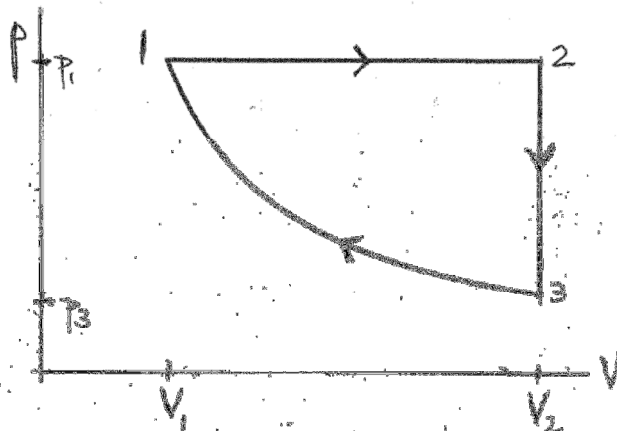


"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

Oct. 29, 2013 Sign Honor Pledge: _____

Don't get bogged down on any problem you find difficult. Skip ahead and go through all 4 pages, then come back to it afterwards!! Note that not all later parts of problems depend on the answers to earlier parts, so you should read through entire problems. You may detach the equation sheet from the back of the exam for easier use.

1) Consider the *reversible* cycle in which a mole of an *ideal* gas of *atoms* expands isobarically from initial point 1, which has volume V_1 , pressure p_1 and temperature T_1 , until point 2 where $V_2 = b V_1$ (where b is some number [unrelated to the van der Waals b] greater than 1). The gas then decreases pressure isochromically till point 3 and returns to point 1 isothermally. See picture.



a) What are the pressure p_2 and the temperature T_2 at point 2?

b) What are the pressure p_3 and the temperature T_3 at point 3?

c) Find the work done *by* the gas on each leg of the cycle and, from that, the work done in the entire 3-leg cycle.

d) What is change ΔU in internal energy on each cycle? Express your answer in terms of temperatures.

e) How much heat in total enters the gas during one cycle? (You do not need to compute each leg to answer this.)

f) Show that heat enters (rather than leaves) the gas during only one of the legs. Which leg is it?

g) How does the efficiency e of this engine compare to $1 - (T_c/T_h) = 1 - (T_1/T_2)$? On what, briefly, do you base your answer? (You do *not* need to (and should not) compute e to answer this part.)

h) Is there any leg on which there is *no* change in entropy? Justify your answer very briefly.

i) Suppose the system expands irreversibly (like freely, but with an increasing temperature) rather than reversibly from point 1 to point 2.

Compare ΔS_{free} , ΔU_{free} , and $W^{\text{by}}_{\text{free}}$ with your answers for the reversible case. (You can answer this part without knowing the values of those three quantities from the previous parts.)

2) Using Stirling's approximation, work out the entropy of the N -spin paramagnet in the macrostate in which $1/3$ of the spins are in one direction (say up) and $2/3$ in the opposite direction (down), simplifying as much as possible and showing that this entropy is extensive.

3) a) Starting from the thermodynamic identity for $dU(S,V)$ or $dG(T,p)$, find the identity for $dH(S,p)$.

b) At fixed p and N , find $\partial G/\partial T$ and $\partial^2 G/\partial T^2$ and from these, whether the slope and the curvature of G are positive or negative.

