ln(n\lambda^3).$ 

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3.3 The force on the bead is  $(P - P_a)A - mg$ , where  $P =$  pressure in gas,  $P_a = 1$  atm. The equation of motion for the displacement x is  $m\ddot{x} = (P - P_a)A - mg$ . In equilibrium the pressure in the gas is  $P_0 = P_a + (mg/A)$ . The volume is  $V_0 = RT/P_0$ . Assume adiabatic oscillations:  $PV^{\gamma} = \text{const.}$ This implies  $dP = -\gamma (P/V) dV \approx -\gamma (P_0/V_0) Ax$ .  $P = P_0 + dP \approx P_0 - \gamma (P_0/V_0)Ax.$ Thus  $m\ddot{x} + (\gamma A^2 P_0^2 / RT) x = 0.$ The frequency of oscillations is

$$
\omega = AP_0 \sqrt{\gamma/RT}
$$

3.4

Let the equilibrium pressure and temperature be  $P_0$ ,  $T_0$ . Under an infinitesimal displacement  $x$ , suppose the pressure of compartment 1 changes by dP. Since the process is adiabatic, we have  $PV^{\gamma} = \text{constant}$ , or  $(dP/P)$  +  $\gamma(dV/V) = 0$ . In terms of the temperature, we have  $TV^{\gamma-1} = \text{constant}$ , or  $(dT/T) + (\gamma - 1)(dV/V) = 0.$ (a)

For compartment 1, we have to first order

$$
dP = -\frac{\gamma P_0 x}{L}
$$

$$
dT = -\frac{(\gamma - 1)T_0 x}{L}
$$

For compartment 2, replace x by  $-x$ . (b)

The force acting on the piston is  $dF = AdP$ . The equation of motion for x is  $dF = M\ddot{x}$ , where M is the mass of the piston. Thus  $\ddot{x} + (\gamma AP_0/ML)x = 0$ , and the frequency of small oscillations is

$$
\omega=\sqrt{\gamma AP_0/ML}
$$

(c)

Due to the finite thermal conductivity of the piston, heat flows back and forth between the two compartment, because of the oscillation in the temperature difference.Assume that the temperatures change so slowly that at any moment we regard heat conduction as taking place between two heat reservoirs of fixed temperatures. When an amount of heat  $dQ$  flows from 1 to 2, the entropy increase is  $dS = (dQ/T_2) - (dQ/T_1)$ . Thus

$$
\frac{dS}{dt} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \frac{dQ}{dt} = \frac{k_B(\Delta T)^2}{T_1 T_2} \approx k_B \left(\frac{\Delta T}{T_0}\right)^2
$$

The temperature difference is

$$
(\Delta T)^{2} = (T_{1} - T_{2})^{2} = (2dT)^{2} = \frac{4(\gamma - 1)^{2}T_{0}^{2}x^{2}}{L^{2}}
$$

Hence

$$
\frac{dS}{dt} = ax^2
$$

where  $a = 4k_B(\gamma - 1)^2/L^2$ . (d)

Energy dissipation, which has so far been ignored, occurs at the rate  $T_0 dS/dt =$  $aT_0x^2$ . The time average of this rate is  $\frac{1}{2}aT_0x_0^2$ , where  $x_0$  is the amplitude of oscillation. The energy of oscillation is  $\bar{E} = \frac{1}{2}M\omega^2 x_0^2$ . In one period of oscillation, the energy dissipated is  $\Delta E = (2\pi/\omega) \frac{1}{2} a T_0 x_0^2$ . This gives a fractional dissipation per cycle

$$
\frac{\Delta E}{E} = \frac{2\pi T_0}{aM\omega^3}
$$

3.5 (a)

$$
P = -\left(\frac{\partial A}{\partial V}\right)_T = a_0(v_0 - v)
$$

(b)  $\kappa_T = -v^{-1}(\partial v/\partial P)_T = (a_0v)^{-1}$  $\alpha = v^{-1}(\partial v/\partial T)P = -v^{-1}(\partial P/\partial T)V(\partial v/\partial P)T$ , by chain rule.  $\alpha = \frac{1}{a_0 v}$  $da_0$  $dT$ 

(c)

$$
\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = a_0 (v_0^2 - v^2) - f
$$



For this problem it is important to use the entropy expression with arbitrary  $C_V$ , instead of setting it to  $(3/2)k_B$ . Write the adiabatic condition as

