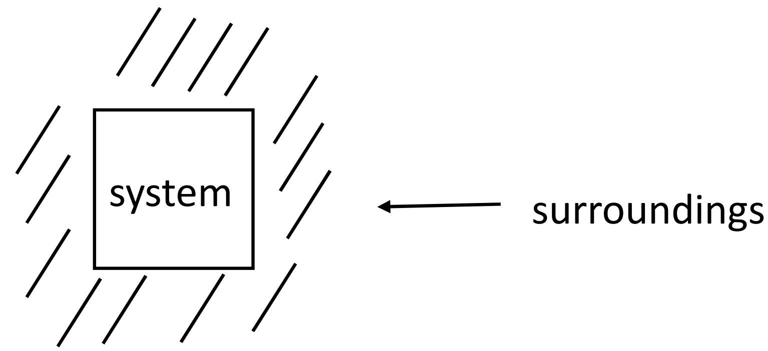
CHAPTER 6 – THERMODYNAMIC DRIVING FORCES

1ST Law: Conservation of energy

2nd Law: Maximum entropy principle



open system – can exchange *E, V*, matter with surroundings

closed system – can exchange *E*, but not matter

isolated – neither *E* nor matter can exchange; *V* fixed

semipermeable membrane – allows some materials to pass

adiabatic boundary – no heat flow allowed

phase – homogenous part of a system that is mechanically separable from rest (e.g., solid + liquid)

simple system – single phase, surface effects unimportant

Extensive properties – depend on size of system

S, V, U (internal energy)

$$U = \sum N_i \varepsilon_i$$ non-interacting particles

Intensive – independent of size of system

e.g., *p*, concentration

$$S = S(U, V, N) \qquad \{N = N_1, N_2, \ldots\}$$

$$U = U\left(S, V, N\right)$$

S(V) when *V* can change – expansion of gases

S(N) when *N* can change – changes in composition

S(U) when *U* can change – heat flow

Fundamental equations of thermodynamics written in terms of *U*

this is historical

what drives changes is better understood in terms of *S*

$$S = S(U, V, N)$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \sum \left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_{i\neq j}} dN_j$$

$$dU = \left(\frac{\partial U}{dS}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{i\neq j}} dN_j$$

↑ T ↑ -p ↑ μ_j

We replace each derivative with a new variable, that we will see later correspond to temperature, pressure, chemical potential

T, S conjugate

p, V conjugate

μ_j, N_j conjugate

↑ intensive ↖ extensive

$$dU = TdS - pdV + \sum \mu_j dN_j$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum \frac{\mu_j}{T}dN_j$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} \quad -\left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_{i\neq j}}$$

Ideal gas law $pV = NkT$

We can derive this from a lattice model

$$S = k\ell nW = k\ell n\left[\frac{M!}{N!(M-N)!}\right]$$

M sites with
N particles

Uses Stirling
Approximation

$$S/k \approx -N\ell n\left(\frac{N}{M}\right) - (M-N)\,\ell n\left(\frac{M-N}{M}\right)$$

$V = M\, v_0 =$ (#sites)*(vol per site)

$$\left(\frac{\partial S}{\partial V}\right)_N = \left(\frac{\partial S}{\partial M}\right)_N \frac{1}{v_0}$$

$$\frac{1}{k}\left(\frac{\partial S}{\partial M}\right) = \frac{N}{M} - \ell n\left(\frac{M-N}{M}\right) - (M-N)\left[\frac{1}{M-N} - \frac{1}{M}\right]$$

$$\frac{1}{k}\frac{\partial S}{\partial M} = \frac{N}{M} - \ell n\frac{M-N}{M} - 1 + \frac{M-N}{M}$$

$$= -\ell n\left(\frac{M-N}{M}\right)$$

$$\left(\frac{\partial S}{\partial M}\right) = -k\ell n\left(\frac{M-N}{M}\right)$$

$$= -k\ell n\left(1 - \frac{N}{M}\right)$$

$$= k\frac{N}{M}$$

$$\ell n(1-x) = -x - \frac{x^2}{2} - \ldots$$

Recall $\left(\frac{\partial S}{\partial V}\right) = \frac{-p}{T}$

$$\frac{\partial S}{\partial M} = V$$

$$v_0\left(\frac{\partial S}{\partial V}\right) = \frac{p v_0}{T} = \frac{kN}{M}$$

$$\Rightarrow \frac{pV}{M} = \frac{NkT}{M} \Rightarrow pV = NkT$$

What are *T, p,* μ?

