

Agenda: Information, Probability, Statistical Entropy

- Information and probability
 - simple combinatorics, stochastic variables.
 - Probability distributions, joint probabilities, correlations
 - Statistical entropy
 - Statistical entropy for bi- & multi-partitions
 - Microstates,
 - Stationary states defined by extreme statistical entropy, asymptotic stationary states
 - Constraints: in particle number, total energy,...
 - The Boltzmann factor, probability distribution
- Partition of probability, thermodynamic connection
- Gibbs stability criteria, equilibrium
 - Canonical Observables, Free Energy A
 - Grand Canonical Observables, Free Energy G
 - Application to chemical reactions
- Partition functions for other degrees of freedom
- Phase space evolution (Eta Theorem)

Reading Assignments

Weeks 6 & 7

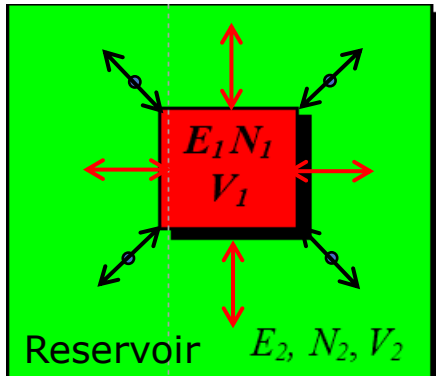
LN III.1- III.6:

Kondepudi Ch. 20
Additional Material

McQuarrie & Simon
Ch. 3 & 4

Math Chapters
MC B, E

Open Systems: Grand-Canonical Ensembles



Open system: Exchanges of energy and particles occur with surrounding “Particle Reservoir” and “Heat Bath.”

→ Combined, (system + reservoirs) = isolated system

→ Conservation laws in mass and energy

Stationary macro-state is characterized by

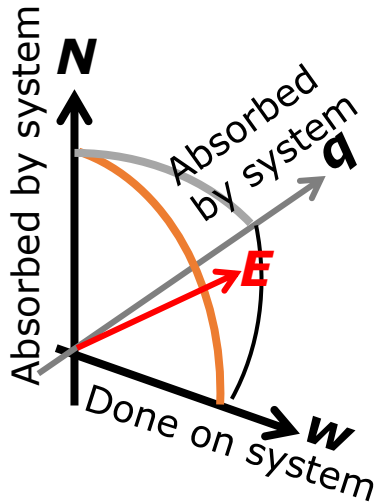
N: constituent (particle) number, $0 \leq N < \infty$

V: containment volume.

T: temperature ~ mean internal energy per particle,

Differential energy change $E(N, V, T)$:

$$dE = \underbrace{\left(\frac{dE}{dT}\right)_{V,N}}_{C_V} \cdot dT + \underbrace{\left(\frac{dE}{dV}\right)_{T,N}}_{-p} \cdot dV + \underbrace{\left(\frac{dE}{dN}\right)_{V,T}}_{\mu} \cdot dN$$



C_V: heat capacity at $V=\text{const.}$, **p**: internal pressure
μ: “chemical potential” = energy gain per absorbed particle

Grand Canonical Ensemble

Grand canonical ensembles: μ states (\mathbf{N}, i) have different energies $E_{Ni}(V)$ and different numbers \mathbf{N} of particles \rightarrow occupation probabilities $\{p_{Ni}\}$

Maximize entropy $dS(\{p_{Ni}\}) = 0$, boundary conditions (constraints)

$$\sum_{N,i} p_{Ni} = 1 \quad \sum_{N,i} E_{Ni} \cdot p_{Ni} = \langle E \rangle, \quad \text{and} \quad \sum_{N,i} N \cdot p_{Ni} = \langle N \rangle$$

\uparrow μ state #
 \uparrow # of particles

Sum over # of particles: $N=1,2,\dots$

$$\frac{\partial}{\partial p_{Nn}} \left\{ -k_B \sum_{M,m=1}^{\Omega_M} p_{Mm} \ln(p_{Mm}) - \lambda_1 \left(\sum_{M,i=1}^{\Omega_M} p_{Mi} \right) - \lambda_2 \left(\sum_{M,j=1}^{\Omega_M} E_{Mj} p_{Mj} \right) - \lambda_3 \left(\sum_{M,k=1}^{\Omega_M} M p_{Mk} \right) \right\} = 0$$

