Solvation.
Free energies of transfer

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Phase equilibria and phase transitions
Phase diagrams

Conditions \((p,T)\) can define phases. Phase diagrams map phases versus \((p,T)\).

Phase boundaries indicate where phases are in equilibrium.

- Solid-gas: sublimation/deposition
- Liquid-gas: boiling/condensation
- Solid-liquid: melting/freezing

Boiling temperature rises with pressure. What is the slope \(dp/dT\)?
The shape of phase boundaries

Take two nearby points \((T_1, p_1)\) and \((T_2, p_2)\) on the liquid-gas phase boundary.

\[
\begin{align*}
\mu_L(T_1, p_1) &= \mu_G(T_1, p_1) \\
\mu_L(T_2, p_2) &= \mu_G(T_2, p_2) \\
\mu_L(T_2, p_2) &= \mu_L(T_1, p_1) + d\mu_L(T, p) \\
\mu_G(T_2, p_2) &= \mu_G(T_1, p_1) + d\mu_G(T, p)
\end{align*}
\]

\[
d\mu_L(T, p) = d\mu_G(T, p)
\]

\[
d\mu(T, p) = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} dT + \left(\frac{\partial \mu}{\partial p}\right)_{T,N} dp
\]

Maxwell relations

\[
d\mu(T, p) = -\left(\frac{\partial S}{\partial N}\right)_{T,p} dT + \left(\frac{\partial V}{\partial N}\right)_{T,p} dp
\]

\[
d\mu(T, p) = -s dT + v dp
\]
The Clapeyron and Clausius-Clapeyron Equations

For two nearby points \((T_1, p_1)\) and \((T_2, p_2)\) on the liquid-gas phase boundary:

\[
d\mu_G = -s_GdT + v_Gdp = -s_LdT + v_Ldp = d\mu_L
\]

\[
(s_L - s_G)dT = (v_L - v_G)dp
\]

\[
\frac{dp}{dT} = \frac{s_G - s_L}{v_G - v_L} = \frac{\Delta s}{\Delta v}
\]

At the phase transition boundary: \(\Delta \mu = \Delta h - T\Delta s = 0 \Rightarrow \Delta h = T\Delta s\)

Clapeyron equation:

\[
\frac{dp}{dT} = \frac{\Delta h}{T\Delta v}
\]

Clausius-Clapeyron equation:

\[
\frac{d \ln(p)}{dT} = \frac{\Delta h}{RT^2}
\]

\[
\Delta v = v_G - v_L \approx v_G = \frac{RT}{p}
\]
Clausius-Clapeyron equation: Applications

Starting with the Clausius-Clapeyron equation:

\[
\frac{d \ln(p)}{dT} = \frac{\Delta h}{RT^2} \quad \Rightarrow \quad \int_{p_1}^{p_2} d \ln(p) = \int_{p_1}^{p_2} \frac{\Delta h}{RT^2} dT \quad \Rightarrow \quad \ln \left( \frac{p_2}{p_1} \right) = \frac{\Delta h}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

The boiling point of water is 373 K at 1 atm. What is the boiling point of water at 0.5 atm?

\[\Delta h = 40.66 \, \text{kJ/mol}\]

\[
\ln \left( \frac{1}{2} \right) = \frac{40.66}{8314} \left( \frac{1}{T_2} - \frac{1}{373} \right)
\]

\[T_2 = 354 \, \text{K} = 81 \, ^{\circ}\text{C}\]

Linearity of the following graph indicates that \(\Delta h\) does not depend on temperature \(T\):

Vapor pressure of benzene vs. \(1/T\)
Surface tension

Surface = boundary between condensed phase and vapor.

Surface tension arises from the energy cost of increasing the surface area. \( \gamma = \left( \frac{\partial U}{\partial A} \right)_{T,V,N} \)

Consider the lattice shown below.
Bulk particles have \( z \) neighbors. Surface particles have \( z-1 \) neighbors.