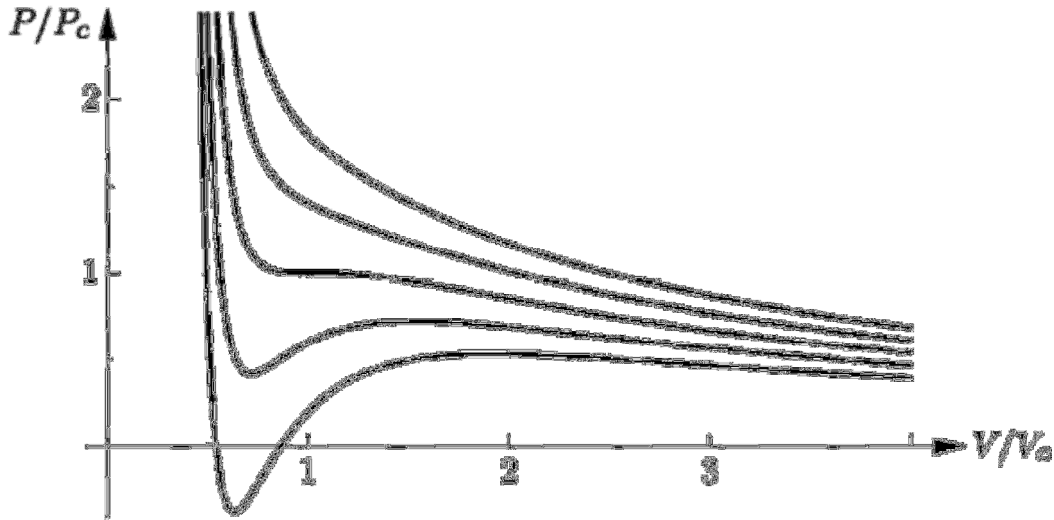
4) a) Recall that $dU(S,L) = TdS + \mathcal{F} dL$ for a rubber band. Find the Maxwell relation for $\partial \mathcal{F}/\partial S$.

b) Find the thermodynamic identity for associated Helmholtz free energy $F(T,L)$. (\mathcal{F} is the force, to be distinguished from F .)

5) In a system that is in a regime with negative temperature, **circle** those of the following which are positive. (Note that $U(0^+)$ is the energy of the “ground state,” the limit of $U(T)$ as $T \rightarrow 0$ from above.)

Entropy S Energy $U(T) - U(0^+)$ $\partial S/\partial U$ dU/dT $(dU/dT) / [T(dS/dT)]$

6) a) Consider the depicted family of isotherms for the van der Waals (vdW) equation (cf. Study Sheet).



i) What are the conditions on $p(V)$ at the critical point? Draw an X at it in the plot.

ii) For the second lowest (second from bottom) isotherm, indicate the region of volumes over which the system is unstable, i.e. $\kappa_T = -V^{-1}(\partial V/\partial p)_T < 0$. (You may thicken the horizontal axis over this region.)

iii) Draw the Maxwell construction for this isotherm. Indicate clearly the two values of the volumes of the coexisting phases.

b) i) What is the physical origin of the two additions to the ideal gas equation that result in the vdW equation of state?

ii) As in homework, find the second virial coefficient $B(T)$ for the vdW equation of state. Compare with temperature at which it vanishes to $T_{cr} = 8a/27bk_B$

Study Guide for Midterm, PHYS404, Fall 2013

ver. 1.00

Heat, work (on or by), temperature, [internal] energy, heat capacity, latent heat, entropy, enthalpy

3 basic models: paramagnet (2-state), Einstein solid, ideal gas

– What N and q (or U) mean for each, and the resulting multiplicities $\Omega(N, \dots)$

$$\Omega(N, N_{\uparrow}) = \frac{N!}{N_{\uparrow}!(N - N_{\uparrow})!}$$

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

$$\Omega(U, V, N) = f(N)V^N U^{fN/2}$$

2 weakly interacting systems, thermodynamic limit
Application of models to other physical systems

Equipartition theorem at thermal equilibrium:

$U = (f/2) Nk_B T$; determining f : 3 for atoms,
5 for diatomic molecules at room T , 7 at higher T ,
2 for each direction of an Einstein oscillator

