

You are graded on your work (with partial credit where it is deserved) so please do not just write down answers with no explanation (or skip important steps)!

Please give clear, well-organized, understandable solutions.

$$\begin{array}{llll}
 h = 6.63 \times 10^{-34} \text{ J s} & \text{[Planck's constant]} & k = 1.38 \times 10^{-23} \text{ J/K} & \text{[Boltzmann constant]} \\
 c = 3.00 \times 10^8 \text{ m/s} & \text{[speed of light]} & m_e = 9.11 \times 10^{-31} \text{ kg} & \text{[mass of electron]} \\
 \sigma_B = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \cdot \text{K}^4} & \text{[Stefan-Boltzmann constant]} & G = 6.67 \times 10^{-11} \frac{\text{N m}^2}{\text{kg}^2} & \text{[gravitational constant]} \\
 1 \text{ eV} = 1.60 \times 10^{-19} \text{ J} & \text{and} & \frac{1 \text{ eV}}{k} = 11,600 \text{ K} & 0 \text{ }^\circ\text{C} = 273 \text{ K}
 \end{array}$$


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The variables have their usual meanings:  $E$  = energy,  $S$  = entropy,  $V$  = volume,  $N$  = number of particles,  $T$  = temperature,  $P$  = pressure,  $\mu$  = chemical potential,  $B$  = applied magnetic field,  $C_V$  = heat capacity at constant volume,  $k$  = Boltzmann constant. Also,  $\langle \dots \rangle$  represents an average.

You should know this, but:

$$\langle n(\epsilon_i) \rangle = \frac{1}{e^{(\epsilon_i - \mu)/kT} \pm 1} ; \quad dE = TdS - PdV + \mu dN ; \quad E = TS - PV + \mu N$$

$$PV^\gamma = \text{constant} \quad \text{for process in which entropy is constant} \quad PV = NkT$$


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1. **Stefan-Boltzmann law from thermodynamics alone.** Here we will employ only the *thermodynamics* of a classical radiation field, with no reference to statistical mechanics.

(a) (4) Use the first law of thermodynamics,

$$dE = dq - dw,$$

with  $dq$  and  $dw$  written in terms of  $dS$  and  $dV$  respectively, to obtain the familiar relation between  $dE$ ,  $dS$ , and  $dV$ .

For a quasiequilibrium process,  $dq = TdS$  &  $dw = PdV$ :

$$dE = TdS - PdV$$

(b) (4) Recall that the Helmholtz free energy is defined by  $F = E - TS$ . Use this definition and the result of part (a) to obtain  $dF$  in terms of  $dT$  and  $dV$ .

$$\begin{aligned} dF &= (TdS - PdV) - TdS - SdT \\ &= -SdT - PdV \end{aligned}$$

(c) (4) Using the result of part (b), obtain the Maxwell relation that relates  $\left(\frac{\partial S}{\partial V}\right)_T$  to  $\left(\frac{\partial P}{\partial T}\right)_V$ .

$$S = -\frac{\partial F}{\partial T} \quad \& \quad P = -\frac{\partial F}{\partial V}$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T} = -\frac{\partial^2 F}{\partial V \partial T} = -\frac{\partial^2 F}{\partial T \partial V} = \boxed{\left(\frac{\partial P}{\partial T}\right)_V}$$

(d) (4) Use the result of part (a) and the Maxwell relation in part (c) to obtain a relation between

$\left(\frac{\partial E}{\partial V}\right)_T$ ,  $\left(\frac{\partial P}{\partial T}\right)_V$ , and  $P$ .

With  $T$  constant, result in (a) implies

$$\frac{dE}{dV} = T \frac{dS}{dV} - P$$

$$\begin{aligned} \text{or } \boxed{\left(\frac{\partial E}{\partial V}\right)_T} &= T \left(\frac{\partial S}{\partial V}\right)_T - P \\ &= \boxed{T \left(\frac{\partial P}{\partial T}\right)_V - P} \end{aligned}$$

(e) (1) It is conventional to write  $E = Vu(T)$ , where the energy density  $u(T)$  is a function of only the temperature  $T$ . Rewrite the result of (d) in terms of  $u(T)$ ,  $\left(\frac{\partial P}{\partial T}\right)_V$ , and  $P$ .