 $\Delta S = \Delta S_1 + \Delta S_2 = 0$ , or  $(N_1 + N_2)k_B \ln(V_f/V_i) + (N_1C_{V1} + N_2C_{V2}) \ln(T_f/T_i) = 0.$ Thus,  $T_f/T_i = (V_i/V_f)^5$ , where  $\zeta = k_B(N_1 + N_2)/(N_1C_{V1} + N_2C_{V2})$ . This means  $TV^{\zeta}$  = constant. Putting  $T = PV/Nk_BT$ , where  $N = N_1 + N_2T$ , we have

$$
PV^{\xi} = \text{constant}
$$

where

$$
\xi = \zeta + 1 = \frac{N_1(C_{V1} + k_B) + N_2(C_{V2} + k_B)}{N_1C_{V1} + N_2C_{V2}} = \frac{n_1C_{P1} + n_2C_{P2}}{n_1C_{V1} + n_2C_{V2}}
$$

3.7

(a)

Since the disks are thin, we can assume that their temperatures always remain uniform.

Let the final temperature be T.

The changes in temperatures are respectively  $\Delta T_1 = T - T_1$ ,  $\Delta T_2 = T - T_2$ . For simplicity write  $C_{P1} = C_1$ ,  $C_{P2} = C_2$ .

The amounts of heat absorbed are respectively  $\Delta Q_1 = C_1 \Delta T_1$ ,  $\Delta Q_2 =$  $C_2\Delta T_2$ .

Since the system is isolated  $\Delta Q_1 + \Delta Q_2 = 0$ . This gives

$$
T = \frac{C_1 T_1 + C_2 T_2}{C_1 + C_2}
$$

(b)

Consider the instant when the two temperatures are  $T_2', T_1', (T_2' > T_1')$ . When an amount of heat  $dQ$  flows from 2 to 1, the entropy increase is  $dS = (dQ/T'_1) - (dQ/T'_2).$ 

We can express  $dQ$  in terms of the  $dT'$  through  $dQ = C_1 dT_1' = -C_2 dT_2'$ . Thus we can rewrite  $dS = C_1(dT_1'/T_1') + C_2(dT_2'/T_2')$ .

$$
\Delta S = C_1 \int_{T_1}^{T} \frac{dT_1'}{T_1'} + C_2 \int_{T_2}^{T} \frac{dT_2'}{T_2'} = C_1 \ln \frac{T}{T_1} + C_2 \ln \frac{T}{T_2}
$$

3.8

The relations are straightforward mappings from a  $PV$  system to a magnetic system.

3.9

(a)

The desired expression are straightforward mappings of those for a  $PV$  system.

(b)

The first relation is the condition that  $dA$  be an exact differential. The second is obtained by using the equation of state  $M = \kappa H/T$ .

(c)

The chain rule states  $(\partial T/\partial H)_{S}(\partial H/\partial S)_{T}(\partial S/\partial T)_{H} = -1$ .

From (b) we have  $(\partial H/\partial S)_T = -T^2/(\kappa H)$ .

By definition, the heat absorbed at constant H is given by  $TdS = C_H dT$ . Thus  $(\partial S/\partial T)_H = C_H/T$ .

3.10

(a)

The important property to verify is that at constant  $T$  the entropy decreases as the magnetic field  $H$  increases.

(b)

Isothermal magnetization:  $dT = 0$ . The heat absorbed is The near absorbed is<br> $dQ = C_M dT - H dM = -H dM$ . Therefore

$$
Q = C_M dT - H dM = -H dM.
$$
 Therefore

$$
\Delta Q = -\int_0^H H dM = -\frac{\kappa H^2}{2T_0}
$$

(c)

Adiabatic cooling:  $dQ = 0$ . From  $dQ = C_M dT - H dM$  we obtain

 $dT = (H/C_M) dM = (\kappa/aT^2) M dM$ . Multiply both sides by  $T^2$  and integrate:

 $\int_{T_0}^{T_1} T^2 dT = (\kappa/a) \int_M^0 M dM.$ This gives  $T_1^3 = T_0^3 - (\kappa/2a) M^2$ , or

$$
T_1^3 = T_0^3 - \frac{\kappa^3 H^2}{2aT_0^2}
$$

This becomes negative when the magnetic field  $H$  is sufficiently large. However, the equation becomes invalid long before that happens, for it is based on Curie's law, which is valid only for weak fields.

 $\,$  CHAPTER 3.

#### 4.1

The system is in contact with a heat reservoir, but initially not in equilibrium with it. Let the stages of the process be labeled A,B,C:. We first calculate the heat absorbed  $\Delta Q$ , and the entropy change  $\Delta S$  of the system.

(A) Water cools from  $20^{\circ}$ C to  $0^{\circ}$ C.

