$$N_i = \frac{N_{tot} e^{(U_i/k_B T)}}{Q}$$

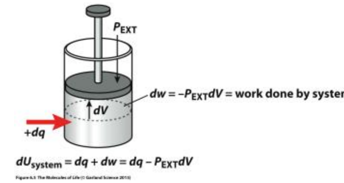
$$Q = \sum_i e^{(U_i/k_B T)}$$

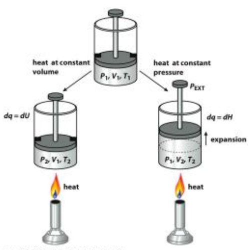
- $k_B = 1.4\ 10^{-23}\ J\ K^{-1}$ = Boltzmann constant

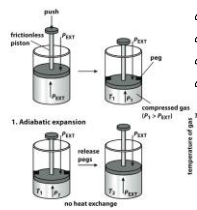
$$p_i = \frac{e^{-\epsilon_i/k_B T}}{\sum_{i=1} e^{-\epsilon_i/k_B T}}$$

- When binding occurs, energy is exchanged through heat (q) and work (w)
- **First law of thermodynamics: Energy is conserved**
- **$dU_{system} = -dU_{surroundings}$**
  - **Is this obvious?**
- **dU = dq + dw**
  - **Note sign convention**
- **What is dq?**
- **What is dw?**
  - **($-P_{ext}$ dV)**
  - **(F dx)**

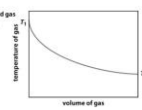
- For reactions occurring at constant pressure, but not constant volume, it is convenient to define Enthalpy as:
- **H = U + PV**
- **dH = dU + Pdv + VdP**
- **dH = dU + PdV**
  - **Noting that P is constant**
- **Since dU = dq + dw = dq - PdV**
- **dH = dq**
  - **Heat released by a reaction at constant pressure (e.g. bench top conditions)**
- **So H is just energy, but with a correction for PV work under bench top (constant pressure) conditions**







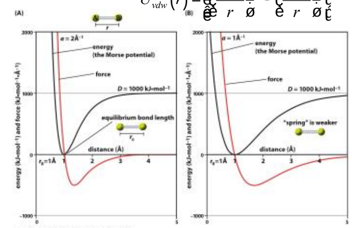
$$dq = 0$$
$$dw = -P_{ext}dV$$
$$dU = dq + dw = -P_{ext}dV$$
$$dT = ?$$



$$U_{vdw}(r) = \left[\left(\frac{R_{min}}{r}\right)^{12} - \left(\frac{R_{min}}{r}\right)^{6}\right]$$

$$U_p(r) = -\int F(r)dr$$

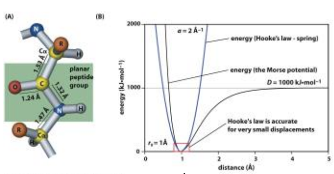
$$F(r) = \frac{-dU_p(r)}{dr}$$



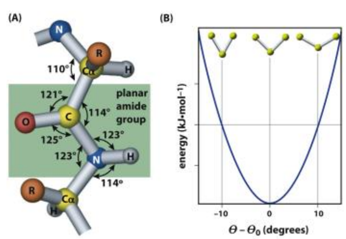
$$U_{electrostatic} = \left(\frac{1}{4\pi\epsilon\epsilon_0}\right)$$

$\epsilon_0 = 8.854 \times 10^{-12} C^2 \cdot$

ϵ = relative dielectric

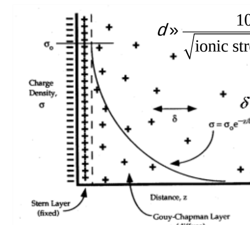


$$U_{bond} = \frac{1}{2}K_b(r - r_0)^2$$



$$d \approx \frac{10\text{ nm}}{\sqrt{\text{ionic strength (mM)}}}$$

$$\delta = \left[\frac{\varepsilon kT}{e^2 \sum_i z_i n_{\infty,i}}\right]^{\frac{1}{2}}$$



Gaussian distribution $p(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{\left(\frac{(x-\mu)^2}{2\sigma^2}\right)}$

