

Interface Thermodynamics

Surface tension (or surface energy, γ) is work (w), needed for unit increase of interfacial area (S)

$$\gamma = \frac{dw}{dS} \quad \Rightarrow \quad dw = \gamma dS$$

Estimation Methods: Surface tension of (mainly) organic liquids can be derived from **parachor**

$$[P] = \frac{M\gamma^{1/4}}{\rho^l - \rho^g}$$

where M is molar mass, ρ density in respective phases (density of a gas above its critical point may be neglected). Structure-activity relationships using group contributions are available for parachor, e.g. Vogel A.I.: J. Chem. Soc. 1833, 1948.

Data Sources: Cdata (software, available at the Dept. of Chem.)

Jasper, J.J.: The Surface Tension of Pure Liquid Compounds, J. Phys. Chem. Ref. Data, 1, 841, 1972.

Parachor values were tabulated e.g. in

Escobedo J., Mansoori G.A.: Surface Tension Prediction for Pure Fluids, AIChE J., 42, 1425-1433, 1996.

Temperature dependence of surface tension follows from parachor, more accurate description is provided by the **Eötvös equation**

$$\gamma(V^l)^{2/3} = k(T_c - T - \delta)$$

where V^l is molar volume of a liquid, T_c its critical temperature and parameter δ is constant for most compounds with the value of 6 K.

Surface tension of mixtures also follows from the parachor

$$\gamma^{1/4} = \rho^l \sum_{i=1}^k \frac{x_i \gamma_i^{1/4}}{\rho_i^l}$$

ρ_i^l is density of a liquid component and ρ^l density of the mixture. Surface tension of dilute solutions is often described by the **Szyszkowski equation**

$$\gamma = \gamma^o - a \ln(1 + bc)$$

where γ^o is surface tension of pure solvent, a , b are parameters and c concentration of a solute.

Shape of the interface affects the pressures on both sides of the interface (phases α and β)

$$\gamma dS = dw^\alpha - dw^\beta = p^\beta dV - p^\alpha dV \quad \Rightarrow \quad p^\beta - p^\alpha = \gamma \kappa$$

where $\kappa = dS/dV$ is the mean curvature, characterized by two principal radii of curvature R_1 and R_2 , $\kappa = 1/R_1 + 1/R_2$. This pressure difference across the interface (**Laplace-Young equation**) describes e.g. the capillary elevation/depression (for spherical surface with radius r it holds that $\kappa = 2/r$ – spherical surface is acceptable approximation for non-wetting liquids). Thermodynamic equilibrium condition requires equal molar Gibbs energy in phases α and β , $G^\alpha = G^\beta$

$$\begin{aligned} dG^\alpha &= -S^\alpha dT + V^\alpha dp^\alpha & dG^\beta &= -S^\beta dT + V^\beta dp^\beta = -S^\beta dT + V^\beta (dp^\alpha + \gamma d\kappa) \\ dG^\alpha &= dG^\beta & \Rightarrow & (S^\beta - S^\alpha) dT - (V^\beta - V^\alpha) dp^\alpha = V^\beta \gamma d\kappa \end{aligned}$$

At constant temperature in a system gas-liquid (i.e. droplets in the vapor phase)

$$-(V^l - V^g) dp^\circ = V^l \gamma d\kappa$$

where p° is vapor pressure. Integrating this equation with the assumption of ideal gas EOS for the gas phase we get the **Kelvin equation**. The pressure over the surface of a droplet with radius r , p_r° , is higher than the pressure over flat surface, p_∞° (infinite radius of curvature)

$$RT \ln \frac{p_r^\circ}{p_\infty^\circ} = V^l \gamma \kappa$$

Small droplets thus evaporate more easily than larger ones. The same conclusion can be made for small crystals in a dispersion system. An analogue of Kelvin equation can be applied for multicomponent systems with activities instead of vapor pressures. Activities are often approximated by concentrations for this purpose.

Cohesion is the work needed for separating unit area of a material (i.e. column of material with unit cross section),
 $w_k = 2\gamma = 2\gamma^{lg}$.

Adhesion is the work needed for separating unit area of two phases from each other, e.g. liquid from solid,
 $w_a = \gamma^{lg} + \gamma^{sg} - \gamma^{sl}$. The difference between adhesion and cohesion ($S_R = \gamma^{sg} - \gamma^{lg} - \gamma^{sl}$) is directly related to the liquid wettability with respect to the solid surface. If this difference is negative, the shape of liquid drops formed on the surface follows from the balance of forces expressed by interfacial tensions, leading to **Young equation**
 $\gamma^{sg} = \gamma^{lg} \cos \vartheta + \gamma^{sl}$, where ϑ is the contact angle.

Interfacial Adsorption

Accumulation of solute molecules in near-surface layer relative to bulk liquid – **adsorption** – can lead to a substantial change in the interfacial tension. The difference is sometimes called the surface pressure

$$\pi = \gamma - \gamma^\circ$$

Adsorption is characterized by a relative excess of the solute in the near-surface layer compared to bulk composition. This surface excess $\Gamma_{i,1}$ can be described by the **Gibbs adsorption isotherm**

$$\Gamma_{i,1} = - \left(\frac{\partial \gamma}{\partial \mu_i} \right)_T = - \left(\frac{\partial \gamma}{\partial (RT \ln a_i)} \right)_T \approx - \frac{c_i}{RT} \left(\frac{\partial \gamma}{\partial c_i} \right)_T$$

Experimental data on adsorption are generally expressed in the format of adsorption isotherms, which relate the adsorbed amount a of a given component to its partial pressure (adsorption from the gas phase) or to its concentration (adsorption from solutions).

Freundlich Isotherm $a = kp^{1/n}$

where k, n are parameters, typically decreasing with temperature,

Langmuir Isotherm $a = a_m \frac{bp}{1+bp}$

where a_m is the maximum adsorbed amount of a component and b is parameter,

BET Isotherm

$$a = a_m \frac{Cp_{rel}}{(1-p_{rel})[1+(C-1)p_{rel}]}$$

where $p_{rel} = p/p^\circ$ and C is parameter. BET isotherm describes multilayer adsorption.

Adsorption on the electrically charged surface of a solid leads to the difference of potentials on the surface and in the bulk solution – **electrical double layer**. This adsorption always includes multiple layers, attracted to the surface by chemical interaction (first layer) and by long-range electrostatic forces (further layers, often called the diffuse layer).

Homework 9:

Solute A is removed from aqueous solution by adsorption on activated carbon. In two experiments 3 g of adsorbent were added to 250 ml of a solution

- with initial concentration $c_A^\circ = 0,5$ mol/l, equilibrium concentration (after adsorption) was found $c_A = 0,35$ mol/l
- with initial concentration $c_A^\circ = 1$ mol/l, equilibrium concentration (after adsorption) was found $c_A = 0,8$ mol/l

Find the parameters of Langmuir adsorption isotherm (take care about appropriate units).