$$u(T) = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

(f) (4) From Maxwell's equations of electromagnetism, it can be shown that  $P = \frac{1}{3}u$  for radiation. Use this relation and the result of part (e) to get a relation between  $u$  and  $\left(\frac{\partial u}{\partial T}\right)_V$ .

$$u(T) = T \cdot \frac{1}{3} \left( \frac{\partial u}{\partial T} \right)_V - \frac{1}{3} u$$

$$\Rightarrow \boxed{4u = T \left( \frac{\partial u}{\partial T} \right)_V}$$

(f) (4) Integrate this equation of part (f) (at constant volume) to obtain  $u = aT^n$ , while at the same time determining the constant  $n$ . This is essentially the Stefan-Boltzmann law, derived through a thermodynamic rather than a statistical-mechanics argument.

$$T \frac{du}{dT} = 4u \quad \text{with } V \text{ constant}$$

$$\Rightarrow \frac{du}{u} = 4 \frac{dT}{T}$$

$$\Rightarrow \ln u = 4 \ln T + \text{const}$$

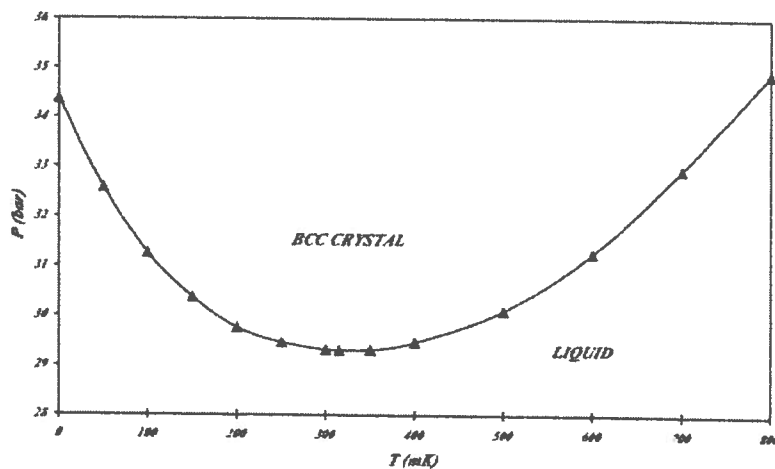
$$= \ln (\underbrace{\text{const}'}_{=a} \times T^4)$$

$$\Rightarrow \boxed{u = a T^4}$$

2. **The Pomeranchuk refrigerator.** On the right you will see the experimentally determined melting curve for  $^3\text{He}$ , in the neighborhood of its pressure minimum at  $T = 0.32 \text{ K}$  and  $P = 29.3 \text{ atm}$ .

(From <https://www.princeton.edu/~lhs/kecurve/kecurve.htm>, adapted from E.R. Dobbs. *Helium Three* (Oxford University Press, 2002).)

Let us start with general ideas and then consider this solid-liquid coexistence curve from 320 mK down to a few mK, temperatures that can be reached with the cooling technique below. ( $1 \text{ mK} = 10^{-3} \text{ K}$  of course)



(a) (3) Give a qualitative explanation of the fact that  $^3\text{He}$  remains a liquid at low temperature and  $P = 1 \text{ atm}$ . How many other substances have this property?

*Small mass  $\Rightarrow$  large zero-point vibrations  
only  $^3\text{He}$  &  $^4\text{He}$*

(b) (3) For a general system, use Euler's theorem and the expression for  $dE$  on the front page of this exam to obtain the (Gibbs-Duhem) relation between  $d\mu$ ,  $dT$ , and  $dP$ , or small  $\Delta\mu$ ,  $\Delta T$ , and  $\Delta P$ , in terms of the entropy  $s$  per particle and the volume  $v$  per particle.

*Euler's theorem & expression for  $dE$*

$$\Rightarrow Tds - PdV + \mu dN = Tds + SdT - PdV - VdP + \mu dN + Nd\mu$$

$$\Rightarrow Nd\mu = VdP - SdT$$

$$\text{or } N\Delta\mu = V\Delta P - S\Delta T \quad \text{or} \quad \boxed{\Delta\mu = v\Delta P - s\Delta T}$$

(c) (3) Now consider two closely-separated points A and B along a coexistence curve like the one shown in the figure above, and let  $\Delta\mu = \mu_B - \mu_A$ . Use the result of part (b), together with the condition for thermal equilibrium between two phases with the same kind of particles, to obtain the Clausius-Clapeyron equation – which relates the slope  $dP/dT$  along the coexistence curve to the differences  $\Delta s$  and  $\Delta v$  between the quantities  $s$  and  $v$  in the two phases.

