

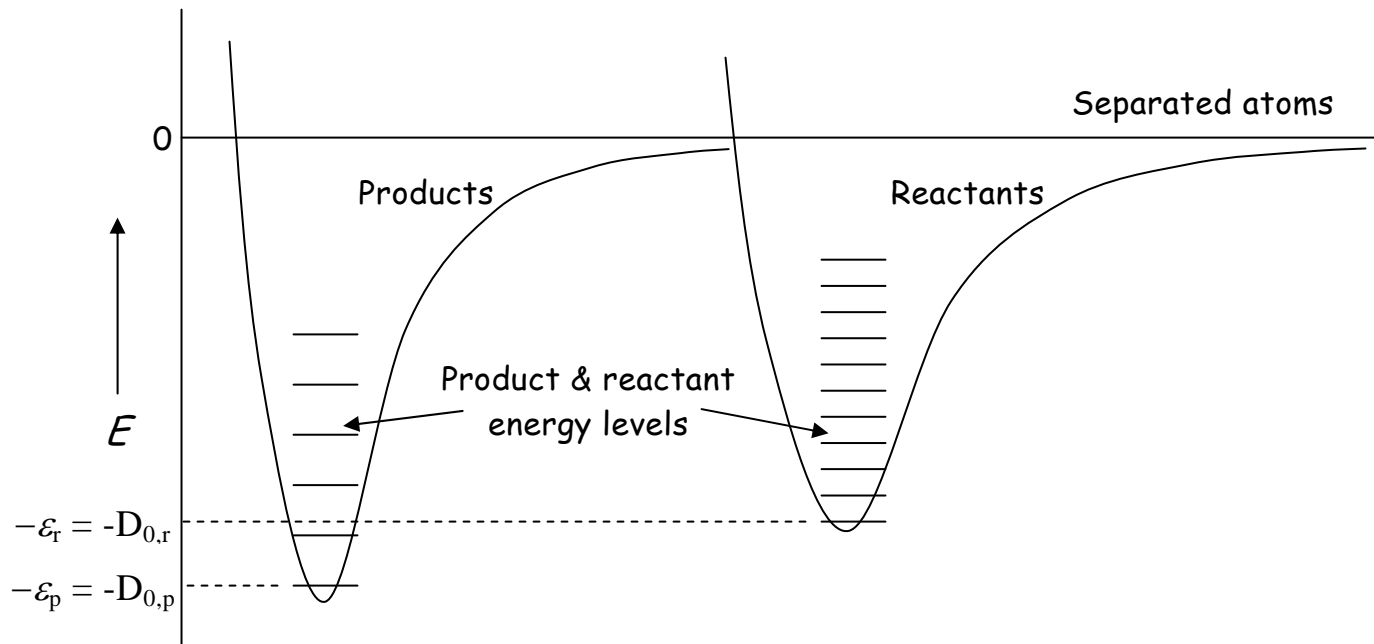
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5.60 Thermodynamics & Kinetics
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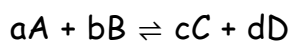
APPLICATIONS: CHEMICAL AND PHASE EQUILIBRIA

Apply statistical mechanics to develop microscopic models for problems you've treated so far with macroscopic thermodynamics



Chemical equilibria

Gas phase: Calculate K_p from microscopic properties



$$\Delta G^0 = -RT \ln K_p = cG_c^0 + dG_d^0 - aG_a^0 - bG_b^0$$

Need G^0 for each species

$$G = A + pV = -kT \ln Q + pV = -kT \ln Q + NkT$$

$$Q = \frac{q_{trans}^N}{N!} q_{int}^N$$

$$\ln Q = N \ln(q_{trans} q_{int}) - \ln N! = N \ln(q_{trans} q_{int}) - N \ln N + N = N \ln(q_{trans} q_{int} / N) + N$$

$$G = -kT \ln Q + NkT = -NkT \ln(q_{trans} q_{int} / N) = -NkT \ln(q/N)$$

For molecules in the gas phase, internal degrees of freedom are rotations and vibrations and electronic states.

