

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

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

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

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

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

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

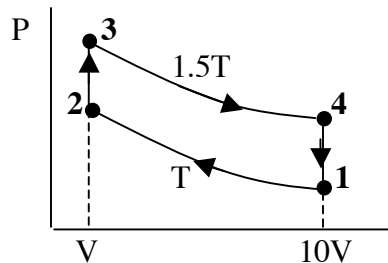
Clausius - Clapeyron: $\frac{dP}{dT} = \frac{L}{T\Delta V}$; for ideal gas $P = P_0 e^{-L/RT}$

Chemical equilibrium: $\sum_i b_i \mu_i = 0$ for reaction $\sum_i b_i B_i = 0$

Justify all your answers to all (6) problems

Problem 1

Consider a heat engine that uses a monoatomic ideal gas undergoing the cycle through points 1, 2, 3 and 4 shown in the pressure-volume diagram below:



Steps 1-2 and 3-4 are at constant temperature T and $1.5T$, steps 2-3 and 4-1 are at constant volume V and $10V$. The gas has N atoms.

- Find the work done by this engine in one cycle in terms of T and N .
- Find the heat absorbed in the step 3-4 in terms of T and N .
- Find the heat absorbed in the step 2-3 in terms of T and N .
- Find the efficiency of this engine, defined as: $e = (\text{work performed}) / (\text{heat absorbed})$ per cycle.
- Show that the efficiency found is lower than that of a Carnot engine operating between temperatures T and $1.5T$. Explain why.

Problem 2

Consider a system of N (N is large) distinguishable atoms, each of which can be in only one of two states: the lowest energy state with energy 0 , and an excited state with energy $\epsilon > 0$. When there are n atoms in the excited state (and $N-n$ in the lowest state) the total energy is $U = n\epsilon$.

- Give the multiplicity of this system $\Omega(n)$ for (i) $n=0$, (ii) $n=1$, (iii) $n=2$, (iv) $n=N-1$ and (v) $n=N$. Multiplicity = number of different states for given n .
- Give the general formula for $\Omega(n)$ for any n value, and a simplified form using Stirling's approximation (ignore the square root terms).
- Calculate $\ln(\Omega(n))$ from the approximate form found in (b) and find the value of n for which $\ln(\Omega(n))$ is maximum.
- Using the definition of temperature $1/T = k \partial(\ln \Omega) / \partial U$ and $U = n\epsilon$, find an expression for T as function of n , N and ϵ .
- Inverting the result in (d), find an expression for n in terms of ϵ , T and N .
- Suppose two such systems are in contact so that they can interchange energy. System 1 has $N_1 = 1,000$ atoms, system 2 has $N_2 = 1,000,000$ atoms. If initially system 1 has $n_1 = 10$ atoms in the excited state and system 2 has $n_2 = 1,000$ atoms in the excited state, in which direction is energy most likely to flow? From 1 to 2 or from 2 to 1? Explain your answer.

Problem 3

The Joule-Thomson coefficient, giving the change in temperature in a throttling process, is defined as $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$, where H, the enthalpy, is held constant. To derive a formula for μ_{JT} :

- Write an expression for dH in terms of dS and dP. Hint: use the thermodynamic identity $dU=TdS-PdV$.
- By considering S as function of T and P, write the expression for dH obtained in (a) in terms of dT and dP and partial derivatives of S.
- Replace the partial derivatives in your expression for dH in terms of measurable quantities such as C_V , C_P , $\beta = \left(\frac{1}{V} \frac{\partial V}{\partial T}\right)_P$, $\kappa_T = -\left(\frac{1}{V} \frac{\partial V}{\partial P}\right)_T$, $\kappa_S = -\left(\frac{1}{V} \frac{\partial V}{\partial P}\right)_S$ given in the formula sheet. You will have to use a Maxwell relation.
- From the obtained expression for dH, derive an expression for μ_{JT} that involves only measurable quantities such as those given in (c) as well as possibly volume, temperature and / or pressure.
- Evaluate the expression for μ_{JT} found in (d) for the case of a monoatomic ideal gas, with equation of state $PV=NkT$.