The total energy is:
\[
U = \left( \frac{zw_{AA}}{2} \right) (N - n) + \left[ \frac{(z-1)w_{AA}}{2} \right] n = \frac{w_{AA}}{2} (NZ - n)
\]
Relating surface tension to binding energies

\[ U = \frac{w_{AA}}{2} (N_Z - n) \]

\[ \gamma = \left( \frac{\partial U}{\partial A} \right)_{T,V,N} = \left( \frac{\partial U}{\partial n} \right)_{T,V,N} \left( \frac{\partial n}{\partial A} \right) = -\frac{w_{AA}}{2a} \]

Here, \( a \) is the area associated with a surface particle.

\[ \gamma a (\text{J mol}^{-1}) \]

This plot indicates that \( \sim 6 \)-fold more bonds are broken in vaporization than in creating a surface.
Solutions and mixtures

Salt + water

Tin + copper = bronze
Solutions and mixtures

We will model mixtures as molecules filling lattice sites.

For liquids and solids, the ensembles \((T,V,N)\) and \((T,p,N)\) are approximately equivalent. So \(F \approx G\).

The entropy of mixtures is greater than that of pure materials.
A lattice model: the entropy of solution

Assume that $N_A$ molecules $A$ and $N_B$ molecules $B$ fill $N=N_A+N_B$ lattice sites. The multiplicity of states is given by:

$$W = \frac{N!}{N_A! N_B!} \text{ Stirling’s approx.}$$

$$\Delta S_{mix} \approx k [N \ln(N) - N_A \ln(N_A) - N_B \ln(N_B)]$$

$$\frac{\Delta S_{mix}}{Nk} \approx -x \ln(x) - (1-x) \ln(1-x)$$

where $x = \frac{N_A}{N}$

Ideal solutions form with no energy change. For ideal solutions entropy dominates the free energy:

$$F = -T \Delta S_{mix}$$
A lattice model: the energy of solution

Real solutions usually involve an energy change. This is the sum of all bond energies, \( w \).

\[
U = m_{AA}w_{AA} + m_{BB}w_{BB} + m_{AB}w_{AB}
\]

How do we calculate \( m_{AA}, m_{BB}, m_{AB} \)? (Each site has \( z \) bonds).

The number of A-A bonds would be:

\[
zN_A - m_{AB}
\]

To avoid overcounting, we divide by 2:

\[
m_{AA} = \frac{zN_A - m_{AB}}{2} \quad m_{BB} = \frac{zN_B - m_{AB}}{2}
\]
A lattice model: the internal energy of solution

\[ U = \frac{z w_{\text{AA}}}{2} N_A + \frac{z w_{\text{BB}}}{2} N_B + m_{\text{AB}} \left( w_{\text{AB}} - \frac{w_{\text{AA}} + w_{\text{BB}}}{2} \right) \]

How can we estimate \( m_{\text{AB}} \)?

Take a site next to an A molecule. What is the chance to find a B molecule there?

\[ p_B = \frac{N_B}{N} = x_B = 1 - x \]

\[ m_{\text{AB}} = z N x p_B = z N x (1 - x) \]

\[ U = \frac{z w_{\text{AA}}}{2} N_A + \frac{z w_{\text{BB}}}{2} N_B + \frac{N_A N_B}{N} \left( w_{\text{AB}} - \frac{w_{\text{AA}} + w_{\text{BB}}}{2} \right)\]

\[ U = \frac{z w_{\text{AA}}}{2} N_A + \frac{z w_{\text{BB}}}{2} N_B + kT \chi_{\text{AB}} \frac{N_A N_B}{N} \]

Exchange parameter \( \chi_{\text{AB}} \)
The Helmholtz free energy of solution

Next we substitute $U$ and $S$ into $F = U - TS$:

$$\frac{F}{NkT} = \left[ \frac{ZW_{AA}}{2kT} + \ln(x) \right] x + \left[ \frac{ZW_{BB}}{2kT} + \ln(1-x) \right] (1-x) + \chi_{AB} x(1-x)$$

