

Notes:

Exam: - Friday Oct. 29, 6 PM, **Room 205** MPHY.

- Coverage through section 6.4. You can make one page formula sheet. 8.5*11 inch, both sides.

Canvas grades & lecture links: sample exams on Canvas now have solutions.

Tomorrow I intend to review; I will accept requests for previous questions from HW etc. to address.

Problem 4 I didn't finish:

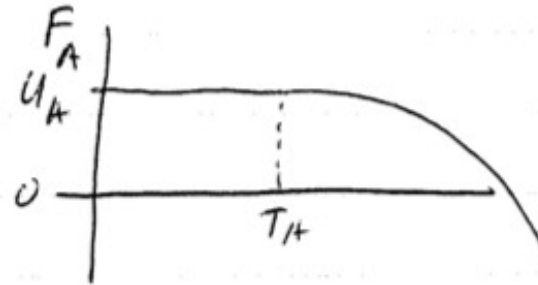
$$\text{so } F = U - TS = U_A + C(T - T_A) - CT \ln(T/T_A), \quad T > T_A \\ = U_A, \quad T < T_A$$

For plotting, note that:

$$\frac{F}{T_A} = \frac{U_A}{T_A} + C \left[x - 1 - x \ln x \right]$$

$$\frac{d}{dx} \Rightarrow C(1 - \ln x - 1)$$

[slope = 0 at $x=1$ & decreasing]



$$U_A + C(2T_A - T_A) - C(2T_A) \ln 2 = U_B$$

$$\text{so } U_A - U_B = C T_A (2 \ln 2 - 1)$$

(d) Normally for transformations at constant P, the enthalpy is $(\Delta U - \text{work}) = \Delta Q$ but here with $V = \text{constant}$, ΔH is just ΔU .

(note the ST term doesn't go in)

$$\text{this is, } \Delta H = U_A + C(2T_A - T_A) - U_B = U_A - U_B + C T_A \\ = C T_A (2 \ln 2)$$

$$a) S = \left(\frac{R^2}{v_0 \theta} \right)^{1/3} (NVU)^{1/3}$$

$$b) S = \left(\frac{R}{\theta^2} \right)^{1/3} \left(\frac{NU}{V} \right)^{2/3}$$

$$c) S = \left(\frac{R}{\theta} \right)^{1/2} \left(NU + \frac{R\theta V^2}{v_0^2} \right)^{1/2}$$

$$d) S = \left(\frac{R^2 \theta}{v_0^3} \right) V^3 / NU$$

$$e) S = \left(\frac{R^3}{v_0 \theta^2} \right)^{1/5} [N^2 V U^2]^{1/5}$$

Which of these is not physically reasonable? (Callen chapter 1)

Find equations of state?

Find C_v ?

P vs V for isostatic isotherm?

ΔS for free expansion?

Problem set 4 note how the equations of state derived:

Given by the equation:

$$S = \sum_J N_J s_{J0} + \left(\sum_J N_J c_J \right) R \ln \frac{T}{T_0} + \sum_J N_J R \ln \left(\frac{V}{N_J v_0} \right)$$

$$U = \left(\sum_J N_J c_J \right) RT$$

Because the mixture is a two-component mixture of simple ideal gases. the four equation of state is :

$$S = N_1 s_1 + N_2 s_2 + (N_1 c_1 + N_2 c_2) R \ln \frac{T}{T_0} + N_1 R \ln \left(\frac{V}{N_1 v_0} \right) + N_2 R \ln \left(\frac{V}{N_2 v_0} \right)$$

$$\frac{1}{T} = \frac{(N_1 c_1 + N_2 c_2) R}{U}$$

$$\frac{P}{T} = \frac{(N_1 + N_2) R}{V}$$

$$\frac{\mu_1}{T} = -S_1 + R c_1 + R - c_1 R \ln \frac{T}{T_0} - R \ln \left(\frac{V}{N_1 v_0} \right)$$

$$\frac{\mu_2}{T} = -S_2 + R c_1 + R - c_2 R \ln \frac{T}{T_0} - R \ln \left(\frac{V}{N_2 v_0} \right)$$

3) Given a system that exhibits the equations of state $P = A s^3/v^2$, and $T = 3A s^2/v$,

a) Determine α , c_V , c_P , κ_T , and κ_S .

b) Show that $c_P = c_V + \frac{Tv\alpha^2}{\kappa_T}$.

c) Show that $\kappa_T = \kappa_S + \frac{Tv\alpha^2}{c_P}$.