$$q_{\text{int}} = q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$$

$$q_{\text{elec}} = e^{D_0/kT} \quad \text{Dissociation energy } D_0 \text{ from ground electronic level}$$

Usually no other electronic levels matter

$$q_{\text{vib}} = \sum_n e^{-n\varepsilon_0/kT} = 1 + e^{-\varepsilon_0/kT} + e^{-2\varepsilon_0/kT} + e^{-3\varepsilon_0/kT} + \dots = \frac{1}{1 - e^{-\varepsilon_0/kT}}$$

Note we've set the zero of vibrational energy as the lowest vibrational level. The zero-point vibrational energy has been included in q_{elec} by using the dissociation energy rather than the bottom of the electronic potential energy.

$$kT (300 \text{ K}) \leftrightarrow 200 \text{ cm}^{-1}$$

Most molecular vibrational frequencies $> 500 \text{ cm}^{-1}$

$q_{\text{vib}} \approx 1$ - Need to calculate it, but it's not large

We have not treated q_{rot} . Levels are NOT evenly spaced: $\varepsilon_{\text{rot}} = J(J+1)\varepsilon_{0,\text{rot}}$ where $J = 0, 1, 2, \dots$, and $\varepsilon_{0,\text{rot}} \approx 1 \text{ cm}^{-1}$.

High-T limit: $q_{\text{rot}} = kT/\varepsilon_{0,\text{rot}} \approx 100\text{-}1000$.

We've seen that $q_{\text{trans}} \approx 10^{30}$, $q_{\text{trans}}/N \approx 10^6$.

For multiple species in chemical equilibrium, need to use N_i for each species and use partial pressure values in pV term.

$$G_i = -N_i kT \ln(q_i/N_i) = -n_i RT \ln(q_i/N_i)$$

$$\bar{G}_i = -RT \ln(q_i/N_i) = \bar{G}_i^\circ + RT \ln(p_i/p^\circ)$$

$$\bar{G}_i^\circ = -RT \ln\left(\frac{q_i}{N_i} \frac{N_i kT}{p^\circ V}\right) = -RT \ln\left(\frac{q_i kT}{p^\circ V}\right)$$

Example: simple reaction at 300 K: $A\text{-}B + C\text{-}D \rightarrow A\text{-}C + B\text{-}D$

Assume all molecules have high vibrational frequencies $\Rightarrow q_{\text{vib}} \approx 1$ for all species

Translational & rotation: high-T limits

Assume similar rotational energies (depends on moments of inertia)

$\Rightarrow q_{\text{trans}}$ & q_{rot} contributions are all equal

$$\Delta \bar{G}_i^\circ = -RT \ln \left(\frac{q_{AC} q_{BD}}{q_{AB} q_{CD}} \right) = -RT \ln K_p$$

$$K_p = \frac{q_{AC} q_{BD}}{q_{AB} q_{CD}} = \frac{e^{D_{0,AC}/kT} e^{D_{0,BD}/kT}}{e^{D_{0,AB}/kT} e^{D_{0,CD}/kT}} = e^{(D_{0,AC} + D_{0,BD} - D_{0,AB} - D_{0,CD})/kT}$$

Only dissociation energies matter since the other degrees of freedom contribute equally.

Usually energy effects dominate in chemical equilibria.

Relatively simple case: Solid-state chemical reaction $aA \rightleftharpoons bB$

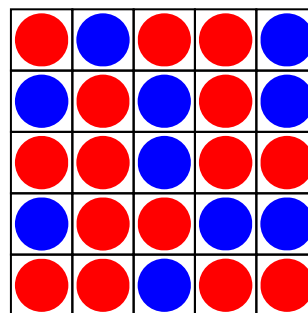
e.g. isomerization in an organic molecular crystal

N_A molecules of A, N_B molecules of B, $N_A + N_B = N$

No translation or rotation, no change in $pV \Rightarrow$ all the change is in the electronic and vibrational energy

If vibrational frequencies are the same, then only the difference in dissociation energies is needed.