Independent variation rel # of particles: $0 \leq N < \infty$; μ state # $1 \leq i \leq \Omega_N$

$$-k_B (\ln(\bar{p}_{Nn}) + 1) - \lambda_1 - \lambda_2 E_{Nn} - \lambda_3 N = 0 \quad \text{for all } \{\bar{p}_{Nn}\}_{S=S_{max}}$$

$$\ln(\bar{p}_{Nn}) = \frac{1}{k_B} (-\lambda_1 - k_B - \lambda_2 E_{Nn} - \lambda_3 N) \rightarrow p_{Nn} = \exp \left\{ \underbrace{-\left(\frac{\lambda_1}{k_B} + 1 \right)}_{-\alpha} - \underbrace{\frac{\lambda_2}{k_B} E_{Nn}}_{-\beta} - \underbrace{\frac{\lambda_3}{k_B} N}_{-\gamma} \right\}$$

Maximizing entropy



$$\bar{p}_{Nn} = e^{-\alpha} \cdot e^{-\beta \cdot E_{Nn}} \cdot e^{-\gamma \cdot N}$$

Grand Canonical Partition Sum

Most likely occupation probabilities $\bar{p}_{Nn} = e^{-\alpha} \cdot e^{-\beta \cdot E_{Nn}} \cdot e^{-\gamma \cdot N}$

Normalization (boundary) : $1 = \sum_{Nn} \bar{p}_{Nn} = \exp\{-\alpha\} \cdot \sum_{Nn} \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$

Define gc partition sum $\Xi(V, \beta, \gamma) = \exp\{\alpha\}$

**Grand canonical
partition sum/function**

$$\Xi(V, \beta, \gamma) = \sum_{N,n} \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$$

Grand canonical partition sum over all energies and particle numbers

Parameter $\beta = 1/k_B T$ was determined, γ remains to be determined

Grand canonical
probabilities

$$p_{Nn} = \frac{1}{\Xi(\beta, \gamma)} \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\} = -\frac{1}{\beta} \frac{d}{dE_{Nn}} \ln \Xi(\beta, \gamma)$$

PF is generating function of probability for microstate \mathbf{n} with \mathbf{N} particles

Grand Canonical Entropy

Proceed like for the canonical ensemble:

$$\ln(\bar{p}_{Nn}) = \frac{1}{k_B} (-\lambda_1 - k_B - \lambda_2 E_{Nn} - \lambda_3 N) \rightarrow p_{Nn} = \exp \left\{ \underbrace{-\left(\frac{\lambda_1}{k_B} + 1\right)}_{-\alpha} - \underbrace{\frac{\lambda_2}{k_B} E_{Nn}}_{-\beta} - \underbrace{\frac{\lambda_3}{k_B} N}_{-\gamma} \right\}$$

$$\Xi = e^\alpha \rightarrow \alpha = \ln \Xi \quad \text{and} \quad p_{Nn} = e^{-\alpha} \cdot e^{-\beta \cdot E_{Nn}} \cdot e^{-\gamma \cdot N}$$

$$S = -k_B \sum_{N,n} p_{Nn} \cdot \ln p_{Nn} =$$

$$k_B e^{-\alpha} \cdot \sum_{N,n} \left(e^{-\beta \cdot E_{Nn}} \cdot e^{-\gamma \cdot N} \right) \cdot (\alpha + \beta \cdot E_{Nn} + \gamma \cdot N)$$

$$S = k_B \cdot \left\{ \ln \Xi + \beta \langle E \rangle + \gamma \cdot \langle N \rangle \right\}$$

Average Properties of Grand Canonical Ensembles

Grand canonical ensembles: μ states (N, i) have different energies $E_{Ni}(V)$ and different numbers N of particles \rightarrow occupation probabilities $\{p_{Ni}\}$

Grand canonical PF

$$\Xi(V, \beta, \gamma) = \sum_{Nn} \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$$



$$S = k_B \cdot \{ \text{Ln} \Xi + \beta \langle E \rangle + \gamma \cdot \langle N \rangle \}$$

$$\langle E(V, \beta, \gamma) \rangle = \frac{1}{\Xi} \sum_{Nn} E_{Nn} \cdot \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\} = - \left(\frac{\partial}{\partial \beta} \text{Ln} \Xi \right)_{V, \gamma}$$

$$\langle p(N, V, T) \rangle = \frac{-1}{\Xi} \sum_{Nn} \left(\frac{\partial E_{Nn}(V)}{\partial V} \right) \cdot \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\} = \frac{1}{\beta} \left(\frac{\partial}{\partial V} \text{Ln} \Xi \right)_{\beta, \gamma}$$

$$\langle N(V, \beta, \gamma) \rangle = \frac{1}{\Xi} \sum_{Nn} N \cdot \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\} = - \left(\frac{\partial}{\partial \gamma} \text{Ln} \Xi \right)_{V, \beta}$$

Entropy and Heat in Grand Canonical Ensemble

Grand canonical partition sum

$$\Xi(V, \beta, \gamma) = \sum_{Nn} \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$$

Internal energy @ $S = S_{\max}$:

= Energy in its most randomized distribution over many states, all d.o.f.