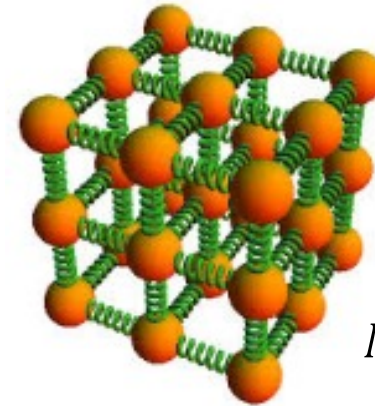
Find fundamental equation?

Does F increase or decrease vs T?

Einstein oscillator problem:

binomial with q quanta, $3N$ oscillators:

$$\Omega = \frac{(3N+q-1)!}{(q)!(3N-1)!}$$



N atoms

Find, $S = k_B \left[3N \ln \left(1 + \frac{q}{3N} \right) + \overset{U/\hbar\omega_0}{q} \ln \left(1 + \frac{3N}{q} \right) \right]$

$$\frac{1}{T} = \frac{k_B}{\hbar\omega_0} \ln \left(1 + \frac{3N}{q} \right)$$



$$U = \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1}$$

- Sketch S vs U ?
- Place two isolated equal- N solids with different ω_0 in thermal contact; one has $U = 0$. What is final situation in low- T and high- T limit?

Results:

Continuum
limit in cavity,

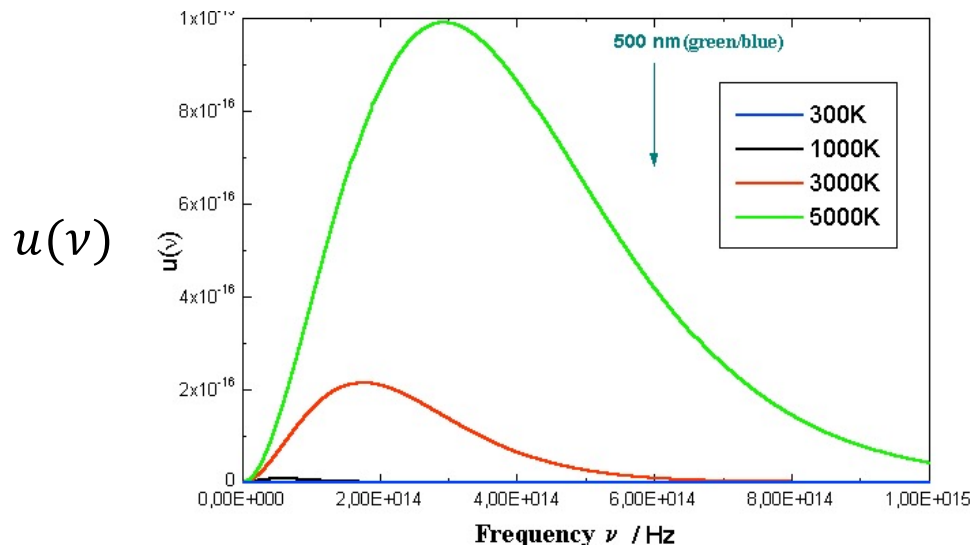
$$U = \sum_{\text{all modes}} \frac{\hbar\omega_i}{(e^{\beta\hbar\omega_i} - 1)} \Rightarrow 2 \int_0^\infty \frac{\pi V k^2 dk}{\pi^3} \frac{\hbar kc}{(e^{\beta\hbar kc} - 1)}$$

$$U = \frac{V\pi^2(kT)^4}{15(\hbar c)^3}$$

← $\frac{U}{V}$ independent of cavity details, recovers thermodynamic result showed last time.

