

$$g(N, s) = \frac{N!}{\left(\frac{1}{2}N + s\right) \left(\frac{1}{2}N - s\right)} = \frac{N!}{N_{\uparrow}! N_{\downarrow}!}$$

$$g(N, s) \approx \sqrt{\frac{2}{\pi N}} 2^N e^{-\frac{2s^2}{N}}$$

$$U(s) = -2smB$$

$$2s = N_{\uparrow} - N_{\downarrow}$$

$$\sigma(N, s) = \ln(g(N, s))$$

$$S = k_B \sigma$$

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U} \right)_{N, V}$$

$$\tau = k_B T$$

Accessible States ($s = s_1 + s_2$) :

$$g(s) = \sum_s g_1(s_1) g_2(s - s_1)$$

System/Reservoir State Probability:

$$P(\varepsilon_s) = \frac{1}{z} e^{-\frac{\varepsilon_s}{\tau}}$$

$$z = \sum_s e^{-\frac{\varepsilon_s}{\tau}}$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_{\sigma} = \tau \left(\frac{\partial \sigma}{\partial V} \right)_U = - \left(\frac{\partial F}{\partial V} \right)_{\tau}$$

$$F = U - \tau \sigma \quad \text{min. in eq. with const } \tau, V$$

$$F = -\tau \ln(z) \quad \text{to derive } P, \sigma$$

Ideal Monatomic Gas

Given N atoms: $z_N = \frac{(n_Q V)^N}{N!}$

If $n = \frac{N}{V} \ll n_Q$, $n_Q = \left(\frac{M\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}}$

$$PV = N\tau$$

$$\sigma = N \left[\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right]$$

$$C_V = \frac{3}{2} N$$

A process is reversible if the system remains infinitesimally close to the equilibrium state at all times during the process.

Average in Mode at freq. ω : $\langle s \rangle = \frac{1}{e^{\frac{\hbar\omega}{\tau}} - 1}$ Energy Density at τ : $\langle s \rangle = \frac{U}{V} = \frac{\pi^2}{15\hbar^3 c^3} \tau^4$

Radiant energy per vol: $U_{\omega} = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar\omega}{\tau}} - 1}$ Flux Density: $J_U = \sigma_B T^4$, $\sigma_B = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}$

Heat Capacity of Dielectric Solid: $C_V = \frac{12\pi^4 N k_B}{5} \left(\frac{T}{\theta} \right)^3 \rightarrow \theta = \left(\frac{\hbar\omega}{k_B} \right) \left(\frac{6\pi^2 N}{V} \right)^{\frac{1}{3}}$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{\tau, V} = \left(\frac{\partial U}{\partial N} \right)_{\sigma, V} = -\tau \left(\frac{\partial \sigma}{\partial N} \right)_{U, V}$$

In diffusive equilibrium if: $\mu_1 = \mu_2$

$$\mu = \mu_{int} + \mu_{ext}$$

$$\mu_{int} = \tau \ln \left(\frac{n}{n_Q} \right)$$

$$\mu_{ext} = \frac{U_{ext}}{N}$$

$$3 = \sum_N \sum_s e^{\frac{N\mu - \varepsilon_s}{\tau}}$$

$$\text{Gibbs Factor: } P(N, \varepsilon_s) = \frac{e^{\frac{N\mu - \varepsilon_s}{\tau}}}{3}$$

Prob. chem. potential μ and temp τ has N particles in q.s. s of energy ε_s

$$\lambda = e^{\frac{\mu}{\tau}} \rightarrow 3 = \sum \lambda^N e^{-\frac{\varepsilon_s}{\tau}}$$

$$\text{Therm. Average: } \langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \ln(3)$$

$$\text{Quant. Particle in Box: } \varepsilon = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

$$U = \tau^2 \left(\frac{\partial \ln(3)}{\partial \tau} \right)_V$$

$$W = PA\Delta x = P\Delta V$$

$$\tau d\sigma = dU + P dV$$

$$\int_{-\infty}^{\infty} e^{-\alpha^2 n^2} dn = \frac{\sqrt{\pi}}{2\alpha}$$

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_{V, N}$$

$$\langle N \rangle = \sum_N \sum_s N(N, \varepsilon_s) = \tau \left(\frac{\partial \ln(3)}{\partial \mu} \right)_{\tau, V}$$

$$\langle \varepsilon_s \rangle = \sum_N \sum_s \varepsilon_s(N, \varepsilon_s) = \tau^2 \left(\frac{\partial \ln(3)}{\partial \tau} \right)_{\mu, V} + \tau \mu \left(\frac{\partial \ln(3)}{\partial \mu} \right)_{\tau, V} \quad f(\varepsilon_n) \text{ avg. occupancy}$$

