

Thermodynamics of Surfaces

- Surface atoms are very different from atoms in the bulk.
- The fewer neighbors of the surface cause it to have a very different and anisotropic chemical environment compared with the bulk.
- The thermodynamics of the surface is most likely to be quite different from the thermodynamic properties of the bulk.
- Often certain atoms in multicomponent systems selectively accumulate on the surface as a result of these properties and impart rather different surface properties compared with the bulk.
- The balance of energies at the surface is the reason why small drops are curved and why liquid interfaces may rise when placed in capillaries

Surface Thermodynamic Functions

- Consider a large crystalline solid containing a total of N atoms, which is bounded by surface planes. We can determine various thermodynamic properties by including a term that accounts for excesses from the surface properties.
- Let E^0 , S^0 be the energy and entropy of the solid per atom, respectively. Also, E^s = specific surface energy (energy per unit area):
- $E = NE^0 + \alpha E^s$ where
 - N = # of atoms in the solid;
 - E = total energy of the solid and
 - α = surface area
- Similarly, for entropy the total entropy is
- $S = NS^0 + \alpha S^s$
- Total free energy is: $G = NG^0 + \alpha G^s$
- Surface work content is: $A^s = E^s - TS^s$
- Surface free energy is: $G^s = H^s - TS^s$

Work Needed to Create A Surface of one Component: Surface Tension

- Surface area is increased by moving atoms from the bulk to the surface and then to move surface atoms out of the way to make room for the new surface atoms.
- At const. T and P, the reversible surface work, δW , required to increase the surface area, α , by an amount $d\alpha$ of a one component system is

$$dW_{T,P}^S = \gamma da$$

where γ = called “surface tension” and is two dimensional equivalent of pressure. Note volume change is replaced with change in the surface area.

- Units:
 - Pressure, P = force per unit area = N/m²;
 - Surface tension, γ = force per unit length = N/m = J/m²
- Rough estimate of surface tension can be obtained by assuming the work is of the same magnitude as heat of sublimation
- The ΔH_{sub} is about 4×10^5 J/mol = 7×10^{-24} J/atom and the typical concentration of atoms on a surface is 10^{15} atoms/cm² = 10^{19} atoms/m²

$$\begin{aligned} g_{\text{est}} &\approx 7 \times 10^{-24} \text{ J/atom} \times 10^{19} \text{ atoms/m}^2 \\ &\approx 7 \text{ J/m}^2 \end{aligned}$$

- Experimentally the equation is best described as

$$g_{\text{est}} \approx 0.16 \cdot \Delta H_{\text{sub}}$$

- Small coefficient that metal – metal bonds in the bulk are not all broken when the surface is created.
- Also due to a relaxation where surface atoms move their equilibrium positions to maximize their bonding with the remaining neighbors.

Surface Tension and Work2

- Experimental values of surface tensions of a few metals and other substances are shown below.

Material	γ , J/m ²	T, °C
W (solid)	2.900	1727
Au(solid)	1.410	1027
NaCl	0.227	25
Water	0.07275	20
Ethanol (liquid)	0.02275	20

- Estimation of three dimensional pressure, P, for a solid surface.

- Divide by the thickness of the interaction assuming a few atomic layers ($d \approx 1$ nm)
- For W: $\gamma = 2.900$ J/m²

$$P = \frac{g}{d} = \frac{2.900 \text{ J/m}^2}{1 \times 10^{-9} \text{ m}} \cdot \left(\frac{1 \times 10^{-2} \text{ m}}{\text{cm}} \right)^3 \cdot \frac{1000 \text{ cm}^3}{1 \text{ L}} \cdot \frac{9.9 \times 10^{-3} \text{ L} \cdot \text{atm}}{\text{J}}$$

$$\approx 2.9 \times 10^4 \text{ atm}$$

- Conclusion metal surface experiences very large compressive forces.

Surface Free Energy: Positive

- Total free energy change dG of a one component system can include the contribution from surface work:

$$dG = -SdT + VdP + gda$$

- At constant T and P: $dG_{T,P} = gda$
- Two ways of increasing the surface area:
 - Adding new atoms from the bulk and
 - Stretching the already existing surface so that the number of atoms is fixed and only the state of strain changes (changes γ).
- Earlier we said that $G = NG^0 + \alpha G^s$, but when any change free energy is due only to a change in the surface free energy, this equation becomes: $dG_{T,P} = d(\alpha G^s)$. This can be rewritten in terms of the total differential at constant T, P:

$$dG_{T,P} = \left(\frac{\partial(G^s a)}{\partial a} \right)_{T,P} da = \left[G^s + a \left(\frac{\partial G^s}{\partial a} \right)_{T,P} \right] da$$

