



PHY 410 - Reference Sheet

Stirling's approximation - for very large N :

$$\log N! \approx N \log N - N$$

$$N! \approx \sqrt{2\pi N} N^N e^{-N}$$

Fractional uncertainty of \bar{X} is uncertainty of expected value per particle.

$$\frac{\Delta \bar{X}}{N} = \frac{\sqrt{\langle \bar{X}^2 \rangle - \langle \bar{X} \rangle^2}}{N}$$

Boltzmann's constant

$$k_B = 1.380649 \times 10^{-23} \text{ m}^2 \text{ s}^{-2} \text{ K}^{-1}$$

Entropy $S = k_B \sigma$, $\sigma_{TOT} = \sigma_1 + \sigma_2$

Temperature $T = \tau/k_B$

Microcanonical Ensemble

Multiplicity function

$$g = \# \text{ of microstates}, \quad \mathcal{P}(n) = \frac{1}{g}$$

Expected value of \bar{X} is the average across all microstates.

$$\langle \bar{X} \rangle = \sum_n \bar{X}(n) \mathcal{P}(n) = \frac{1}{g} \sum_n \bar{X}(n)$$

Entropy can be written in terms of the multiplicity function.

$$\sigma(N, T, U, V, P) \equiv \log[g(N, T, U, V, P)]$$

Binary System

A **binary system** is a system of N particles where each particles has two possible states. Let N_\uparrow is the number of particle in the up state and N_\downarrow be the number of particles in the down state.

$$g(N, N_\uparrow) = \frac{N!}{N_\uparrow!(N-N_\uparrow)!}, \quad \sum_{N_\uparrow=0}^N g(N, N_\uparrow) = 2^N$$

The binary system can be rewritten in terms of the difference between up states and down states this is the **spin excess**.

$$2S = N_\uparrow - N_\downarrow$$

$$g(N, S) = \frac{N!}{(\frac{N}{2} + S)!(\frac{N}{2} - S)!}$$

$$\sum_{S=-\frac{N}{2}}^{\frac{N}{2}} g(N, N_\uparrow) = 2^N$$

Applying Stirling's approximation to the binary model, for large N the multiplicity function and fractional uncertainty are

$$g(N, S) \approx g(N, 0) e^{-2s^2/N}$$

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

$$\frac{\Delta S}{N} \approx \frac{1}{\sqrt{N}}$$

An example of a binary system is N spin 1/2 particles in an external **magnetic field** B . The total energy U and magnetization M of the system are

$$U = \sum_{i=1}^N -\vec{m}_i \cdot \vec{B} = -(N_\uparrow - N_\downarrow)mB = -2SmB$$

$$M = 2Sm = -U/B$$

$$g(N, U) = \frac{N!}{(\frac{N}{2} - \frac{U}{2mB})! (\frac{N}{2} + \frac{U}{2mB})!}$$

$$\sigma(N, S) \approx -\left(\frac{N}{2} + S\right) \log\left(\frac{1}{2} + \frac{S}{N}\right) - \left(\frac{N}{2} - S\right) \log\left(\frac{1}{2} - \frac{S}{N}\right)$$

$$M = Nm \tanh(mB/\tau)$$

Einstein Solid

An **einstein solid** is a system of N atoms where each atom is modeled as a harmonic oscillator the energy of the system is determined by the number of atoms n oscillating at frequency ω .

$$U = n\hbar\omega$$

$$g(N, n) = \frac{(n+N-1)!}{n!(N-1)!}$$

$$g(N, n) \approx \frac{\left(\frac{n+N}{n}\right)^n \left(\frac{n+N}{n}\right)^N}{\sqrt{2\pi n(n+N)/N}}$$

Thermal Equilibrium

Temperature

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

Thermal Equilibrium

$$\left(\frac{\partial \sigma_1}{\partial U_1} \right)_{N_1, V_1} = \left(\frac{\partial \sigma_2}{\partial U_2} \right)_{N_2, V_2}$$

$$\frac{1}{\tau_1} = \frac{1}{\tau_2}$$

2nd law of thermo - Change in entropy ≥ 0 .