= "Heat" energy $T \cdot S = k_B \cdot T \cdot \ln \Xi + \langle E \rangle + (k_B T) \cdot \gamma \cdot \langle N \rangle$

Internal energy gain per particle @ const T, V

Chemical potential : $-\mu := \frac{\partial}{\partial \langle N \rangle} (T \cdot S) = (k_B T) \cdot \gamma \quad \rightarrow \quad \gamma = \frac{-\mu}{k_B T}$

Statistical entropy (S_{\max}) : $S = k_B \ln \Xi + \frac{\langle E \rangle}{T} - \frac{\mu}{T} \langle N \rangle$

Grand Canonical PF

Grand canonical partition sum $\Xi(V, \beta, \gamma) = \sum_{Nn} \exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$

GC PF
Representation

$$\Xi(V, N, T) = \sum_{E, N} \omega(E, N) \cdot e^{-\frac{E}{k_B T}} \cdot z^N; \quad \text{fugacity } z = e^{+\frac{\mu}{k_B T}}$$

Statistical entropy from before: $S = S_{\max} = k_B \ln \Xi + \frac{\langle E \rangle}{T} - \frac{\mu}{T} \langle N \rangle$

$\alpha ?$

Internal energy @ $S = S_{\max}$: $T \cdot S = k_B \cdot T \cdot \ln \Xi + \langle E \rangle - \mu \cdot \langle N \rangle$



$T \cdot S = \text{Energy}(N, T, V)$ must also depend on $V \rightarrow p \cdot V = \text{energy}$

Additional $d\langle \text{Energy} \rangle = \dots + d(p \cdot V)$ @ const T, p

Identify
terms

$$p \cdot V = k_B \cdot T \cdot \ln \Xi \rightarrow \Xi = \exp\left\{\frac{p \cdot V}{k_B \cdot T}\right\}$$

GC PF Closed Form

Gibbs Free Energy $G := \mu \cdot \langle N \rangle = \langle E \rangle + p \cdot V - T \cdot S$

Extensive state
variable

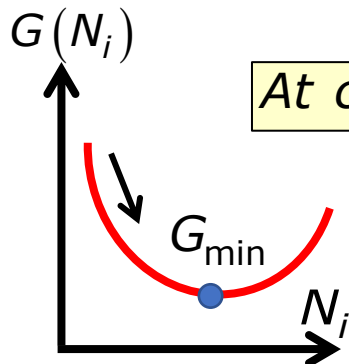
Grand Canonical PF: Chemical Potential

Gibbs Free Energy $G = G(p, T, N) = \mu \cdot \langle N \rangle = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*

Chemical potential $\mu = \left(\frac{\partial G}{\partial N} \right)_{p, T}$; also $V = \left(\frac{\partial G}{\partial p} \right)_T$ note: $N = \langle N \rangle$
 $p = \langle p \rangle$

System with multiple components $\{N_i\}$:

$$G(p, T, \{N_i\})_{p, T} = \sum_i G(p, T, N_i)_{p, T} = \sum_i \mu_i \cdot N_i$$



cut through multi-dimensional energy surface

At constant $p, T \rightarrow G$ decreases with increasing $S \rightarrow S_{\max}$

Stationary state (Equilibrium) $_{p, T} : S = S_{\max} :$

G at minimum \rightarrow

$$\text{solve } dG(p, T, \{N_i\})_{p, T} = \sum_i \mu_i \cdot dN_i = 0$$

Grand Canonical PF: Chemical Potential

Gibbs Free Energy $G = G(p, T, N) = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*

Chemical potential $\mu = \left(\frac{\partial G}{\partial N} \right)_{p, T}$; also $V = \left(\frac{\partial G}{\partial p} \right)_T$ note: $N = \langle N \rangle$
 $p = \langle p \rangle$