The free energy due to mixing is:

$$\Delta F_{mix} = F(N_A, N_B) - F(N_A, 0) - F(0, N_B)$$

$$\frac{F(N_A, 0)}{NkT} = \frac{ZW_{AA}}{2kT} x$$

$$\frac{F(0, N_B)}{NkT} = \frac{ZW_{AA}}{2kT} (1-x)$$

$$\frac{\Delta F_{mix}}{NkT} = x \ln(x) + \ln(1-x)(1-x) + \chi_{AB} x(1-x)$$

This is called the regular solution model. Similar-sized spherical molecules form regular solutions.
The meaning of the exchange parameter

\[
\frac{F}{NkT} = \left[ \frac{\zeta W_{AA}}{2kT} + \ln(x) \right] x + \left[ \frac{\zeta W_{BB}}{2kT} + \ln(1-x) \right] (1-x) + \chi_{AB} x (1-x)
\]

The chemical potential tells about molecular preferences for each component:

\[
\frac{\mu_B}{kT} = \left[ \frac{\partial}{\partial N_B} \left( \frac{F}{kT} \right) \right]_{T,N_A} = \frac{\zeta W_{BB}}{2kT} + \ln(x_B) + \chi_{AB} (1-x_B^2) = \frac{\mu^\circ}{kT} + \ln(\gamma x)
\]

\( \gamma(x) = \) activity coefficient

The exchange parameter describes the energy change associated with moving an A molecule into a medium of pure B-s and vice versa.

\[ A_2 + B_2 \xrightleftharpoons[K_{exch}]{K_{exch}} 2AB \]

\( \chi_{AB} > 0 : \) mixing is not favored energetically

\( \chi_{AB} < 0 : \) mixing is favored energetically
Interfacial tension

Interfaces form at the boundaries of materials. What is the surface tension?

The total energy is:

\[ U = \left( \frac{z w_{AA}}{2} \right) (N_A - n) + \left[ \frac{(z - 1) w_{AA}}{2} \right] n + n w_{AB} + \]
\[ + \left( \frac{z w_{BB}}{2} \right) (N_B - n) + \left[ \frac{(z - 1) w_{BB}}{2} \right] n \]

\[ \gamma \approx \left( \frac{\partial U}{\partial A} \right)_{T,V,N} = \frac{1}{a} \left( w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) = \frac{kT}{za} \chi_{AB} \]

\( \alpha \) is the area associated with a surface particle.
Solvation
**Solvation: Particles inside and across media**

Example: toxins dissolve in water, and then transfer into fish.

Colligative properties: Freezing and boiling temperatures change for solutions.
Example: salt melts the ice.
Example: salt reduces vapor pressure of water.

Assume a liquid mixture of A and B molecules. B is volatile, A is not.

\[ N_B = N_L + N_G = \text{const.} \]

At equilibrium we have:

\[ \mu_{B,\text{liquid}} = \mu_{B,\text{gas}} = kT \ln \left( \frac{p}{p_{B,\text{int}}} \right) \]

\[ \frac{\mu_{B,\text{liquid}}}{kT} = \left[ \frac{\partial}{\partial N_B} \left( \frac{F}{kT} \right) \right]_{T,N_A} \]

\[ = \ln(x_B) + \frac{z w_{BB}}{2kT} + \chi_{AB} (1 - x_B)^2 \]

\[ \frac{p_B}{p_{B,\text{int}}} = x_B e^{\frac{z w_{BB}}{2kT} + \chi_{AB} (1 - x_B)^2} \]
Solvation: transfer of particles across media

\[ p_B = p_B^\circ x_B e^{\chi_{AB}(1-x_B)^2} \]

where \( p_B^\circ \) = \( p_B^{\circ,\text{int}} e^{\frac{zw_{BB}}{2kT}} \) vapor pressure over pure solvent

\( \chi_{AB} = 0 \) is Raoult’s Law. It refers to an ideal solutions (no energy change from mixing).

