

3 Laws of Thermodynamics

- 0) If two systems are in equilibrium with a third, they are in equilibrium with each other.
- 1) Conservation of energy $\Delta E_{th} = W + Q$
 - 2) The entropy of an isolated system never decreases. The entropy either increases until it reaches equilibrium, or if it's in equilibrium, it stays the same.
 - ⇒ given two system $w/\sigma_1 > \tau_2$, heat will be spontaneously transferred from system 1 to 2.
 - ⇒ heat cannot be completely converted into work.

Thermodynamic basics

Partition function: $Z = \sum_s e^{-\epsilon_s / \tau}$

Probability of being in a state w/energy ϵ : $P(\epsilon) = \frac{e^{-\epsilon / \tau}}{Z}$

$$\mu = \frac{\sum_s \epsilon_s e^{-\epsilon_s / \tau}}{Z}$$

The fundamental assumption: a closed system is equally likely to be any of the quantum states accessible to it.

$g(N, U)$ ≡ The multiplicity of a system with N particles and energy

$$S = k_B \sigma = k_B \log g(N, u)$$

Specific case: Hermonic oscillator: $g(N, n) = \frac{(N + n - 1)!}{n! (N - 1)!}$

where N = #oscillators, n = quantum #

Specific case: N magnets with S_p in excess $Z_s = N_+ - N_-$: $g(N, s) = \frac{N!}{N_+! N_-!}$

where $\frac{N_+}{N} = \frac{e^{-SMB}}{e^{-SMB} + e^{SMB}}$ where B is the magnetic field and M is the magnetic moment

Kinds of energy:

$$\tau d\sigma = du + pdV - \mu dN \quad \left(\mu = \tau^2 \frac{\alpha \log Z}{\alpha \tau} \right)$$

Helmholtz Free Energy

(isothermal) $F = u - \tau\sigma = -\tau \log z$ $dF = du - \tau d\sigma + \mu dN$
 $= -\sigma d\tau - PdV + \mu dN$

(isobaric) Enthalpy $H = u + pV$ $dH = \tau d\sigma + V dp - \mu dN$

(isobaric, isothermal) Gibbs Free Energy $G = F + pV = u + pV - \tau\sigma$ $dG = -\sigma d\tau + V dp + \mu dN$

$$C_v = \left(\frac{\alpha u}{\alpha \tau} \right)_v = \tau \left(\frac{\alpha \delta}{\alpha \tau} \right)_v, \quad C_p = \left(\frac{\alpha u}{\alpha \tau} \right)_p + p \left(\frac{\alpha v}{\alpha \tau} \right)_p = \tau \left(\frac{\alpha \sigma}{\alpha \tau} \right)_p$$

Distributions

 Fermi – Dirac : Average occupancy of an orbital w/energy ϵ , for fermions

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau} + 1}$$

 Bose – Einstein: Average occupancy of an orbital w/energy ϵ , bosons

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau} - 1}$$

Plank distribution: Thermal average number of photons in a single mode a

$$\langle s \rangle = \frac{1}{e^{h\nu/\tau} - 1}$$

Ideal gas

$$PV = nRT = Nk_B T \quad \left(\text{if the container is scaled } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \right)$$

$$\mu = KE_{\text{avg}} = \boxed{\frac{3}{2} K_B T} \quad \left(\frac{1}{2} k_B T \text{ for each degree of freedom, note that } f \exists \text{ potential energy, each of those degrees of freedom gets } \frac{1}{2} k_B T \text{ as well by the Equipartition Theorem} \right)$$

Per atom in a monatomic gas

Heat capacity, constant volume : $C_v = \left(\frac{\alpha U}{\alpha \tau} \right)_v = \boxed{\frac{3}{2} N} k_B \quad (\tau = k_B T)$

$$C_p = \left(\frac{\alpha U}{\alpha \tau} \right)_p + P \left(\frac{\alpha U}{\alpha \tau} \right)_p = \tau \left(\frac{\alpha \sigma}{\alpha \tau} \right)_p = \boxed{\frac{5}{2} N k_B}$$

 Partition function of an atom in a box. $Z_1 = n_Q / n = n_Q V$

$$n_a = \left(M \tau / Z \pi \hbar^2 \right)^{3/2}$$

 Partition function of N atoms in a box : $Z_N = \frac{1}{N!} Z_1^N$

Entropy $S = k_B \sigma = k_B N \left[\log \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right]$

Chemical potential : $\mu = \tau \log \left(\frac{n}{n_Q} \right)$

 Average occupancy of an orbital of energy ϵ

$$f(\epsilon) = \lambda e^{-\epsilon/\tau} \quad \text{where } \lambda = e^{1/\tau}$$

Free energy: $F = N \tau \left[\log \left(\frac{n}{n_Q} \right) - 1 \right]$

Reversible isothermal	$u_2 - u_1$	$\sigma_2 - \sigma_1$	W	Q
Reversible isentropic	0	$N \log \frac{V_2}{V_1}$	$-N \log \frac{V_2}{V_1}$	$N \tau \log \frac{V_2}{V_1}$
Irreversible extension into vacuum	0	0	$-\frac{3}{2} N \tau_1 \left[1 - \left(\frac{V_1}{V_2} \right)^{\frac{2}{3}} \right]$	0
	$-\frac{3}{2} N \tau_1 \left[1 - \left(\frac{V_1}{V_2} \right)^{\frac{2}{3}} \right]$	0	0	0
	0	$N \log \frac{V_2}{V_1}$	0	0