Stationary state (Equilibrium)_T: vary pressure (concentration) to find $S = S_{\max}$

$$G(p) - G^0(p_0) = \int_{p_0}^p dG(p, \dots) = \int_{p_0}^p V(p) dp \rightarrow \text{need EoS } V(p) = ?$$

Assume e.g. gas EoS $p \cdot V = N \cdot k_B \cdot T \rightarrow G(p) - G^0(p_0) = N \cdot k_B \cdot T \cdot \ln \left(\frac{p}{p_0} \right)$

$$\mu(p, T) - \mu^0(p_0, T_0) = k_B \cdot T \cdot \ln \left(\frac{p}{p_0} \right)$$

For EoS
 $p \cdot V = N \cdot k_B \cdot T$



conventional standard @
 $p_0 = 10^5 \text{ Pa}$, $T_0 = 298 \text{ K}$, (per mol)

Grand Canonical PF: Application to Reactions

Gibbs Free Energy $G = G(p, T, N) = \mu \cdot \langle N \rangle = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*

Chemical potential $\mu = \left(\frac{\partial G}{\partial N} \right)_{p, T}$; also $V = \left(\frac{\partial G}{\partial p} \right)_T$ note: $N = \langle N \rangle$
 $p = \langle p \rangle$

System with multiple components $\{N_i\}$:

$$G(p, T, \{N_i\})_{p, T} = \sum_i G(p, T, N_i)_{p, T} = \sum_i \mu_i \cdot N_i$$

Stationary state (Equilibrium)_{p, T} : $S = S_{\max}$:

G at minimum \rightarrow solve $dG(p, T, \{N_i\})_{p, T} = \sum_i \mu_i \cdot dN_i = 0$

Grand Canonical PF: Application to Reactions

Gibbs Free Energy $G = G(p, T, N) = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*

Chemical potential $\mu = \left(\frac{\partial G}{\partial N} \right)_{p, T}$; also $V = \left(\frac{\partial G}{\partial p} \right)_T$ note : $N = \langle N \rangle$
 $p = \langle p \rangle$

Stationary state (Equilibrium)_T : vary pressure to find $S = S_{\max}$

$$G(p) - G^0(p_0) = \int_{p_0}^p dG(p, \dots) = \int_{p_0}^p V(p) dp \rightarrow \text{need EoS } V(p) = ?$$

Assume e.g. gas EoS $p \cdot V = N \cdot k_B \cdot T \rightarrow G(p) - G^0(p_0) = N \cdot k_B \cdot T \cdot \text{Ln} \left(\frac{p}{p_0} \right)$

$$\mu(p, T) - \mu^0(\cancel{p_0}, T) = k_B \cdot T \cdot \text{Ln} \left(\frac{p}{p_0} \right)$$

For EoS
 $p \cdot V = N \cdot k_B \cdot T$

Grand Canonical PF: Application to Reactions

Apply to chemical reaction in gas phase (because of EoS used)

$$\mu(p, T) = \mu^0(\cancel{p_0}, T) + k_B \cdot T \cdot \ln\left(\frac{p}{p_0}\right) \quad \text{For EoS } p \cdot V = N \cdot k_B \cdot T$$



Change in chemical potential ($T = \text{const.}$):

$$\Delta\mu = \nu_C \cdot \mu_C - \nu_D \cdot \mu_D - \nu_A \cdot \mu_A + \nu_B \cdot \mu_B \quad \text{similar for } \Delta\mu^0(p_A, \dots, p_D)$$

$$\Delta\mu = \Delta\mu^0 + k_B T \cdot \ln\left[\frac{(p_C)^{\nu_C} (p_C)^{\nu_D}}{(p_A)^{\nu_A} (p_B)^{\nu_B}}\right] \quad \text{all relative to } p_0$$

$$S = S_{\max} \rightarrow \Delta\mu = 0 \rightarrow \Delta\mu^0 = -k_B \cdot T \cdot \ln\left[\frac{(p_C)^{\nu_C} (p_C)^{\nu_D}}{(p_A)^{\nu_A} (p_B)^{\nu_B}}\right] = -k_B T \cdot \ln K_p$$

Equilibrium
Constant

$$K_p = \exp\left\{-\frac{\Delta\mu^0}{k_B \cdot T}\right\}$$

$$K_p = \exp\left\{-\frac{\Delta\mu^0}{R \cdot T}\right\}$$

for ν_i in
moles

Grand Canonical PF: Application to Reactions

Gibbs Free Energy $G = G(p, T, N) = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*