Bose-Einstein:

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

Fermi-Dirac:

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

Classical Limit:

$$f(\varepsilon_n) = e^{\frac{\mu - \varepsilon_n}{\tau}}$$

	ΔU	$\Delta \sigma$	W	Q
Rev. Isothermal	0	$N \ln \left(\frac{V_2}{V_1} \right)$	$-N\tau \ln \left(\frac{V_2}{V_1} \right)$	$N\tau \ln \left(\frac{V_2}{V_1} \right)$
Rev. Isentropic	$-\frac{3}{2}N\tau_1 \left[1 - \left(\frac{V_1}{V_2} \right)^{\frac{2}{3}} \right]$	0	$-\frac{3}{2}N\tau_1 \left[1 - \left(\frac{V_1}{V_2} \right)^{\frac{2}{3}} \right]$	0
Irrev. Expansion	0	$N \ln \left(\frac{V_2}{V_1} \right)$	0	0

Constants

$$k_B = 1.381 \cdot 10^{-23} \left[\frac{\text{J}}{\text{K}} \right]$$

$$\sigma_B = 5.67 \cdot 10^{-8} \left[\frac{\text{J}}{\text{m}^2 \text{sK}^4} \right]$$

$$c = 3 \cdot 10^8 \left[\frac{\text{m}}{\text{s}} \right]$$

Energy of Highest-Filled Orbital
of Fermi Gas (spin 1/2):

$$\varepsilon_f = \frac{\hbar^2}{2M} \left(\frac{3\pi^2 N}{V} \right)^{\frac{2}{3}}$$

Heat Capacity of Electron Gas ($\tau \ll \tau_F$):

$$C_{el} = \frac{1}{3} \pi^2 \mathcal{D}(\varepsilon_f) \tau \approx N \tau / \tau_F$$

Ground State Kinetic Energy:

$$U_o = \frac{3}{5} N \varepsilon_f$$

Density of Orbitals:

$$\mathcal{D}(\varepsilon_f) = 3N/2\varepsilon_f$$

Density of Orbitals (Fermi):

$$\mathcal{D}(\varepsilon_f) = \frac{V}{2\pi^2} \left(\frac{2M}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\varepsilon}$$

Degenerate Gas ($\tau \ll \tau_o$)

$$\mu = \varepsilon_f \left(1 - \frac{\pi^2 \tau^2}{12 \varepsilon_f^2} \right)$$

$$U = \frac{3}{5} N \varepsilon_f \left(1 + \frac{5\pi^2 \tau^2}{12 \varepsilon_f^2} \right)$$

$$\sigma = C_v = \frac{\pi^2 N \tau}{2 \tau_F}$$

Density of Orbitals (Bose):

$$\mathcal{D}(\varepsilon_f) = \frac{V}{4\pi^2} \left(\frac{2M}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\varepsilon}$$

Einstein Condensation Temperature:

$$\tau_E = \frac{2\pi \hbar^2}{M} \left(\frac{N}{2.612V} \right)^{\frac{2}{3}}$$

Carnot Energy Efficiency:

$$\eta_c = \frac{(\tau_h - \tau_l)}{\tau_h} \geq \frac{W_{tot}}{Q_h}$$

Carnot Refrigerator Efficiency:

$$\gamma_c = \frac{\tau_l}{(\tau_h - \tau_l)} \geq \frac{Q_l}{W_{tot}}$$

Gibbs Free Energy:

$$G = U + PV - \tau \sigma = F + PV$$

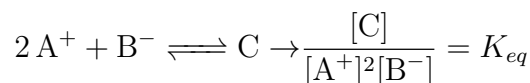
Gibbs Relations:

$$\left(\frac{\partial G}{\partial \tau} \right)_{N,P} = -\sigma; \left(\frac{\partial G}{\partial P} \right)_{N,\tau} = V; \left(\frac{\partial G}{\partial N} \right)_{\tau,P} = \mu$$