Sharpness of Equilibrium For a two binary systems, the number of states in a configuration of deviation δ from equilibrium is

$$g_1 g_2 = (g_1 g_2)_{max} e^{\left(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}\right)}$$

Canonical Ensemble

Partition Function - partition by energy levels for a fixed temperature

$$z = \sum_n e^{-\varepsilon_n/\tau}, \quad \mathcal{P}(n) = \frac{1}{z} e^{-\varepsilon_n/\tau}$$

$$z = \sum_{\alpha} g(\varepsilon_{\alpha}) e^{-\varepsilon_{\alpha}/\tau}, \quad \text{for degeneracy } g(\varepsilon_{\alpha})$$

Expected Value of \bar{X} is the average across all energies (Thermal Average).

$$\langle \bar{X} \rangle = \sum_n \bar{X}(n) \mathcal{P}(n) = \frac{1}{z} \sum_n \bar{X}(n) e^{-\varepsilon_n/\tau}$$

Expected Energy in the canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z} \sum_n \varepsilon_n e^{-\varepsilon_n/\tau}$$

$$U = \langle \varepsilon \rangle = \tau^2 \frac{1}{z} \frac{\partial z}{\partial \tau} = \tau^2 \frac{\partial}{\partial \tau} \log z$$

The total partition function and expected value for N non-interacting particles is simply

$$z_N = z_1^N$$

$$\langle \bar{X} \rangle_N = N \langle \bar{X} \rangle_1 \Rightarrow U_N = N U_1$$

Helmholtz Free Energy

$$F = U - T\sigma = U - ST = -\tau \log z$$

$\Delta F \leq 0$ - helmholtz free energy decreases

$dF = 0$ - helmholtz free energy minimized

$$\text{Entropy } \sigma = -\left(\frac{\partial F}{\partial T}\right)_V, \quad S = k_B \sigma$$

$$\text{Temperature } \tau = \left(\frac{\partial U}{\partial \sigma}\right)_V$$

Pressure

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

$$\text{Energy } U = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F}{\tau}\right)$$

Concentration and DeBroglie Wavelength

$$n = \frac{N}{V}, \quad n_Q = \frac{1}{\lambda_T^3}, \quad \lambda_T = \sqrt{\frac{2\pi\hbar^2}{m\tau}}$$

Single Particle Ideal Gas

A system in the canonical ensemble consisting of a single particle in a box of side lengths L . The energy levels, partition function and average energy are

$$\varepsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

and for the ultra-relativistic case:

$$\varepsilon_n = pc = \frac{\pi\hbar c}{L} n = \frac{\pi\hbar c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$

$$z_1 = \frac{V}{\lambda_T^3}, \quad U_1 = \frac{3}{2}\tau$$

$$\sigma_1 = \log \left(\frac{V}{\lambda_T^3} \right) + \frac{3}{2}, \quad F_1 = -\tau \log \frac{V}{\lambda_T^3}$$

N-Particle Ideal Gas

Gibbs Resolution for systems of N identical particles the partition function is

$$z_N = \frac{1}{N!} (z_1)^N$$

$$PV = N\tau, \quad U = \frac{3}{2} N\tau$$

$$\sigma = N \left[\log \left(\frac{V}{N\lambda_T^3} \right) + \frac{5}{2} \right]$$

$$F = N\tau \left[\log \frac{n}{n_Q} - 1 \right]$$

Thermal Radiation

Single Frequency Photon Gas is a system in the canonical ensemble that considers photons of a specific frequency ω .

$$\varepsilon_s = s\hbar\omega, \quad s = 0, 1, 2, 3, \dots$$

$$z = \sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau} = \frac{1}{1 - e^{-\hbar\omega/\tau}}$$

$$\mathcal{P}(s) = \frac{e^{-s\hbar\omega/\tau}}{z}$$

$$\langle s \rangle = \frac{1}{z} \sum_{s=0}^{\infty} s e^{-s\hbar\omega/\tau} = \frac{1}{e^{\hbar\omega/\tau} - 1}$$

Photon Gas is an expansion of the single frequency photon gas that considers all the possible cavity modes. The modes are 2 fold degenerate for the 2 independent polarizations.

$$\omega_n = \frac{c\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{c\pi n}{L}$$

$$U = \langle \varepsilon \rangle = 2 \sum_n \frac{\hbar\omega_n}{e^{\hbar\omega_n/\tau} - 1} = \frac{\pi^2 V}{15(hc)^3} \tau^4$$