Ideal gas law $pV = Nk_B T = nRT$

Virial exp. $pV = nRT [1 + B(T)/(V/n) + C(T)/(V/n)^2 + \dots]$

Entropy $S = k_B \ln \Omega = \int dQ_{\text{rev}}/T$

Ideal gas $S = Nk_B [(V/(N\lambda^3)) + 5/2]$; $\lambda = h/\sqrt{2\pi m k_B T}$

Paramag $S = Nk_B [\ln(2 \cosh x) - x \tanh x]$; $x = \mu B/k_B T$

$C_i = dQ_i/dT = T dS_i/dT$ $i = V, p, \text{etc.}$

Quasistatic vs. free expansion, microstate vs. macrostate; intensive vs. extensive

Laws of thermodynamics, and what they mean

$$\Delta U = Q + W_{\text{on}} = Q - W_{\text{by}} \quad \Delta S \geq 0 \text{ (when?)}$$

Spreadsheet computations of Ω, S, U, T, C for paramagnets and Einstein solids

Constants: $k_B \approx 10^{-4} \text{ eV/K} = 1.38 \times 10^{-23} \text{ J/K}$

C_V of 1 gm of water (ice) is 1 cal/K ($\sim 1/2$ cal/K)

$R \sim 8.3 \text{ J/K}$ $N_A = 6.02 \times 10^{23}$

Meaning of mole: mass = atomic wgt grams

Heat engines, Carnot cycles, refrigerators, efficiency, coefficient of performance

Very large numbers; Stirling's approximation,

$\ln n! \approx n \ln n - n [+1/2 \ln n + 1/2 \ln(2\pi)]$, and use

Expansions in $\epsilon \ll 1$:

$$\ln(1 \pm \epsilon) \approx \pm \epsilon [-\epsilon^2/2], \quad \exp(\pm \epsilon) \approx 1 \pm \epsilon [+ \epsilon^2/2!]$$

$$1/(1 \pm \epsilon) \approx 1 \mp \epsilon + \epsilon^2 \mp \epsilon^3 + \epsilon^4 \dots$$

pV diagrams: adiabat, isotherm, isobar, isochrom

Change in internal energy, change in temperature, heat, work, during "simple" processes:

isobaric ($\Delta p = 0$), isochoric ($\Delta V = 0 = W$), isothermal ($\Delta U = \Delta T = 0$), adiabatic ($Q = 0$).

Along an isobar, $W_{\text{by}} = p(V_f - V_i)$; along an isotherm $W_{\text{by}} = Nk_B T \ln(V_f/V_i)$

Along an adiabat pV^γ is constant = $Nk_B T V^{\gamma-1}$ (using the ideal gas law) $W_{\text{by}} = (f/2) Nk_B (T_i - T_f)$; $\gamma = (f+2)/f$

Helmholtz and Gibbs free energies $F(T, V, [N]) =$

$$U - TS \quad G(T, p, [N]) = U + pV - TS = H$$

$U(V, S, [N]) \quad H(p, S, [N]) \quad [U, H, F, G \text{ all have } +\mu N]$

$$\Phi = U - TS - \mu N$$

Electrolysis

What does thermal equilibrium mean?

Thermo. identities: $dU = TdS - p dV + \mu dN$

$dG = -S dT + V dp + \mu dN$, etc. & uses

Maxwell relations: 2nd derivatives of thermo functions do not depend on order of derivatives

Graphs of $G(p, T)$ with one held fixed, implications for phase transitions

van der Waals: $p = Nk_B T/(V - Nb) - a(N/V)^2$

or $p = nRT/(V - nB) - \bar{a}(n/V)^2$, $B \equiv N_A b$, $\bar{a} \equiv N_A^2 a$

and its $p(V)$ isotherms, critical point, implications for liquid-gas transitions, coexistence, instability

$$\beta = V^{-1} \partial V / \partial T|_p \quad \kappa_T = -V^{-1} \partial V / \partial p|_T$$

$$\Delta S_{\text{mix}} = -Nk_B [x \ln x + (1-x) \ln(1-x)]$$