- When changing the surface are by addition of atoms to the surface from the bulk, the specific surface free energy, G^s is independent upon the surface are:

$$\left(\frac{\partial G^s}{\partial a} \right)_{T,P} = 0$$

- Simplify: $dG_{T,P} = G^s da$

- Combine with above to get: $dG_{T,P} = G^s da = gda$

- Or $G^s = g$

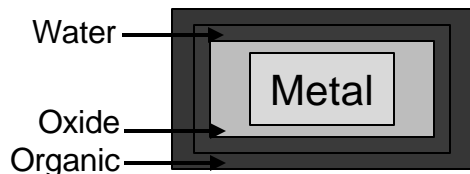
- Thus, for a one component system the surface tension is equal to the specific surface free energy. Only true when surface area changes as a result of the movement of atoms to the surface from the bulk.
- Since surface tension is always positive, the **surface free energy is always positive**.

Surface Free Energy (2)

- G^s is positive; this means that there is reluctance of a surface to form and is the cause of many interfacial properties of condensed phases.
- Surface free energy is minimized by keeping the surface tension to a minimum \Rightarrow closest packing of atoms is preferred.
- If at all possible, a high surface tension surface will be covered with a coating of reduced surface tension.
 - Metals are covered with oxides when the metal – gas interfacial energy, $\gamma_{m-g} > \gamma_{ox-g} + \gamma_{ox-m}$
 - Water will adsorb on and cover the oxide if

$$\gamma_{ox-g} > \gamma_{H_2O-g} + \gamma_{H_2O-ox}$$

- Adsorbed water can be displaced or covered by organic molecules of even lower surface tension



Surface coating will develop when

$$\gamma_{\text{new surface}} + \gamma_{\text{interface}} < \gamma_{\text{old surface}}$$

- Liquids tend to assume a spherical shape to minimize their surface area and surface tension.

Temperature Dependence of Specific Surface Free Energy

- For the temperature range that are typically used in the studies of surface-tension, $G^s = \gamma$. Temperature dependence can be determined by differentiating with respect to temperature.

$$\left(\frac{\partial G^s}{\partial T}\right)_P = \left(\frac{\partial g}{\partial T}\right)_P = -S^s \quad 1$$

- Thus, temperature dependence of surface tension leads to the specific surface entropy.
- Temperature dependence of γ predicting by a semi-empirical equation (van der Waals and Guggenheim:

$$g = g^o (1 - T/T_o)^n \quad 2$$

where $\gamma^o = \gamma$ at $T = 0$ K, T_c = critical temperature (temperature at which condensed phase no longer can exist) and n is a constant that varies from 11/9 for organic substances to 1 for metals.

–Notice $\gamma = 0$ when $T \rightarrow T_c$.

- Another empirical relationship for metals:

$$g_m = \frac{3.6T_m}{V_m^{2/3}} \quad 3$$

where m = melting point of the metal; γ is in dynes per centimeter.

- Specific surface enthalpy can be determined from the specific free energy and entropy (eq. 1):

$$H^s = G^s + TS^s$$

$$H^s = g - T \left(\frac{\partial g}{\partial T}\right)_P \quad 4$$

Specific Surface Energy and Heat Capacity

- At constant pressure the heat absorbed upon creation of unit surface area is given by Eq. 4. If volume is constant, then we can immediately see that the specific surface energy and specific surface enthalpy are equal to each other:

$$E^s = g - T \left(\frac{\partial g}{\partial T} \right)_P \quad 5$$

Specific Heat Capacity

- Remember the heat capacity, C, is defined as $C = dq/dt$. This leads to:

$$C_v = \left(\frac{\partial q}{\partial T} \right)_v = \left(\frac{\partial E}{\partial T} \right)_v \wedge C_p = \left(\frac{\partial q}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

- Take derivative with respect to temperature of equation 4 to find the heat capacity at constant pressure.