$$\Delta\mu_{liq} - \Delta\mu_{sol} = (v_{liq} - v_{sol})\Delta P - (s_{liq} - s_{sol})\Delta T$$

$$\underbrace{\hspace{10em}}_{=0}$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{s_{liq} - s_{sol}}{v_{liq} - v_{sol}}} \quad \text{along coexistence curve}$$

(d) (4) Let us specialize to the case that the particles are  ${}^3\text{He}$  atoms in a **SOLID**, with spin  $\frac{1}{2}$  and thus 2 possible spin states per atom. (We neglect other contributions to the entropy, which become negligibly small at the temperatures considered here, between a few mK and 320 mK.) Based on Boltzmann's expression for the entropy  $S$ , what is  $s = S/N$  in **solid  ${}^3\text{He}$**  if each of the  $N$  atoms independently has the 2 spin states (up and down)?

$$W = \text{number of possible states} = 2^N$$

$$\Rightarrow S = k \ln W = k \ln 2^N = Nk \ln 2$$

$$\Rightarrow \boxed{s = k \ln 2}$$

(e) (4) On the other hand, if the particles are  ${}^3\text{He}$  atoms in a **LIQUID**, and we model this liquid as a quantum ideal gas of spin  $\frac{1}{2}$  fermions, the heat capacity at low temperatures is given by

$$C_V = \frac{\pi^2}{2} Nk \frac{T}{T_F} .$$

Using the fact that  $C_X = T \left( \frac{\partial S}{\partial T} \right)_X$  (with  $X=V$  here) and that  $C_V \rightarrow 0$  as  $T \rightarrow 0$  by the third law of

thermodynamics, integrate to obtain  $S(T)$  and then  $s(T) = \frac{S(T)}{N}$  in **liquid  ${}^3\text{He}$** .

At constant  $V$ ,

$$T \frac{dS}{dT} = AT \quad , \quad A \equiv \frac{\pi^2}{2} Nk \frac{1}{T_F}$$

$$\Rightarrow S = AT + \frac{\text{constant}}{T} \quad \text{by 3rd law}$$

$$\Rightarrow \boxed{s = \frac{\pi^2}{2} k \frac{T}{T_F}}$$

(f) (4) Let  $\Delta S = S_{\text{liq}} - S_{\text{sol}}$ , where  $S_{\text{sol}}$  and  $S_{\text{liq}}$  are the values of  $S$  in parts (d) and (e) respectively. For

$$\frac{T}{T_F} < \text{constant}$$

we will have

$$\Delta S < 0.$$

Calculate this constant using your results from parts (d) and (e).

$$\Delta S < 0 \text{ means } \frac{\pi^2}{2} \cancel{\times} \frac{T}{T_F} - \cancel{\times} \ln 2 < 0$$

$$\text{or } \boxed{\frac{T}{T_F} < \frac{2 \ln 2}{\pi^2}}$$

(g) (4) Now let  $\Delta v$  be the change in volume per atom when  $^3\text{He}$  goes from solid to liquid:  $\Delta v = v_{\text{liq}} - v_{\text{sol}}$ . It turns out that

$$\Delta v > 0.$$

**Clearly** explain why the temperature will fall along the coexistence curve, for  $T < \text{constant} \times T_F$ , as the pressure is increased. I.e., why does  $\Delta P > 0$  imply that  $\Delta T < 0$  at low  $T$ ? (We thus cool the system by squeezing it.)

$$\text{For } T < \frac{2 \ln 2}{\pi^2} T_F, \text{ we have } \Delta S < 0$$

$$\text{and } \frac{dP}{dT} = \frac{\Delta S}{\Delta v} < 0 \quad [\text{by part (c) in this new notation}]$$

so  $\Delta P > 0$  implies that  $\Delta T < 0$

and compression  $\Rightarrow$  cooling  
 [if we stay on the coexistence curve]

3. **Adiabatic compression.** A Diesel engine requires no spark plug. Instead the air is compressed so much that the fuel ignites spontaneously. Recall that air is composed 99% of the diatomic molecules  $N_2$  and  $O_2$  and that we can ignore the contribution of molecular vibrations to the energy and heat capacity in a problem like the one below.

