

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

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

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, isochrome

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 $F(T, V, [N]) =$

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

$U(V, S, [N])$ $H(p, S, [N])$ [U, H, F, G 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 $p = nRT/(V - nB) - \bar{d}(n/V)^2$, $B \equiv N_A b$, $\bar{d} \equiv N_A^2 a$

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

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

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