$$C_p^s = \left(\frac{\partial H^s}{\partial T} \right)_p = \frac{\partial}{\partial T} \left[g - T \left(\frac{\partial g}{\partial T} \right)_p \right]_p = \left(\frac{\partial g}{\partial T} \right)_p - \left(\frac{\partial T}{\partial T} \right)_p \left(\frac{\partial g}{\partial T} \right)_p - T \left(\frac{\partial^2 g}{\partial T^2} \right)_p$$

$$C_p^s = -T \left(\frac{\partial^2 g}{\partial T^2} \right)_p \quad 6$$

- Also, using $H = G + TS$ and taking the derivative of both sides with respect to T leads to

$$\left(\frac{\partial H}{\partial T} \right)_p = \frac{\partial}{\partial T} (G + TS)_p = \left(\frac{\partial G}{\partial T} \right)_p + \left(\frac{\partial T}{\partial T} \right)_p S + T \left(\frac{\partial S}{\partial T} \right)_p = -S + S + T \left(\frac{\partial S}{\partial T} \right)_p$$

$$\left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = \quad 7$$

- Surface heat capacity is equal to T times temperature derivative of entropy at constant pressure.
- On metal surfaces C_v and C_p are usually considered approximately equal to each other.
- Accurate surface tension measurements should lead to accurate estimates of surface heat capacity.

Surface Heat Capacity 2

- Direct Surface Heat capacities are often not reliable since the data is often not accurate enough.
- Better results are obtained from direct measurements of surface heat capacity measurements on finely divided powders with large surface – to – volume ratio.
- Difference between this and heat capacity of large crystallites of the same material yield the surface heat capacity.

Theoretical Estimation of Surface Heat Capacity

- Bulk heat capacities: C_p varies in a regular fashion with temperature. At low temperatures, it is often estimated using Debye extrapolation, which
 - assumes a T^3 dependence,
 - fits the data to the expression: $C_p = aT^3$
 - uses the value of a obtained above to determine heat capacities where they could not be measured.
- Surface heat capacities: Frequencies of vibration is given by

$$\frac{dn}{dv} = f(v) = \frac{2\alpha v}{C_2} \quad 8$$

where α = surface area, v = frequency and C_2 = velocity of sound in two dimensions, n = number of frequencies.

- If N surface atoms still have $3N$ vibrational modes, we have (after integration of eq 8):

$$\int_0^{3N} dn = \int_0^{v_D} \frac{2\alpha v}{C_2} dv$$

$$3N = \frac{\alpha v_D^2}{C_2} \quad 9$$

where v_D is the limiting Debye frequency.

Surface Heat Capacity: Theoretical

- In 9 solve for C_2 and substitute into 8 to get:

$$C_2 = \frac{pav_D^2}{3N} \Rightarrow f(v) = \frac{2pav}{\frac{pav_D^2}{3N}}$$

$$f(v) = \frac{6Nv}{v_D^2} \quad 10$$

- The total surface energy is given by

$$E = \frac{6Nh}{v_D^2} \int_0^{v_D} \frac{v^2}{\exp(hv/kT) - 1} dv \quad 11$$

- Use the approximation for high temperatures

$$\exp\left(\frac{hv}{kT}\right) \approx 1 + \frac{hv}{kT} \quad 12$$

where $kT \gg hv$

$$E = \frac{6Nh}{v_D^2} \int_0^{v_D} \frac{v^2}{1 + hv/kT - 1} dv = \frac{6N}{v_D^2} \int_0^{v_D} kTv dv = \frac{6NkT}{v_D^2} \frac{v_D^2}{2}$$

$$E = 3NkT \quad 13$$

and

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V$$

$$\left(\frac{\partial E}{\partial T}\right)_V = 3Nk \quad 14$$

so that $C_V(T \rightarrow \infty) = 3Nk$

- These limiting values at high temperature are the same as is seen for 3-dimensional solids.
- We do the same for low temperatures. First use the following substitutions

$$x = \frac{hv}{kT} \wedge x_{\max} = \frac{hv_D}{kT} \wedge v_D = \frac{kq_D}{h}$$

Surface Heat Capacity: Theoretical (2)

- Find a substitute for variables

$$dv = \frac{kT}{h} \cdot dx \wedge v^2 = \frac{kT}{h} \cdot x^2 \wedge \mathbf{q}_D = \frac{v_D h}{k}$$

- Substitute into eq 11

$$E = \frac{6Nh}{v_D^2} \int_0^{x_{\max} v_D} \left(\frac{kT}{h}\right)^2 \frac{x^2}{e^x - 1} \cdot \left(\frac{kT}{h}\right) \cdot dx = \frac{6Nh}{v_D^2} \left(\frac{kT}{h}\right)^3 \int_0^{x_{\max} v_D} \frac{x^2}{e^x - 1} \cdot dx$$

$$E = \frac{6N}{\mathbf{q}_D^2} \cdot k \cdot T^3 \int_0^{x_{\max}} \frac{x^2}{e^x - 1} \cdot dx \quad 15$$