Up to now, we have not proven that these are temperature, pressure, and chemical potential.

T, p, μ are intensive because $U(S,V,N)$ is a first-order homogenous function

$$f(\lambda x) = \lambda f(x)$$

$U(S,V,N)$ $\quad > S,V,N$ by λ $\quad U >$ by λ

extensive extensive

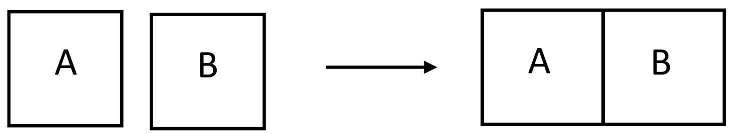
The derivatives $T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}, \quad \mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S,V,N_{i \neq j}}$

are intensive quantities

Second Law of Thermodynamics

Isolated systems tend toward states of maximum entropy

$\frac{1}{T}$ measures a system's tendency for heat exchange



A and B are brought together and only energy exchange is allowed

$$A: \; U_A, S_A \qquad \frac{1}{T_A} = \frac{\partial S_A}{\partial U_A}$$

$$B: \; U_B, S_B \qquad \frac{1}{T_B} = \frac{\partial S_B}{\partial U_B}$$

Before equilibrium

$S_{tot} = S_A + S_B$ not fixed

$U_{tot} = U_A + U_B$ fixed

What variations of U_A, U_B give max entropy *(dS = 0)*?

$$dS_{tot} = dS_A + dS_B = \left(\frac{\partial S_A}{\partial U_A}\right)_{V,N} dU_A + \left(\frac{\partial S_B}{\partial U_B}\right)_{V,N} dU_B = 0$$

$$0 = \left[\left(\frac{\partial S_A}{\partial U_A} \right)_{V,N} - \left(\frac{\partial S_B}{\partial U_B} \right)_{V,N} \right] dU_A$$

$$\Rightarrow \left(\frac{\partial S_A}{\partial U_A} \right)_{V,N} = \left(\frac{\partial S_B}{\partial U_B} \right)_{V,N}$$ or $$\frac{1}{T_A} = \frac{1}{T_B}$$

At equilibrium the two subsystems achieve the same *T*

$$dS_{total} = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dV_A$$

S > as system evolves toward equil.

if $T_A > T_B$, $\frac{1}{T_A} - \frac{1}{T_B}$ negative so dU_A negative

energy goes from higher *T* to lower *T* object entropy is the potential to move energy from one place to another

$\frac{1}{T}$ is the driving force

The greater *T* is, the greater the tendency for energy to escape

heat flows to maximize *S*.

energy no longer flows when *S* has already reached its maximum

When the system stops changing, the two subsystems do not have to have the same values of S or U.

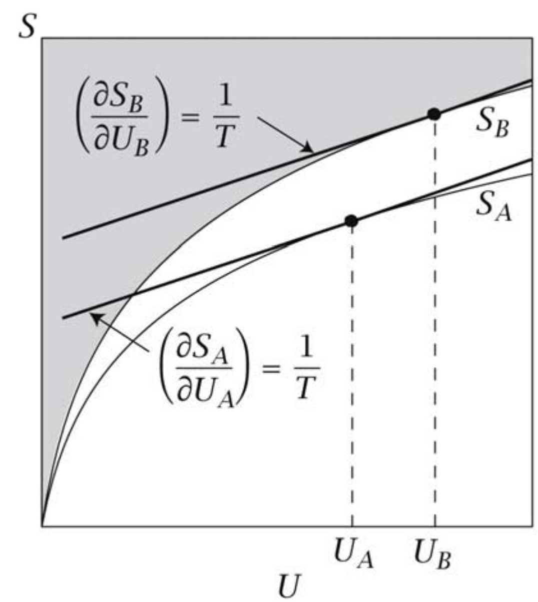


Figure 6.4 Molecular Driving Forces 2/e (© Garland Science 2011)