 $\Delta Q = C_P \Delta T = -10 \times 4180 \times 20 \text{ J} = -8.36 \times 10^5 \text{ J}.$  $\Delta S = \int dQ/T = C_P \int dT/T = C_P \ln(T_f/T_i) = 41800 \ln(273/293) = -2.96 \times$  $10^3$ J/deg.

(B) Solidification at 0◦C.

 $\Delta Q = -10 \times 3.34 \times 10^5$  J =  $-3.34 \times 10^6$  J.  $\Delta S = \Delta Q/T = -3.34 \times 10^6 / 273 = -1.22 \times 10^4$  J/deg.

(C) Ice cools from  $0^{\circ}$ C to -10 $^{\circ}$ C.

 $\Delta Q = C_P' \Delta T = -10 \times 2090 \times 10 \text{ J} = -2.09 \times 10^5 \text{ J}.$  $\Delta S = C_P' \ln(T_f/T_i) = 20900 \ln(263/273) = -7.80 \times 10^2 \text{ J/deg.}$ 

Total heat absorbed by system:  $\Delta Q_{\rm sys} = -4.39 \times 10^6 \text{J}$ Total entropy change of system:  $\Delta S_\mathrm{sys} = -1.39 \times 10^4$  J/deg.

The reservoir has a fixed temperature  $T_0 = -10$ <sup>o</sup>C.. The total heat absorbed by reservoir equals that rejected by the system:  $\Delta Q_{\rm res} = 4.39 \times 10^6$  J. Entropy change of reservoir:  $\Delta S_{\rm res} = \Delta Q_{\rm res}/T_0 = 4.39 \times 10^6 / 263 = 1.67 \times 10^4$  J/deg.

$$
\Delta S_{\text{universe}} = \Delta S_{\text{res}} + \Delta S_{\text{res}} = 2.8 \times 10^3 \text{ J/deg}
$$

4.2

Let  $P_0, T_0$  be the pressure and absolute temperature at the triple point. Let  $L$  be the extensive latent heat (not specific latent heat.) Since the solid-gas

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transition can be made either via a direct path or a solid-liquid-gas path, we must have

$$
L_{\text{sublimation}} = L_{\text{melt}} + L_{\text{vap}}
$$
  
Vaporization: 
$$
dP/dT \approx L_{\text{vap}}/TV = PL_{\text{vap}}/Nk_BT^2.
$$

$$
P = P_0 \exp\left[\frac{L_{\text{vap}}}{Nk_BT_0} \left(1 - \frac{T_0}{T}\right)\right]
$$

Melting:  $dP/dT = L_{\text{vap}}/T\Delta V$ .

$$
P = P_0 + \frac{L_{\text{melt}}}{\Delta V} \ln \frac{T}{T_0}
$$

Sublimation:  $dP/dT \approx P(L_{\text{van}} + L_{\text{melt}})/Nk_BT^2$ .

$$
P = P_0 \exp\left[\frac{L_{\text{vap}} + L_{\text{melt}}}{N k_B T_0} \left(1 - \frac{T_0}{T}\right)\right]
$$

4.3  $dP/dT = \ell/T\Delta v = [1.44 \text{ J}/(18-20) \text{cm}^3]T^{-1}.$  $\therefore dT/dP = -c_0T$ , where  $c_0 = 1.39 \text{ cm}^3/\text{J}$ .

4.4

(a)

At a given  $v > v_0$ , the dashed line lies at a lower free energy than the solid line. The latter represents a "stretched" that fills the whole volume. The former represent a liquid drop at specific volume  $v_0$  that does not fill up the entire volume. This is therefore the preferred state of the liquid. At  $v = v_0$  the pressure is zero.

(b)

Now assume that the liquid coexists with its vapor, treated as an ideal gas. We are in the transition region of a first-order phase transition. At the given temperature, the liquid and gas have fixed densities, which must be consistent with the requirement of equal pressure  $P$  and chemical potential  $\mu$ . Denote quantities for the liquid with subscript 1, and those for the vapor with subscript 2:

 $P_1 = a_0(v_0 - v),$  $\mu_1 = a_0(v_0^2 - v^2) - f,$  $P_2 = n k_B T$ ,  $\mu_2 = k_B T \ln(n\lambda^3).$ 

where  $P_1, \mu_1$  were obtained in Prob.3.5, and  $\mu_2$  was given in Prob.3.2, with  $\lambda = \sqrt{2\pi\hbar^2/mk_BT}$ . Thus, the conditions determining v and n are

$$
a_0(v_0 - v) = nk_BT
$$
  

$$
a_0(v_0^2 - v^2) - f = k_BT \ln(n\lambda^3)
$$