$$Q = \sum_{\text{microstates}} e^{-E_i/kT} = \sum_{E_i} \Omega(E_i) e^{-E_i/kT}$$



Recall the entropy due to mixing of two species

$$\begin{aligned} Q &= \sum_{E_i} \Omega(E_i) e^{-E_i/kT} = \sum_{N_A=0}^N \frac{N!}{N_A! N_B!} e^{(N_A D_A + N_B D_B)/kT} = \sum_{N_A=0}^N \frac{N!}{N_A! N_B!} e^{(D_A/kT)^{N_A}} e^{(D_B/kT)^{N_B}} \\ &= \sum_{N_A=0}^N \frac{N!}{N_A! N_B!} q_A^{N_A} q_B^{N_B} = (q_A + q_B)^N = q_A^N (1 + s)^N \quad \text{where } s = q_B/q_A = e^{(D_B - D_A)/kT} = e^{\Delta D_0/kT} \end{aligned}$$

The binomial theorem gives a simple closed form for the sum.

It's convenient here to redefine the zero of energy as $-D_A$ so $q_A = 1$ and

$$Q = (1 + s)^N = 1 + a_1 s + a_2 s^2 + a_3 s^3 + \dots + a_N s^N$$

The ground state of the system has all A molecules

System energy is $E(N_B) = N_B \Delta D_0$.

Probability that the system has this energy is

$$p(N_A) = a_{N_A} s^{N_A} / Q$$

The average number of B molecules is

$$\langle N_B \rangle = \sum_{N_B} N_B p(N_B) = \frac{a_1 s + 2a_2 s^2 + 3a_3 s^3 + \dots + N a_N s^N}{Q} = \frac{s}{Q} \left(\frac{\partial Q}{\partial s} \right) = \left(\frac{\partial \ln Q}{\partial \ln s} \right)$$

$$\text{and } \langle E \rangle = U = \langle N_B \rangle \Delta D_0$$

If vibrational energies differ then q_{vib} also needs to be included.

In general, low vibrational frequency favors a species since the levels are closely spaced, so there are many low-energy states of that species.

For chemical reactions involving covalent bonds, the bond energies dominate over entropy. But the treatment we've given could also be used for much more subtle changes like rotation of CO molecules in a CO crystal.

Note that this treatment assumes *no interactions* between different unit cells. This gives rise to a fairly gentle T-dependence of the equilibrium.