pressure is a force for changing volume

$$A:\ \ S_A, V_A$$

$$B:\ \ S_B, V_B$$

$V_{tot} = V_A + V_B =$ const,

Also, energy is not allowed to exchange with surroundings

$$dS = \left[\left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B\right] + \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A = 0$$

$$\left[\left(\frac{\partial S_A}{\partial V_A}\right) - \left(\frac{\partial S_B}{\partial V_B}\right)\right] dV_A = 0$$

At equilibrium $T_A = T_B$

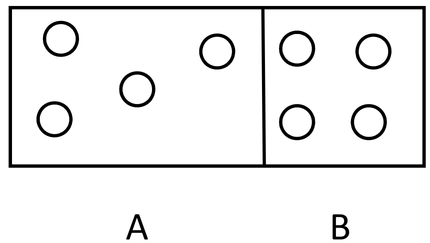
$$\left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right) dV_A = 0 \Rightarrow \frac{p_A}{T_A} = \frac{p_B}{T_B} \Rightarrow p_A = p_B$$

equil. requires pressures of the two subsystems to be equal

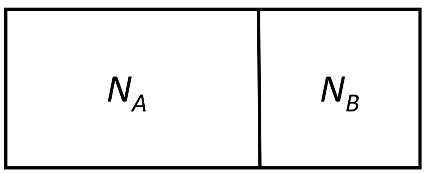
$p_B > p_A \Rightarrow$

$V_A <, \quad V_B >$

until $\quad p_A = p_B$



How to understand this in terms of multiplicities



M_A sites $\qquad M_B$ sites

M = total lattice sites

$$M = M_A + M_B = \text{ constant}$$

suppose $N << M$

$$W(N,M) = \frac{M!}{N!(M-N)!} \sim \frac{M^N}{N!} \qquad \Bigg| \qquad \frac{M!}{(M-N)!} \sim \mathrm{M}^N$$

$$W = W_A W_B = \frac{M_B!}{N_B!(M_B - N_B)!} \frac{M_A!}{N_A!(M_A - N_A)!}$$

$$= \frac{M_B^{N_B}}{N_B!} \frac{M_A^{N_A}}{N_A!} = \frac{M_A^{N_A}(M - M_A)^{N_B}}{N_A! N_B!}$$

Want to maximize

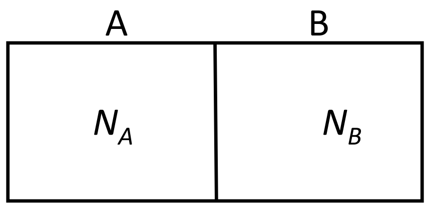
$$\ell n W = N_A \ell n M_A + N_B \ell n(M - M_A) \Rightarrow \frac{N_A}{M_A*} = \frac{N_B}{M_B*}$$

At equilibrium, density is same on both sides

We already know that $\frac{p_A}{T_A} = \frac{p_B}{T_B}$

This plus ideal gas law would also
tell us the densities are equal

Now we have to consider particle #s



$N = N_A + N_B =$ constant

$S_A\left(N_A\right) \quad S_B\left(N_B\right)$

$$dS = \left(\frac{\partial S_A}{\partial N_A}\right) dN_A + \left(\frac{\partial S_B}{\partial N_B}\right) dN_B = 0$$

$$\Rightarrow \left[\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right] dN_A = 0$$

$$\Rightarrow \left(\frac{\mu_B}{T_B} - \frac{\mu_A}{T_A}\right) dN_A = 0$$

equil. $T_A = T_B$

which implies $\mu_A = \mu_B$

$$dS_{tot} = \left(\frac{\mu_B}{T} - \frac{\mu_A}{T} \right) dN_A > 0$$

$\Rightarrow \dfrac{\mu_B - \mu_A}{T}$ and dN_A of same sign

if $N_A >$, then μ_B must be $> \mu_A$

particles move from high chemical potential to low chemical potential