Law of Mass Action:

$$\prod n_j^{v_j} = K(\tau)$$

Example:



Ideal Gas:

$$\mu(P, \tau) = \tau \ln \left(\frac{P}{\tau n_Q} \right)$$

$$G(N, P, \tau) = N \tau \ln \left(\frac{P}{\tau n_Q} \right)$$

Clausius-Clapeyron:

$$\frac{dP}{d\tau} = \frac{L}{\tau \Delta v} = \frac{LP}{\tau^2}$$

Van der Waal's Equation:

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

Free Energy:

$$F_{VdW} = -N\tau \left(\ln \left(\frac{n_Q(V - bN)}{N} \right) + 1 \right) - \frac{N^2 a}{V}$$

Van der Waal's Critical Points:

$$\tau_c = \frac{8a}{27b}$$

$$P_c = \frac{a}{27b^2}$$

$$V_c = 3Nb$$

Van der Waal's Gibbs Energy:

$$G = -N\tau \left(\ln \left(\frac{n_Q(V - bN)}{n} \right) + 1 \right) - \frac{2N^2 a}{V}$$

Gibbs Relations:

$$\left(\frac{\partial G}{\partial P} \right)_{\tau, N} = \frac{V}{N}; \quad \left(\frac{\partial G}{\partial \tau} \right)_{P, N} = -\frac{\sigma}{N} = -S$$

Magnetization:

$$M = \mu n \tanh \left(\frac{\mu \lambda M}{\tau} \right)$$

Conditions:

If $\tau > \tau_c \rightarrow M = 0$; If $\tau < \tau_c \rightarrow M \neq 0$ (stable)

Average Force on Wall:

$$F_{ix} = \frac{2mv_x}{\Delta t}$$

Pressure:

$$P = \frac{Nm}{AL_x} \langle v_x^2 \rangle$$

Gibbs Sum:

$$z(\mu, \tau, N) = \sum_{N=0}^{\infty} \sum_{S(N)} \lambda^N e^{-\varepsilon_s(N)} \tau$$

pH:

$$\text{pH} = -\log_{10} ([\text{H}^+])$$

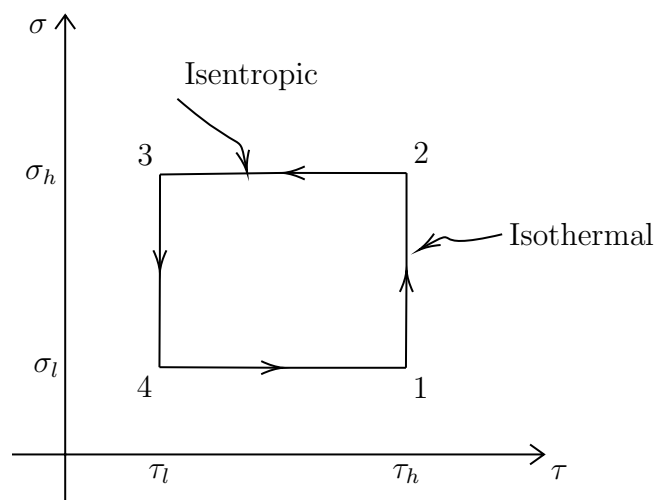


Figure 1: Carnot Cycle

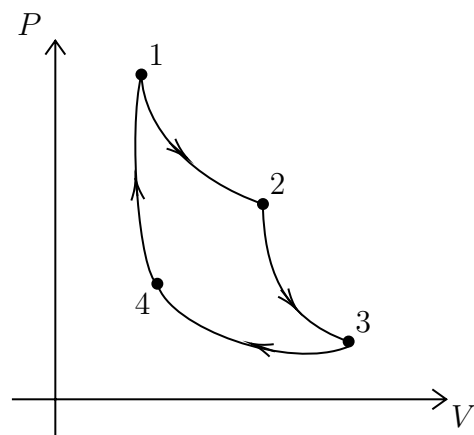


Figure 2: Ideal Gas Carnot Cycle (PV)