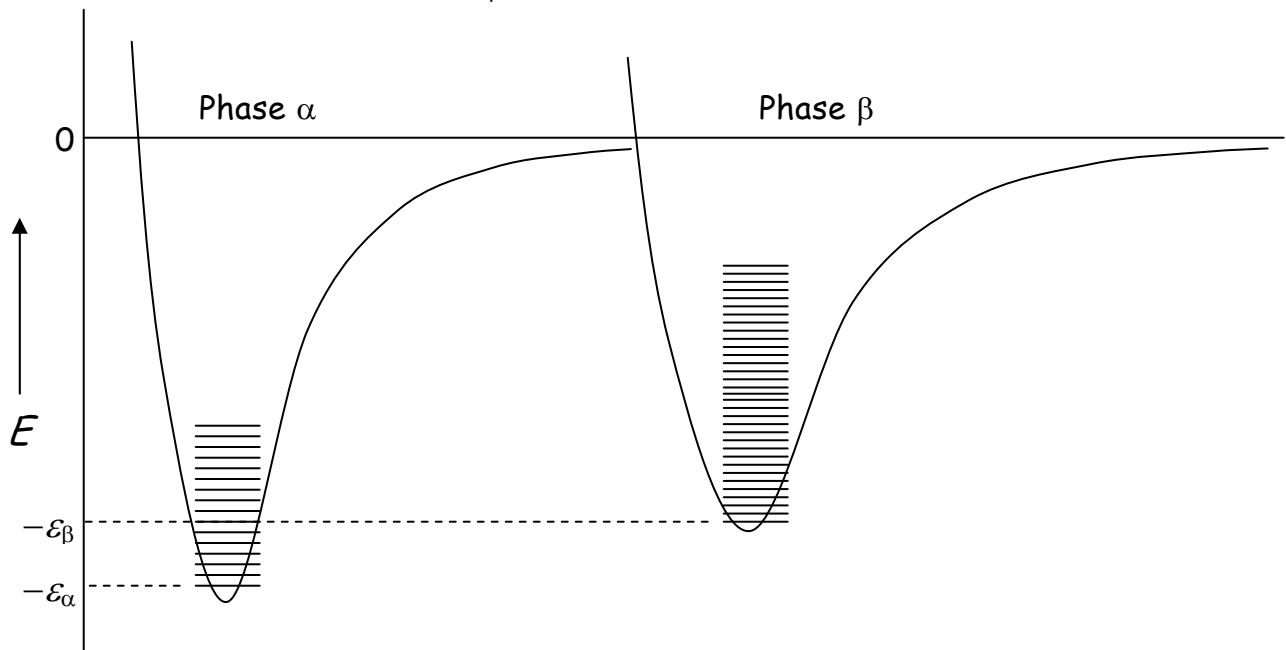
Solid-solid phase equilibria

Phase transitions between different crystalline phases may be easier to treat than chemical reactions, because there is just one state at any temperature: the crystal in phase α or the crystal in phase β .

Problem set problem

Einstein model for crystalline phases α and β , frequencies ν_α , ν_β

Binding energy per atom: $-\varepsilon_\alpha$, $-\varepsilon_\beta$



Binding energy is like dissociation energy. It includes zero-point vibrational energy, so no need to account for this separately.

You can predict the phase transition temperature based on a simple first principles model.

Phase transition only occurs if the crystal with stronger binding energy, e.g. α phase, also has higher vibrational frequency.

Note that this treatment assumes *complete cooperativity*: the crystal is either all one or all the other phase. This gives rise to an abrupt T-dependence of the equilibrium.

Many intermediate cases occur.

Example: helix-coil transition in biopolymers. Interactions make few long segments of helix or coil more stable than many short segments. (Similar for magnetic and nonmagnetic domains in a ferromagnetic crystal, and in all sorts of interacting systems). In this case the T-dependence is not completely abrupt, but not nearly as gradual as in the non-interacting limit.

Extra example (using QM result for q_{trans})

Can also calculate solid-gas phase equilibria, i.e. *vapor pressure* over the crystal. Assume monatomic ideal gas - only translational partition function.

$$Q^g = q_{\text{trans}}^N / N! = \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right]^N / N! \quad A^g = -kT \ln Q^g \quad \mu^g = \left(\frac{\partial A^g}{\partial N} \right)_{T,V}$$

$$\ln Q^g = N \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V - N \ln N + N$$

$$\left(\frac{\partial \ln Q^g}{\partial N} \right)_{T,V} = \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V - \ln N - 1 + 1 = \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N}$$

$$\mu^g = -kT \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{p} \quad (\text{ideal gas})$$

Condition for phase equilibrium: $\mu^s = \mu^g$

$$\mu^s = -\varepsilon - 3kT \ln \left(\frac{kT}{h\nu_E} \right) = \mu^g = -kT \ln \left(\frac{2\pi m}{h^2} \right)^{3/2} \frac{(kT)^{5/2}}{p}$$

$$\varepsilon = kT \ln \left(\frac{2\pi m}{h^2} \right)^{3/2} \frac{(kT)^{5/2}}{p} \left(\frac{h\nu_E}{kT} \right)^3 = kT \ln \frac{(2\pi m)^{3/2} \nu_E^3}{(kT)^{1/2} p}$$

$$p = \frac{(2\pi m)^{3/2} \nu_E^3}{(kT)^{1/2} e^{\varepsilon/kT}}$$

gives vapor pressure $p(T)$ over the crystal! Strong binding energy or low T give low pressure as expected. Low vibrational frequency also gives low p , since this allows higher entropy in the crystal.

So you can calculate the p-T phase diagram that you described before in macroscopic terms only.