Stefan-Boltzmann Law

$$\frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} d\omega = \frac{\pi^2}{15(hc)^3} \tau^4$$

Spectral Density Function

$$\frac{\partial U}{\partial \omega} V = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1}$$

Flux Density (σ_B =Stefan-Boltzmann constant)

$$J_{\mu} = \frac{1}{4} \frac{cU}{V} = \sigma_B \tau^4 = \frac{\pi^2}{60(hc)^3} \tau^4$$

Phonons in a Solid (Debye Model)

Phonons in a solid is a system in the canonical ensemble that is very similar to thermal radiation except there is 3 fold degeneracy from 3 polarizations of phonons and an upper cutoff frequency ω_D due to the separation distance between atoms.

$$\omega_n = \frac{\pi c_S}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{\pi c_S}{L} n$$

Debye cutoff frequency

$$\omega_D = c_S \left(\frac{6\pi^2 N}{V} \right)^{1/3}, \quad \omega_D = \frac{\pi c_S}{L} n_D$$

Grand Canonical Ensemble

Chemical Potential

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

$$\mu = \tau \log \left(\frac{N \lambda_T^3}{V} \right) = \tau \log \left(\frac{n}{n_Q} \right)$$

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

Grand Partition Function - partition by energy levels for a fixed temperature and all possible values of N

$$z = \sum_N \sum_{n(N)} e^{-(\varepsilon_n^N - \mu N)/\tau}$$

$$\mathcal{P}(N, \varepsilon_n) = \frac{1}{z} e^{-(\varepsilon_n^N - \mu N)/\tau}$$

Fugacity

$$\lambda = e^{\mu/\tau}$$

$$z = \sum_N \lambda^N \sum_{s(N)} e^{-\varepsilon_s^N/\tau} = \sum_N \lambda^N z_N$$

Expected Value of \mathbb{X} is the average across all energies (Diffusive Average).

$$\langle \mathbb{X} \rangle = \frac{1}{z} \sum_N \sum_s \mathbb{X}(N, s) e^{-(\varepsilon_s^N - \mu N)/\tau}$$

Expected Number of Particles in the grand canonical ensemble is

$$N = \langle N \rangle = \frac{1}{z} \sum_N \sum_s N e^{-(\varepsilon_s^N - \mu N)/\tau}$$

$$N = \langle N \rangle = \tau \frac{\partial}{\partial \mu} \log z = \lambda \frac{\partial}{\partial \lambda} \log z$$

Expected Energy in the grand canonical ensemble is

$$U = \langle \varepsilon \rangle = \frac{1}{z} \sum_N \sum_{n(N)} \varepsilon_n^N e^{-(\varepsilon_n^N - \mu N)/\tau}$$

$$U = \langle \varepsilon \rangle = \tau^2 \left(\frac{\partial}{\partial \tau} \log z \right)_\lambda$$

Grand Potential

$$\Omega = U - \sigma \tau - \mu N$$

$$\Omega = -\tau \log z$$

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

System of Non-interacting Particles

The grand partition function for a system with M energy states where n_α is the number of particles occupying a state is

$$z = \prod_{\alpha=1}^M z_\alpha, \quad z_\alpha = \sum_{n_\alpha} e^{-n_\alpha(\varepsilon_\alpha - \mu)/\tau}$$

$$U = \sum_{\alpha=1}^M \varepsilon_\alpha f(\varepsilon_\alpha), \quad N = \sum_{\alpha=1}^M f(\varepsilon_\alpha)$$

Fermions

$$n_\alpha = 0, 1$$

$$z_\alpha = 1 + e^{-(\varepsilon_\alpha - \mu)/\tau} = 1 + \lambda e^{-\varepsilon_\alpha/\tau}$$

Fermi-Dirac Distribution is the expected number of α particles in a particular energy ε_α .

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = \frac{1}{e^{(\varepsilon_\alpha - \mu)/\tau} + 1} = \frac{1}{\lambda^{-1} e^{\varepsilon_\alpha/\tau} + 1}$$

For $\tau \rightarrow 0$: $f(\varepsilon_\alpha) = \theta(\varepsilon_\alpha - \mu)$

Bosons

$$n_\alpha = 0, 1, 2, 3, \dots$$

$$z_\alpha = \frac{1}{1 - e^{-(\varepsilon_\alpha - \mu)/\tau}} = \frac{1}{1 - \lambda e^{-\varepsilon_\alpha/\tau}}$$

Boson Distribution is the expected number of α particles in a particular energy ε_α .