- It can be shown that $\int_0^{\infty} \frac{x^2}{e^x - 1} \cdot dx \approx 2.404$
- Substitution into eq 12

$$E \approx \frac{6 \cdot 2.404 \cdot Nk}{\mathbf{q}_D^2} \cdot T^3$$

$$E \approx \frac{14.4 \cdot N \cdot k}{\mathbf{q}_D^2} \cdot T^3 \quad 16$$

- Heat capacity is then determined

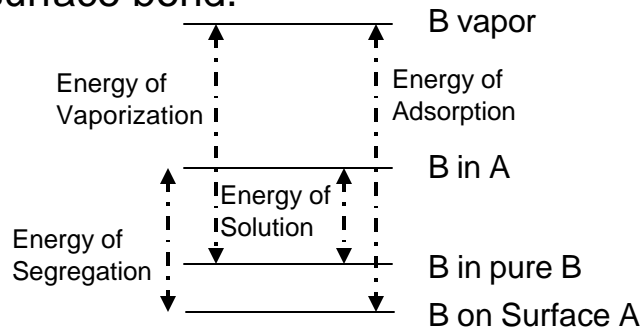
$$C_P^s \approx \left(\frac{\partial E}{\partial T}\right)_V \approx 3 \cdot \frac{14.4Nk}{\mathbf{q}_D^2} \cdot T^2$$

$$C_P^s \approx \left(\frac{\partial E}{\partial T}\right)_V \approx \frac{43.2Nk}{\mathbf{q}_D^2} \cdot T^2 \quad 17$$

- Thus at low temperature C_P^s is proportional to T^2 instead of T^3 as is the case in the bulk.

Surface Energy and Surface Composition of Two Component Systems

- A metal B dissolved in low concentrations in metal A will have a tendency to segregate to the surface of A, if it forms a strong surface bond.



- At all bulk concentrations of B, some of the B atoms will be at the surface of A as a result of the surface – bulk equilibrium.
 - Formation of a strong surface chemical bond between A and B, greatly enhances concentration of B.
 - Enhancement in concentration of B occurs when heat of desorption of B from the surface of A > heat of vaporization of pure B
 - If B atoms form weaker chemical bonds with A surface atoms compared to the bulk, B atoms will be repelled from the surface and the surface concentration; surface concentration will be less than predicted by bulk concentrations.
 - Strength of A – B bond strongly depends upon the reactivity of the surface, which strongly depends upon the crystal orientation.
- Concentration of B in the surface region is compared to its concentration in the bulk. The surface excess is

$$\Gamma_B = \frac{n_B}{a}$$

where n_B = number of moles of B in the surface above the number of moles in the bulk region what would contain the same number of moles of atoms as that part of the surface.

Surface Segregation in Binary Alloys

- Dilute binary system exhibiting ideal solution behavior

$$m_2^b = m_2^{0,b} + RT \ln x_2^b \quad 18$$

where m_2^b and $m_2^{0,b}$ are the chemical potentials of the second component in the bulk solution and pure component and x_2^b is mole fraction of the second component in the bulk.

- Since the mole fraction < 1 , the natural log term is negative and the chemical potential of this component in the bulk is less than in pure solid.
- Driving force of surface segregation is difference in bonding energies between the two metal atoms, A – B, compared to bonds, A – A and B – B, for the pure metals.
- Change in chemical bonding is also responsible to a change in surface tension in solution compared to the surfaces of the pure substances.
- At equilibrium chemical potentials of bulk and surface must be equal

$$m_2^b = m_2^s$$

$$m_2^{0,b} + RT \ln x_2^b = m_2^{0,s} + RT \ln x_2^s - g a_2 \quad 19$$

where a_2 = surface area covered by 1 mole of the component 2 of the binary system.

- For pure component 2 $x_2^b = x_2^s = 1$ and eq 19 produces:

$$m_2^{0,s} - m_2^{0,b} = g_2 a_2 \quad 20$$

- Substitute eq 20 into eq 19 and assume $a_1 = a_2 = a$

$$m_2^{0,s} - m_2^{0,b} = RT \ln x_2^b - RT \ln x_2^s + g a_2$$

$$g_2 a_2 =$$

$$g a = g_2 a - RT \ln x_2^b + RT \ln x_2^s \quad 21$$

Surface Segregation in Binary Alloy Systems (2)

Using the same logic for the first component

$$g_a = g_1 a - RT \ln x_1^b + RT \ln x_1^s \quad 22$$

- Combining 21 and 22 gives equation for the *monolayer ideal-solution model*.
$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \cdot \exp\left[\frac{(g_1 - g_2)a}{RT}\right] \quad 23$$

where γ_2 and γ_1 are surface tensions of pure 2 and 1.