Also : internal energy $\langle E \rangle = U$

Chemical potential $\mu = (\partial G / \partial N)_{p, T}$; also $V = (\partial G / \partial p)_T$

Extensive \rightarrow additivity & scalability of chemical rxns \rightarrow Thermochemistry

Customary definition

Enthalpy (heat content) $H(p, T) = U + p \cdot V \rightarrow G(p, T, N) = H - T \cdot S$

Grand Canonical PF: Application to Reactions

Customary definition

Enthalpy (heat content) $H(p, T) = U + p \cdot V \rightarrow G(p, T, N) = H - T \cdot S$

Reaction **1** \rightarrow **2** \rightarrow constant p , volume V can expand or contract

Heat energy Q_p emitted or absorbed

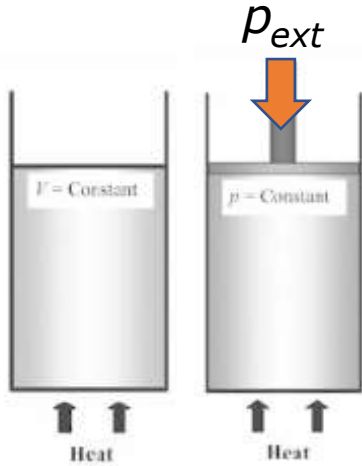
$$\Delta Q_p = H_2(p, T) - H_1(p, T) = \int_{U_1}^{U_2} dU + \int_{V_1}^{V_2} p \cdot dV = (U_2 - U_1) + p \cdot (V_2 - V_1)$$



$$dU(V, T) = \left(\frac{\partial U}{\partial T} \right)_V \cdot dT + \left(\frac{\partial U}{\partial V} \right)_T \cdot dV = dQ_p - p \cdot dV \quad \text{always}$$

Grand Canonical PF: Application to Reactions

Gibbs Free Energy $G = G(p, T, N) = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*



$$dU(V, T) = \left(\frac{\partial U}{\partial T} \right)_V \cdot dT + \left(\frac{\partial U}{\partial V} \right)_T \cdot dV = dQ_p - p \cdot dV \rightarrow$$

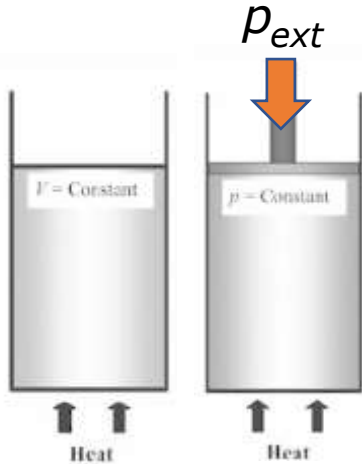
$$dQ_p = dU(V, T) + p \cdot dV = \left(\frac{\partial U}{\partial T} \right)_V \cdot dT + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \cdot dV$$

$$Q_p = C_p \cdot T$$

$$C_p = \left(\frac{\partial Q_p}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_V + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \cdot \left(\frac{\partial V}{\partial T} \right)_p$$

Grand Canonical PF: Application to Reactions

Gibbs Free Energy $G = G(p, T, N) = \langle E \rangle - T \cdot S + p \cdot V$ *extensive*



$$C_p = \left(\frac{\partial Q_p}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_V + \left[p + \left(\frac{\partial U}{\partial V} \right)_T \right] \cdot \left(\frac{\partial V}{\partial T} \right)_p$$



Ideal gas: non-interacting point-like particles:

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \text{and} \quad \text{EoS: } V(T) = (Nk_B/p) \cdot T$$

$$Q_p = C_p \cdot T$$

$$\text{Ideal gas: } C_p = \left(\frac{\partial Q_p}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_V + p \cdot \left(\frac{\partial V}{\partial T} \right)_p$$

Heat capacity @ p = const.

$$C_p = C_V + Nk_B; \quad C_p = C_V + R \quad (\text{per mol})$$

Agenda: Information, Probability, Statistical Entropy

- Information and probability
 - simple combinatorics, random variables.
 - Probability distributions, joint probabilities, correlations
 - Statistical entropy
 - Monte Carlo simulations
- Partition of probability
 - Multiple partitions, max entropy, stationary states, stability
 - Canonical and grand canonical ensembles
 - Applications to chem. reactions
 - Decomposition of partition functions for independent particles, external & internal degrees of freedom
 - Gibbs' stability criteria, equilibrium
- Phase space evolution (Eta Theorem)