Statistical definition of entropy

$$S = k_B \ln W$$

$$W = \frac{N_{total}!}{n_1! n_2! \cdots n_t!} \qquad W = \frac{M!}{N!(M-N)!}$$

$$\sum_{i=1}^{t} n_i = N_{total}$$

Stirling's approximation

$\ln(N!) \approx N \ln(N) - N$

$N! \approx N^N / e^N$

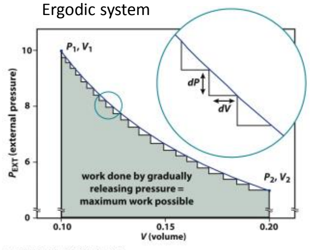
$$W = \frac{N_{total}!}{n_1! n_2! \cdots n_t!} \Rightarrow$$

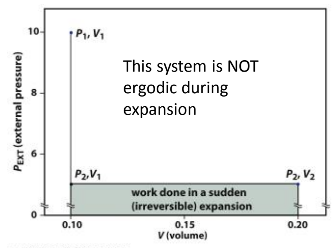
$$\ln W = -N \sum_{i=1}^{t} p_i \ln p_i$$

$$p_i = n_i / N_{total}$$

$$S = k_B \ln W = -N k_B \sum_{i=1}^{t} p_i \ln p_i$$

Ergodic system





Reversible work & thermodynamic definition of entropy

$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$P_{int} = \frac{nRT}{V}$$

$$dV = Adx$$

$$PA = F \Rightarrow PdV = Fdx$$

Area = A
Movement = dx

For isothermal process:

$$w_{rev} = -q_{rev}$$

$$\Delta S = \frac{q_{rev}}{T} \qquad \Delta S = \frac{q_{rev}}{T} = \frac{1}{T} \int_{V_1}^{V_2} \frac{nRT}{V} dV =$$

$$S = k_B \ln W = -N k_B \sum_{i=1}^{t} p_i \ln p_i$$

Entropy of mixing: binary mixture

$$\Delta S = \Delta S_A + \Delta S_B$$

$$V_A = N_A V_m; V_B = N_B V_m; N_A + N_B = N$$

$$\Delta S_A = N_A k_B \ln\left(\frac{V_2}{V_1}\right) = N_A k_B \ln\left(\frac{(N_A + N_B) V_m}{N_A V_m}\right)$$

$$\Delta S = -N k_B \left[\frac{N_A}{N_A + N_B} \ln\left(\frac{N_A}{N_A + N_B}\right) + \frac{N_B}{N_A + N_B} \ln\left(\frac{N_B}{N_A + N_B}\right)\right]$$

$$W = \frac{N!}{N_A! N_B!}; \quad N = N_A + N_B$$

$\ln(N!) \approx N \ln(N) - N$

$N! \approx N^N / e^N$

$$W = \frac{N^N / e^N}{\frac{N_A^{N_A}}{e^{N_A}} \frac{N_B^{N_B}}{e^{N_B}}} = \frac{N^N}{N_A^{N_A} N_B^{N_B}}$$

$$\ln W = N \ln N - N_A \ln N_A - N_B \ln N_B$$

$$\ln W = (N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B$$

$$\ln W = N_A \left(\ln \frac{N_A + N_B}{N_A}\right) + N_B \left(\ln \frac{N_A + N_B}{N_B}\right)$$

$$\ln W = N \left[\frac{N_A}{N} \left(\ln \frac{N_A + N_B}{N_A}\right) + \frac{N_B}{N} \left(\ln \frac{N_A + N_B}{N_B}\right)\right]$$

$$\Delta S = \frac{q_{rev}}{T}$$

$$dS = \frac{dq_{rev}}{T}$$

$$dq_{rev} = C_p dT \quad \text{(constant pressure)}$$

$$dS = \frac{C_p dT}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

If no change in multiplicity, then: $\frac{p_u}{p_f} = e^{-\Delta U / k_B T}$

If change in multiplicity, then: $\frac{p_u}{p_f} = \frac{W_u}{W_f} \cdot e^{-\Delta U / k_B T}$

$$\frac{p_u}{p_f} = \frac{W_u}{W_f} \cdot e^{-\Delta U / k_B T} = e^{\Delta S / k_B} \cdot e^{-\Delta U / k_B T} = e^{-(\Delta U - T\Delta S) / k_B T}$$

$\Delta U - T\Delta S$ factors changes in multiplicity into the probability equation