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = \frac{1}{e^{(\varepsilon_\alpha - \mu)/\tau} - 1} = \frac{1}{\lambda^{-1} e^{\varepsilon_\alpha/\tau} - 1}$$

Ideal Gas

Both fermions and bosons behave identically at the classical limit $\varepsilon_\alpha - \mu \gg \tau$.

$$\langle n_\alpha \rangle = f(\varepsilon_\alpha) = e^{-(\varepsilon_\alpha - \mu)/\tau}$$

$$z = \sum_N \lambda^N z_N = \sum_N \lambda^N \frac{1}{N!} z_1^N = e^{\lambda z_1}$$

$$\lambda = \frac{n}{n_Q}, \quad PV = N\tau, \quad U = \frac{3}{2} N\tau, \quad \mu = \tau \log \frac{n}{n_Q}$$

Heat Capacity measures the change in heat energy per unit temperature

$$C_P > C_V, \quad C_V = \left(\frac{\partial U}{\partial T} \right)_V = \tau \left(\frac{\partial \sigma}{\partial T} \right)_V$$

$$C_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P = \tau \left(\frac{\partial \sigma}{\partial T} \right)_P$$

Monoatmc gas $C_V = \frac{3}{2} Nk_B$, $C_P = \frac{5}{2} Nk_B$

Isothermal Expansion $\sigma_f - \sigma_i = N \log \frac{V_f}{V_i}$

$$Q = N\tau \log \frac{V_f}{V_i}$$

$$\text{Isoentropic Expansion } \frac{\tau_f}{\tau_i} = \left(\frac{V_i}{V_f} \right)^{2/3}$$

Internal Excitations

Expansion of the ideal gas to take into account the additional energy states from internal excitations.

$$z_{int} = \sum_\alpha e^{-\varepsilon_\alpha/\tau}, \quad z_\alpha = 1 + \lambda z_{int} e^{-\varepsilon_\alpha/\tau}$$

Internal Excitation Corrections

$$\lambda = \frac{n}{n_Q z_{int}}, \quad \mu = \tau \left(\log \frac{n}{n_Q} - \log z_{int} \right)$$

$$F = N\tau \left[\log \frac{n}{n_Q} - 1 \right] - N\tau \log z_{int}$$

$$\sigma = N \left[\log \frac{n}{n_Q} + \frac{5}{2} \right] - \left(\frac{\partial F_{int}}{\partial \tau} \right)_V$$

Density of States

$$\sum_n f(\varepsilon_n) \approx \int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon$$

$$\langle \mathbb{X} \rangle = \sum_n f(\varepsilon_n) \mathbb{X}_n = \int_0^\infty D(\varepsilon) f(\varepsilon) \mathbb{X}(\varepsilon) d\varepsilon$$

Finding Density of States

$$\Sigma(\varepsilon) = g_S \sum_n \theta(\varepsilon - \varepsilon_n)$$

$$D(\varepsilon) = \frac{d\Sigma(\varepsilon)}{d\varepsilon}$$

Expected Energy and **Expected Number of Particles** written in terms of the density of states:

$$U = \int_0^\infty \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon$$

$$N = \int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon$$

At $\tau \ll \varepsilon_F$, the integrals can be reduced

$$U(\tau = 0) = \int_0^{\varepsilon_F} \varepsilon D(\varepsilon) d\varepsilon$$

$$N(\tau = 0) = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon$$

Degenerate Fermi Gas

Fermions behave differently at quantum concentrations.

Fermi Energy - $\varepsilon_F = \tau_f = \mu(\tau = 0)$

$$N = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon$$

Groud State Energy - $U_0 = U(\tau = 0)$

Sommerfeld Expansion

for finite $\tau \ll \varepsilon_F$:

$$\mu(\tau \ll \varepsilon_F) \approx \varepsilon_F + \left(\frac{\tau}{\varepsilon_F} \right)^2 \varepsilon_F$$

$$U(\tau \ll \varepsilon_F) \approx U_0 + \left(\frac{\tau}{\varepsilon_F} \right)^2 U_0$$