Vapor pressure decreases because of entropic effects.

\[ \chi_{AB} = 0 \]
Solvation: transfer of particles across media

\( \chi_{AB} > 0 \) : A and B dislike each other. Vapor pressure is higher than for ideal solution.

\( \chi_{AB} < 0 \) : A and B prefer each other. Vapor pressure is lower than for ideal solution.
Thermodynamic model of activity

$$\mu_{B,\text{gas}} = \mu_{B,\text{gas}}^\circ + kT \ln (p_B)$$

$$\mu_{B,\text{liquid}} = \mu_{B,\text{liquid}}^\circ + kT \ln \left[ x_B \gamma_B (x_B) \right]$$

After setting the chemical potentials equal, we get:

$$\frac{p_B}{x_B} = \gamma_B (x_B) e^{\frac{\mu_{B,\text{liquid}}^\circ - \mu_{B,\text{gas}}^\circ}{kT}}$$

If solvent is volatile, use the solvent convention:

$$\lim_{x_B \to 1} \gamma_B (x_B) = 1$$

If solute is volatile, use the solute convention:

$$\lim_{x_B \to 0} \gamma_B (x_B) = 1$$

\(\gamma(x)\) = activity coefficient

\(x\gamma(x)\) = activity

These are defined to make the formula similar to:

$$\mu = \mu^\circ + kT \ln (p)$$
Using the solvent and solute conventions

\[
\frac{zW_{BB}}{2kT} + \chi_{AB}(1 - x_B)^2 = \frac{\mu_B^\circ}{kT} + \ln(\gamma_B)
\]

1. Solvent convention:

\[
\lim_{x_B \to 1} \gamma_B(x_B) = 1 \quad \Rightarrow \quad \frac{\mu_B^\circ}{kT} = \frac{zW_{BB}}{2kT} \quad \Rightarrow \quad \gamma_B = e^{\chi_{AB}(1-x_B)^2}
\]

(Open cavity in pure B and insert a B)

2. Solute convention:

\[
\lim_{x_B \to 0} \gamma_B(x_B) = 1 \quad \Rightarrow \quad \frac{\mu_B^\circ}{kT} = \frac{zW_{BB}}{2kT} + \chi_{AB} \quad \Rightarrow \quad \gamma_B = e^{\chi_{AB}x_B(2-x_B)}
\]
Solute elevates boiling temperature of solvent

For example, saltwater boils at higher temperature than pure water.

Why?
1) pure water boils at 100°C
2) salt reduces vapor pressure of water
3) to boil water, we need to increase the temperature

\[ p_B = p_B^\circ e^{\frac{zW_{BB}}{2RT_{b,0}}} \]

\[ p_B \approx p_{B,int} x_B e^{\frac{zW_{BB}}{2RT_{b,1}}} \]

\[ \ln(x_B) = \frac{zW_{BB}}{2R} \left( \frac{1}{T_{b,0}} - \frac{1}{T_{b,1}} \right) \]

\[ \ln(x_B) \approx \frac{zW_{BB}}{2R} \frac{\Delta T}{T_{b,0}^2} \]

\[ \ln(x_B) \approx -x_A \]

\[ \Delta T_b = -\frac{2}{zW_{BB}} RT_{b,0}^2 x_A = \frac{RT_{b,0}^2 x_A}{\Delta h_{vap}} \]

This is the change in boiling temperature.
Salt helps ice melting
Solute lowers freezing temperature of solvent

For example, saltwater freezes at lower temperature than pure water.

Why?
1) pure water freezes at 0°C
2) salt reduces the escape of molecules from the liquid phase
3) for ice to form, temperature must drop

Freezing temperature drops proportional to solute concentration $x_A$: $\Delta T_f = \frac{RT_f^2 x_A}{\Delta h^\circ_{fus}} < 0$