Infinite number of “oscillators” but finite result due to exponential.
result closely related to Stefan-Boltzmann intensity law.

Peak $\hbar\omega \cong 2.8kT$



- Identify # photons in a given mode above?
- Can we find pressure and entropy from what is given above?
- If P_s is total power from sun to earth, what is *rate of entropy increase* due to radiation in/out of earth?

Blackbody radiation, thermodynamic solution

- Experimental quantities:

$$U = bVT^4$$
$$P = U/(3V)$$

$I = \sigma T^4$ Stefan-Boltzmann
intensity relation

- Then can easily solve for $S = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}$,
using methods we have seen.

- Also note, $S = \frac{4U}{3T}$ simpler form.

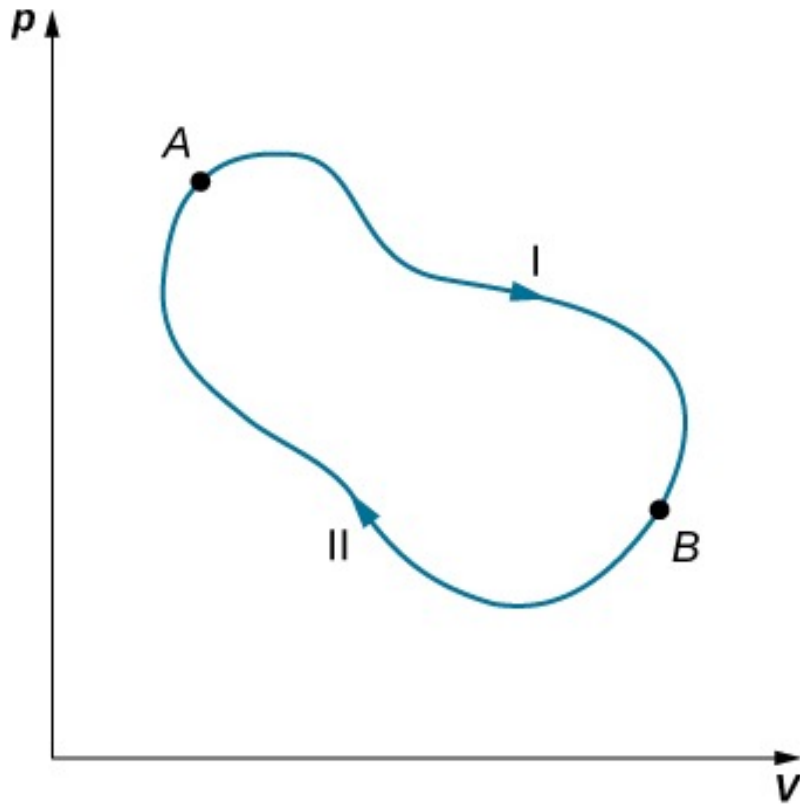
$S \cong 3.6 \langle N \rangle k_B$
“independent of T ”
form

- Note N is formally zero (or can treat N as number of photons; $\mu = 0$ since U independent of N).

also note, $PV \approx NkT$



- For this cycle, if the work per cycle equals the heat expelled per cycle, what is the efficiency?
- Could this cycle be run as a reversible cycle? How?
- Suppose an ideal gas is the working fluid. How would a cycle be configured (in a P-V plot) to have the same work output per cycle, but maximum efficiency?



- For the ideal gas case, identify the parts of the path with heat flow into the gas, and out of the gas. (Think of constructing adiabatic PV curves for comparison.)

- 1 and 2 are two different states occurring for the same material, and g is the per-mole Gibbs free energy. Under what external conditions will the crossing point correspond to a phase transition?
- Which phase has the larger entropy per mole?
- Why are the shapes of the two curves shown (they are straight lines) not reasonable?