Ideal Fermi Gas

$$\varepsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} \vec{n}^2, \quad \vec{n} = 1, 2, 3, 4, \dots$$

$$N = \left(\frac{1}{2^3} \frac{4\pi}{3} n_F \right) n_F^2 = \pi \frac{n_F^3}{3} \Rightarrow n_f = \left(\frac{3N}{\pi} \right)^{1/3}$$

$$\varepsilon_F = \frac{\hbar^2 \pi^2}{2mL^2} n_F^2 = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} = \tau_F$$

$$U_0 = \frac{3}{5} N \varepsilon_F$$

$$P_0 = \frac{2}{3} \frac{U_0}{V}$$

$$D(\varepsilon) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

Bose-Einstain Condensate

Bosons behave differently at quantum concentrations.

$N_0(\tau)$ is the number of ground state particles.
 $N_e(\tau)$ is the number of excited state particles.

$$N_0(\tau) = \langle n_{\varepsilon_0} \rangle = f(\varepsilon_0, \tau) = \frac{1}{e^{(\varepsilon_0 - \mu)/\tau} - 1}$$

$$N_e(\tau) = \int_0^\infty f(\varepsilon) D(\varepsilon) d\varepsilon$$

Limits at ($\tau \approx 0$):

$$N_0(\tau) \approx \frac{\tau}{\varepsilon_0 - \mu}$$

$$\mu \approx \varepsilon_0 - \frac{\tau}{N}$$

BEC Possible? N_e converges \Rightarrow BEC
 N_e diverges \Rightarrow NO BEC

Critical Temperature The maximum temperature τ_E where BEC is possible.

$$N = N_e(\tau)|_{\mu=0}$$

For $\tau < \tau_E$ the normal phase and condensate are approximately

$$N_e(\tau) = N \left(\frac{\tau}{\tau_E} \right)^{3/2}$$

$$N_0(\tau) = N \left(1 - \left(\frac{\tau}{\tau_E} \right)^{3/2} \right)$$

Ideal Boson Gas

$$\varepsilon_n = \frac{\hbar^2 \pi^2}{2mL^2} \vec{n}^2, \quad \vec{n} = 1, 2, 3, 4, \dots$$

$$N_0 = \frac{1}{e^{-\mu/\tau} - 1} = \frac{1}{\lambda^{-1} - 1}$$

$$N_e = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar} \right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{\lambda^{-1} e^{\varepsilon/\tau} - 1}$$

$$(N_e)_{max} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \tau^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1}$$

$$(N_e)_{max} \approx 2.612 \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} = 2.612 n_Q V$$

$$\frac{N_e(\tau)}{N} = 2.612 \frac{n_Q}{n}$$

$$n_E = \frac{(N_e)_{max}}{V} = 2.612 n_Q$$

$$\tau_E = \frac{2\pi\hbar^2}{m} \left(\frac{n}{2.612} \right)^{3/2}$$

Thermodynamics

First Law - $dU = dQ + dW$

Reversible process: $dU = \tau d\sigma + dW$

Heat Engines

A **heat engine** is any devices that converts transfer of heat into work, Q_H/σ_H denotes the heat/entropy transferred from the hot reservoir, Q_C/σ_C denotes the heat/entropy transferred to the cold reservoir, and W denotes the work extracted.

Reversible Heat Engine

$$\sigma_H = \frac{Q_H}{\tau_H}, \quad \sigma_C = \frac{Q_C}{\tau_C}$$

Engine Efficiency the amount of work extracted per unit of heat transferred.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

Carnot Efficiency the engine efficiency of a reversible heat engine.

$$\eta_c = 1 - \frac{Q_C}{Q_H} = 1 - \frac{\tau_C}{\tau_H}$$

The engine efficiency of an engine is less than or equal to the carnot efficiency.

$$\eta \leq \eta_c, \quad \left(\frac{Q_C}{Q_H} \right)_{real} \geq \left(\frac{\tau_C}{\tau_H} \right)_{rev}$$

Carnot Cycle Counterclockwise = Heat Engine, Clockwise = Refrigerator

1. Isothermal expansion from σ_L to σ_H .
2. Isoentropic expansion from τ_H to τ_C .
3. Isothermal compression from σ_H to σ_L .
4. Isoentropic compression from τ_C to τ_H .



Refrigerators

A **refrigerator** is any device that converts work into transfer of heat, Q_H/σ_H denotes the heat/entropy transferred to the hot reservoir, Q_C/σ_C denotes the heat/entropy transferred from the cold reservoir, and W denotes the work used.