(a) (5) In preparation, use the equipartition theorem to determine the energy  $E$  of a diatomic ideal gas with  $N$  molecules at temperature  $T$ , bearing in mind that there are 3 translational and 2 relevant rotational degrees of freedom per molecule.

only kinetic energy for these degrees of freedom  
(which are nonrelativistic and nearly classical  
for the usual temperatures)

$$\Rightarrow 5 \times \frac{1}{2} kT \text{ per molecule} \Rightarrow \boxed{E = \frac{5}{2} NkT}$$

(b) (5) Use the result of part (a), plus the fact that  $C_p = C_v + Nk$ , to obtain  $C_v$ ,  $C_p$ , and the approximate value of the ratio  $\gamma = C_p / C_v$  for air.

$$C_v = \frac{\partial E}{\partial T} = \frac{5}{2} Nk$$

$$C_p = C_v + Nk = \frac{7}{2} Nk$$

$$\boxed{\gamma} = \frac{C_p}{C_v} = \boxed{\frac{7}{5}} \text{ or } 1.4$$

(c) (10) The air in a cylinder of a Diesel engine starts at a temperature of  $20^\circ\text{C}$  and a pressure of 1 atm. It is then adiabatically compressed by a factor of 15. (I.e., the final volume is  $1/15$  of the initial volume.) What is the final pressure, in atm?

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

$$\Rightarrow \frac{P_{\text{final}}}{P_{\text{initial}}} = \left( \frac{V_{\text{initial}}}{V_{\text{final}}} \right)^\gamma = (15)^{1.4} = 44.3$$

$$\Rightarrow \boxed{P_{\text{final}} = 44.3 \text{ atm}}$$

(d) (5) What is the final temperature?

$$PV = NkT$$

$$\begin{aligned} \Rightarrow \frac{T_{\text{final}}}{T_{\text{initial}}} &= \frac{(PV)_{\text{final}}}{(PV)_{\text{initial}}} \\ &= \frac{44.3 \text{ atm}}{1 \text{ atm}} \cdot \frac{1}{15} \\ &= 2.95 \end{aligned}$$

$$\Rightarrow \boxed{T_{\text{final}} = (2.95)(273 + 20) \text{ K}} \\ = \boxed{866 \text{ K}} = \boxed{593^\circ\text{C}}$$

4. **Minimum free energy.** Let us demonstrate that the appropriate free energy is minimized in thermodynamic equilibrium by considering a system at constant temperature  $T$  and pressure  $P$ , for which the Gibbs free energy  $G = E - TS + PV$  is appropriate. (The proof for other cases is very similar.)

(a) (5) Write down the first law of thermodynamics, relating  $q$  to  $\Delta E$  and  $w$ , where  $q$  is the heat added,  $\Delta E$  is the change in internal energy, and  $w$  is the work done by the system.

$$q = \Delta E + w$$

(b) (5) Write down an inequality relating  $T\Delta S$  to  $q$ , where  $\Delta S$  is the change in entropy. Why is  $T\Delta S$  not equal to  $q$  when an ideal gas undergoes a free expansion?

$$T\Delta S \geq q$$

free expansion  $\Rightarrow \Delta S > 0$  with  $q = 0$

(c) (5) Use the results of parts (a) and (b) to write down an inequality relating  $T\Delta S$  to  $\Delta E$  and  $P\Delta V$ .

$$T\Delta S \geq \Delta E + P\Delta V$$

(d) (5) Use the result of part (c) to obtain an inequality for  $\Delta G$  when the system is released out of equilibrium and undergoes spontaneous random changes.

$$\Delta E - T\Delta S + P\Delta V \leq 0$$

&  $\Delta G = \Delta E - T\Delta S + P\Delta V$  with  $T$  &  $P$  constant

$$\Rightarrow \Delta G \leq 0$$

(e) (5) Explain **clearly** why your result in part (d) implies that the system has reached a state of thermal equilibrium if  $G$  has reached a minimum.

When  $G$  has reached a minimum, a change in the thermodynamic state would mean that  $\Delta G > 0$ . This is impossible because  $\Delta G \leq 0$ , so we have thermal equilibrium. [This argument is good enough here. A more rigorous argument involves the entropy of a full system with a reservoir.]

Merry Christmas and Happy Holidays!