Problem 4

A particle can be in one of 3 energy states, of energy 0, ϵ and 10ϵ , with $\epsilon>0$. All states are doubly degenerate. A system of N such particles (distinguishable) is in contact with a heat reservoir at temperature T.

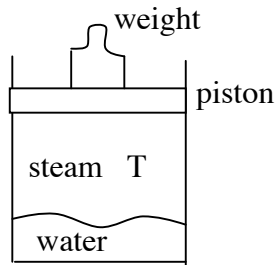
- Give an expression for the average energy of a particle. What is the value of the average energy for (i) $T\rightarrow\infty$ and (ii) $T=0$? (iii) For what value of T is the average energy of this particle equal to ϵ ?
- Give expressions for the total energy of this system of N particles, U, for the free energy F and for the entropy S, all at temperature T.
- Find the limiting values of the entropy of this system for $T\rightarrow 0$ and for $T\rightarrow\infty$.
- Find the limiting values of the heat capacity of this system for $T\rightarrow 0$ and for $T\rightarrow\infty$.
- Find an expression for the heat capacity C of this system at very low (but non-zero) temperatures, and give the value of C in terms of k (Boltzmann constant) for temperature $kT=\epsilon/10$. Hint: simplify the formula for U to a simpler form that is approximately valid at very low temperatures before you compute C.

Problem 5

A new kind of quantum particle has recently been discovered and named "parafermion". Parafermions obey a new quantum statistics, different from fermion and boson statistics. Unlike fermion systems where there can be at most one fermion in each single particle energy state, in a system of identical parafermions each single particle state can be occupied by 0, 1 or 2 parafermions.

- Give the grand partition function for a parafermion system consisting of a single-particle energy state of energy ϵ , in terms of ϵ , the temperature T and the chemical potential μ .
- Give an expression for the probability that the state is occupied by n parafermions.
- Give an expression for the average number of parafermions, \bar{n} , in the single particle state of energy ϵ at temperature T with chemical potential μ .
- Make a plot of \bar{n} versus μ at $T=0$ and at a very low non-zero T . What is the value of \bar{n} for $\mu=\epsilon$ at any temperature?

Problem 6



The water-steam system shown above is in equilibrium. The temperature is $T=150^\circ\text{C}$. The piston can move freely and the external pressure (provided by the weight on top of the piston plus the atmospheric pressure) balances the steam pressure. There is 1 mol of water and 1 mol of steam initially. The latent heat of vaporization of water at this temperature is $38,090\text{ J/mol}$. The gas constant is $R=8.31\text{ J/mol}^\circ\text{K}$. Assume throughout this problem that the temperature dependence of the latent heat can be neglected.

- Assume the temperature is lowered to 140°C . When the system reaches equilibrium, how much water and how much steam is there? Remember the piston can move freely and the external pressure doesn't change. Hints: (1) think about the P-T phase diagram; (2) energy can flow in or out of the system (as heat and/or work) in this process.
- Same as (a) if instead the temperature is raised to 160°C . Justify your answers.
- Instead of changing the temperature, $10,000\text{ J}$ of heat are added to the system, with the temperature fixed at 150°C and the piston free to move. How much water and how much steam is there when the system reaches equilibrium?
- Assume now the piston is clamped into position and cannot move, so the volume occupied by the system doesn't change. The temperature is raised from 150°C to 160°C by adding heat to the system. Calculate how much water and steam there is when the system reaches equilibrium, in moles. Hints: (1) don't forget to convert $^\circ\text{C}$ to $^\circ\text{K}$. (2) Use Clausius-Clapeyron, assume the steam behaves like an ideal gas, and that the volume occupied by the water can be neglected since it is much smaller than that of the steam.

Justify all your answers to all problems