

Formulas:

First law $\Delta U = Q + W$; $C_V = \left(\frac{\partial U}{\partial T}\right)_V$; $H = U + PV$; $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

$k = 1.381 \times 10^{-23} \text{ J/K}$, $N_A = 6.02 \times 10^{23}$, $R = 8.31 \text{ J/(mol}^\circ\text{K)}$

Ideal gas : $PV = NkT$; $U = N \frac{f}{2} kT$; $W = -P\Delta V$, $W = -\int PdV$; $C_P = C_V + Nk$

adiabatic process: $PV^\gamma = \text{const.}$, $\gamma = (f + 2)/f$

$S = k \ln \Omega$; $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$; $dS = \frac{Q}{T} = \frac{C_V dT}{T}$ (constant volume)

Stirling's approximation : $n! = n^n e^{-n} \sqrt{2\pi n}$

Ideal gas (monoatomic) : $\Omega_N = C_N V^N U^{3N/2} / N!$

Einstein solid : $\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!} \sim \left(\frac{eq}{N}\right)^N$ for $q \gg N$

Two - state system : $\Omega = \frac{N!}{N_\uparrow! N_\downarrow!}$

Paramagnetism : $M = N\mu \tanh(\mu B/kT)$, $U = -MB$, $M = \mu(N_\uparrow - N_\downarrow)$

$dU = TdS - PdV$; $Q = TdS$, $W = -PdV$ (quasistatic)

$U(S, V)$; $F(T, V) = U - TS$; $H(S, P) = U + PV$; $G(T, P) = U - TS + PV$

$C_V = T \left(\frac{\partial S}{\partial T}\right)_V$; $C_P = T \left(\frac{\partial S}{\partial T}\right)_P$; $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$; $\kappa_{T,S} = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,S}$; $\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial U}{\partial N}\right)_{S,V}$

$\mu = -kT \ln \left(\frac{V}{N} \left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right)$ Ideal gas (monoatomic)

Heat engines : $e = \frac{W}{Q_h} \leq 1 - \frac{T_c}{T_h}$; Refrigerators : $COP = \frac{Q_c}{W} \leq \frac{T_c}{T_h - T_c}$

Maxwell relations : $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$; $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$; $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$; $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Van der Waals : $(P + a \frac{N^2}{V^2})(V - Nb) = NkT$; Virial : $PV = NkT(1 + \frac{N}{V} B_2(T) + \frac{N^2}{V^2} B_3(T) + \dots)$

Boltzmann distribution : $P(E_i) = C e^{-E_i/kT}$; $C = 1 / \sum_i e^{-E_i/kT} \equiv 1/Z$; $P(E) = C \Omega(E) e^{-E/kT}$

$F = -kT \ln Z$; $\bar{E} = -\frac{\partial}{\partial \beta} \ln Z$; $\sigma_E = kT \sqrt{C_V/k}$; $Z = \frac{Z_1}{N!}$; $Z_1 = \frac{V}{v_Q} Z_{\text{int}}$; $v_Q = \left(\frac{h^2}{2\pi m kT}\right)^{3/2}$

$\mu = -kT \ln(Z_1/N)$; Gaussian integrals : $I_n = \int_{-\infty}^{\infty} dx x^n e^{-\lambda x^2}$; $I_0 = \sqrt{\pi/\lambda}$; $I_{n+2} = -\partial I_n / \partial \lambda$

Grand partition function : $Z = \sum_s e^{-\beta E(s) - \alpha N(s)} = \sum_s e^{-\beta(E(s) - \mu N(s))}$; $P(s) = e^{-\beta(E(s) - \mu N(s))} / Z$

Grand potential : $\phi = -kT \ln Z = U - TS - \mu N$; $\bar{N} = -\frac{\partial}{\partial \alpha} \ln Z$; $\sigma_N = \sqrt{kT \partial \bar{N} / \partial \mu}$

$P(n) = e^{-\beta n(\epsilon - \mu)} / Z$; $\bar{n} = \frac{1}{e^{\beta(\epsilon - \mu)} + s}$, $s = +1$ (FD), $s = -1$ (BE), $s = 0$ (class.)

Justify all your answers to all (3) problems

Problem 1

A particle can be in one of three energy states, of energy 0, 2ϵ and 5ϵ and degeneracy 1, 3 and 1 respectively.

- (a) Find the average energy of this particle at infinite temperature.
- (b) At what temperature is the average energy of this particle 2ϵ ?
- (c) At what temperature is this particle equally likely to have energy 0 and energy 2ϵ ?
- (d) Find the value of the Helmholtz free energy F at temperature $kT=5\epsilon$. Give your answer in terms of ϵ .

Problem 2

A diatomic molecule composed of distinguishable atoms has rotational energy levels $E_r(j) = \epsilon_r j(j+1)$ of degeneracy $(2j+1)$, with $j=0, 1, 2, 3, \dots$, and $\epsilon_r=0.002\text{eV}$. It also can vibrate along the line connecting the two atoms, with the energy difference between two neighboring vibrational energy levels being 0.04eV .

- (a) At temperature $kT=0.02\text{eV}$, give the average rotational and vibrational energies in eV (one of the answers may be slightly approximate).
- (b) Give an approximate value for the rotational partition function at temperature $kT=0.002\text{eV}$ that is accurate to three decimal places.
- (c) Find the heat capacity per molecule from vibration only, at temperatures (i) $kT=0.08\text{eV}$, (ii) $kT=0.8\text{ eV}$, (iii) $kT=800,000\text{ eV}$. Give your answers in terms of k .

Problem 3

A system has three non-degenerate single-particle levels with energy 0, ϵ and 2ϵ respectively.

- (a) Assuming the system has exactly 2 particles, how many states does this system have if the two particles are spinless and (i) fermions, (ii) bosons, (iii) classical distinguishable?
- (b) What is the total number of states that this system can have if the particles are spinless fermions but their number is not fixed?
- (c) If the particles are spinless fermions, what are the possible values for the total energy of this system at zero temperature depending on the number of particles? Assume the system has an integral number of particles.
- (d) What are the possible values of the chemical potential for the answers given in (c)? You should give a range of possible values of the chemical potential, in terms of ϵ , for each of the answers given in (c).

Justify all your answers to all problems