3 translation, 2 rotation

Diatomic Gas: $u = \frac{5}{2} k_B T,$

3 kinetic/translation
3 vibration

Solid*: $u = 3k_B T$

2-D ideal gas

$u = k_B T, \quad C_v = Nk_B \quad C_p = 2Nk_B$

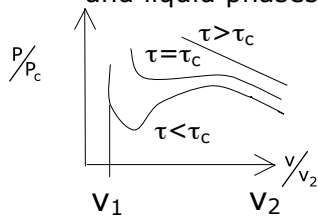
Van DerWalls – attempts to modify the ideal gas law to take into account interactions between atoms or molecules

$$\left(P' + \frac{N^2 a}{V^2} \right) (V - N b) = N \tau$$

where a is a measure of the long-range attractive part (adds to internal pressure) of the interaction and b is a measure of the short-range repulsion (volume of molecules themselves)

Critical points : $P_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad \tau_c = \frac{8a}{27b}$

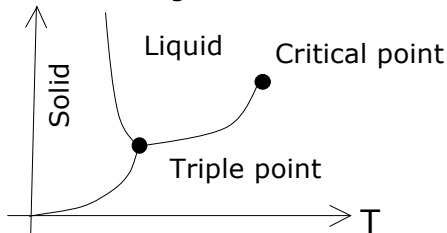
at this point, there is no separation between the vapor and liquid phases (a horizontal point of inflection)



($K \sigma K_1 p^{290}$ Fig. 10.10)

(For a given $\frac{P}{P_c}, \tau < \tau_c, V < V_1 \Rightarrow$ liquid $V > V_2 \Rightarrow$ gas,
 $V_1 < V < V_2 \Rightarrow$ both show that sum of volume of liquid G gas = V)

Phase Diagram



Triple point : The one value of T and P for which all three phases can happily coexist. Happily.

Critical point: below this point \exists a phase change between liquid & gas. Above this point \nexists phase change (fluid Δ continuously between high & low density)

Diffusion

$$\langle V_{rms}^2 \rangle = \left(\frac{3\tau}{M} \right)^{1/2} v^2 e^{-Mv^2/2\tau}, \quad \langle (\Delta R)^2 \rangle = \bar{C}t;$$

Main speed
Main freepath

$$\bar{C} = \left(\frac{\delta\tau}{\pi M} \right)^{1/2}; \quad l = \frac{1}{n\pi d^2}$$

particle density
diameter of particles

Maxwell velocity distribution

$$P(V) = 4\pi \left(\frac{M}{2\pi\tau} \right)^{3/2} v^2 e^{-Mv^2/2\tau}$$

Fick's Law

$$\bar{J}_n = -D\nabla n$$

↑
particle flux density

$$D = \frac{\bar{C}l}{3} \text{ (diffusion constant)}$$

Fourier's Law

$$\bar{J}_n = -K\nabla\tau$$

↑
thermal flux density

$$K = \frac{1}{3} \hat{C}_V \bar{C}l \text{ (Thermal conductivity)}$$

↑
heat capacity per unit volume

Carnot cycle and Work in general

$$\text{Work done on a system} = -\int_1^2 p dV = -(\text{area under pV curve})$$

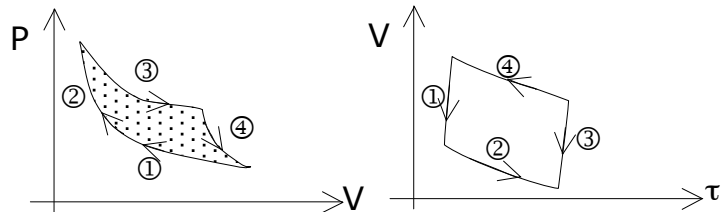
Energy in: heat from reservoir R_H (@ τ_H)

Energy out: heat to reservoir R_L (@ $\tau_L < \tau_H$)

For a reversible engine, $\Delta\sigma_H = \Delta\sigma_L$ (if τ_H, τ_L , only work may be transferred)

efficiency: $Z = \frac{\omega}{Q_H} \leq \left(1 - \frac{\tau_L}{\tau_H} \right)$
(heat engine)

- 1) compress isothermally ($Q \downarrow$)
 - 2) compress isentropically ($\tau \uparrow$)
 - 3) expand isothermally ($Q \uparrow$)
 - 4) expand isentropically ($\tau \downarrow$)
- (for a heat pump, reverse order)



for the carnot cycle, efficiency is at a maximum

$$\zeta_c = 1 - \frac{\tau_L}{\tau_H} \quad \text{or} \quad \gamma_c = \frac{C_L}{\omega} = \frac{\tau_L}{\tau_H - \tau_L}$$

(engine) (pump/refrigerator)

For an ideal gas, isothermal process $\Rightarrow Q_H = \omega = N\tau_H \log \frac{V_2}{V_1}$

$$\text{isentropic process} \Rightarrow \omega = \Delta\mu = \frac{3}{2}N(\tau_H - \tau_L)$$