Reversible Refrigerator

$$\sigma_H = \frac{Q_H}{\tau_H}, \quad \sigma_C = \frac{Q_C}{\tau_C}$$

Coefficient of Performance the amount of heat transferred per unit of work used.

$$\gamma = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$

Carnot Coefficient of Performance the coefficient of performance of a reversible refrigerator.

$$\gamma_c = \frac{1}{\frac{Q_H}{Q_C} - 1} = \frac{1}{\frac{\tau_H}{\tau_C} - 1} = \frac{\tau_C}{\tau_H - \tau_C}$$

The coefficient of performance of a refrigerator is less than or equal to the carnot coefficient of performance.

$$\gamma \leq \gamma_c \quad \left(\frac{Q_H}{Q_C} \right)_{real} \geq \left(\frac{\tau_C}{\tau_H} \right)_{rev}$$

Types of Work

Irreversible Process

$$d\bar{W}_{irr} > dW_{rev}$$

$$dQ_{irr} < dQ_{rev}$$

Isothermal Work

$dW \geq dF$, (= for reversible)

Effective Work

$$dW' = dW - dW_{mech}$$

Gibbs Free Energy

minimized at equilibrium for a system in the isothermal-isobaric ensemble.

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

Reversible Processes: $dW' = dG$

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

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

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

Enthalpy

minimized at equilibrium for a system at constant pressure.

$$H = U + PV$$

Reversible Processes: $dW' = dH - dQ$

$$\tau = \left(\frac{\partial H}{\partial \sigma} \right)_{P,N}$$

$$V = \left(\frac{\partial H}{\partial P} \right)_{\sigma,N}$$

$$\mu = \left(\frac{\partial H}{\partial N} \right)_{\sigma,P}$$

Chemical Reactions

The Gibbs free energy can be written in terms of the chemical potential and particles number.

$$G = N\mu$$

Total Gibbs Free Energy

$$G = \sum_j N_j \mu_j$$

Chemical Equation Number ν is the sign and magnitude of dN relative to the other components of the reaction. For products $\nu < 0$ and for reactants $\nu > 0$.

Chemical Equilibrium

$$\sum_j dN_j \mu_j = 0 = dG$$

$$\sum_j \nu_j \mu_j = 0$$

Ideal Gas Model

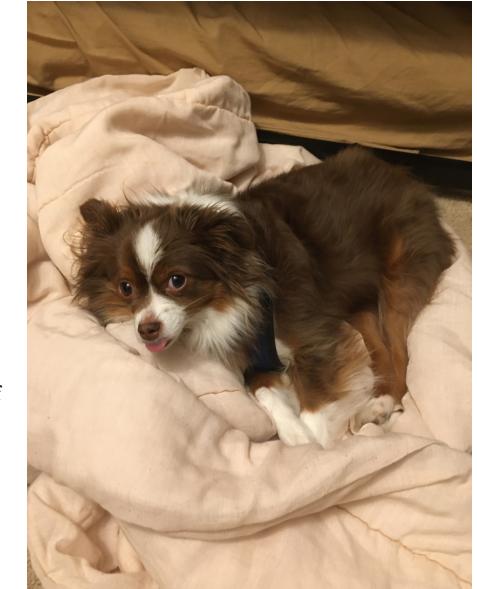
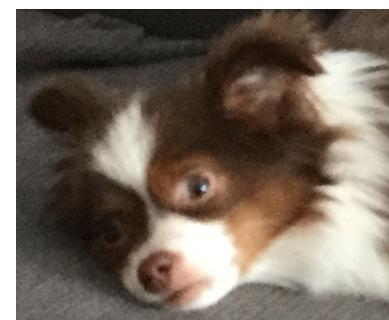
$$\mu_i = \tau(\log n_j - \log c_j)$$

$$c_j = n_{Q,j} z_{j,int}$$

Law of Mass Action $K(\tau)$ only depend on τ .

$$K(\tau) = \prod_j n_j^{\nu_j} = \prod_j n_{Q,j}^{\nu_j} Z_{int,j}^{\nu_j}$$

$$K(\tau) = \prod_j n_{Q,j}^{\nu_j} e^{-\nu_j F_j^{int}/\tau}$$



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