- When $\gamma_2 < \gamma_1$, the surface fraction of 2 will be greater than 1. Component 2 will be concentrated on the surface.
- Whichever component has the lowest surface tension, will segregate to the surface.
- One way of determining the surface tension is from ΔH_{subl} ; a strong correlation exists between surface tension and ΔH_{subl} .
- As discussed earlier for metals, $\gamma_m \approx 0.16 \Delta H_{\text{subl}}$
- Substitute into 23 to get:

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \cdot \exp\left[\frac{0.16(\Delta H_{\text{subl}1} - \Delta H_{\text{subl}2})}{RT}\right] \quad 24$$

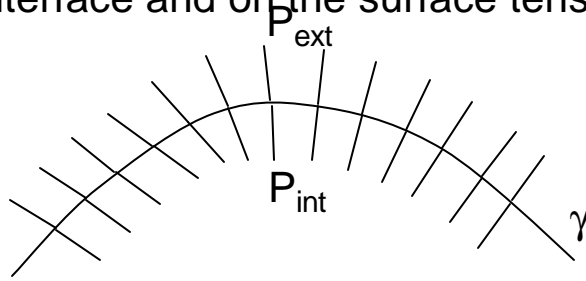
- Surface segregation is exponentially dependent upon the temperature.
- Many metal alloys not ideal solutions, because of finite ΔH_{mix} .
- When including this the ratio in Eq. 24 becomes

$$\frac{x_2^s}{x_1^s} = \frac{x_2^b}{x_1^b} \cdot \exp\left[\frac{a(g_1 - g_2)}{RT}\right] \cdot \exp\left[\frac{\Omega(l+m)}{RT} \left\{ (x_2^b)^2 - (x_1^b)^2 \right\} + \frac{\Omega l}{RT} \left\{ (x_2^s)^2 - (x_1^s)^2 \right\}\right] \quad 25$$

- l = fraction of nearest neighbors to an atom in the plane;
- m = fraction of nearest neighbors below the plane.
- Ω = regular solution parameter containing ΔH_{mix}

Curved Surfaces

- Solids and liquids tend to minimize their surface area to decrease the excess surface free energy.
- Liquids, equilibrium surface is curved and the radius of curvature depends upon the pressure difference on the two sides of the interface and on the surface tension.



- Let r = radius of surface; $V = \frac{4}{3}\pi r^3$
- The change in volume when the bubble changes size will be $dV = 4\pi r^2 dr$
- The force acting on the surface will be given by

$$4\pi r^2 (P_{int} - P_{ext}) dr$$

- Any change in pressure must be balanced by the surface energy $\gamma da = 8\pi r \gamma dr$ to give

$$4\pi r^2 (P_{int} - P_{ext}) dr = 8\pi r \gamma dr$$

$$(P_{int} - P_{ext}) = \frac{2\gamma}{r}$$

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- Pressure inside the bubble is greater than external pressure, because of surface tension.
- Smaller droplets large pressure difference possible (required).

Capillary Rise and Vapor Pressure of Curved Surfaces

- **Capillary Rise:** A liquid contained in a tube with a small radius develops a large pressure difference between internal and external pressures.

- liquid level rises up the tube until the hydrostatic pressure of the rising liquid column balances the internal pressure

$$\Delta P = \Delta \rho g h = \frac{2g}{r} \quad 27$$

where

- $\Delta \rho$ = density difference between liquid and gas phases,
- g = gravitational constant,
- h is the height of the capillary column.

- **Vapor pressure of curved surfaces:** vapor pressure of a droplet depends upon the radius of curvature, r .

- At equilibrium, pressure difference across the droplet is given by Eq. 26.
- Transferring molecules (atoms) for one phase (e.g. liquid phase) to the other is exactly matched by transferring molecules from the other phase to the liquid phase

$$(P_{\text{int}} - P_{\text{ext}}) = \frac{2g}{r} \quad 28$$

$$dP_{\text{int}} - dP_{\text{ext}} = d\left(\frac{2g}{r}\right)$$

- At constant temperature, the free-energy change accompanying transfer across the interface is

$$dG_{\text{int}} = \bar{V}_{\text{int}} dP_{\text{int}} \wedge dG_{\text{ext}} = \bar{V}_{\text{ext}} dP_{\text{ext}}$$

- At equilibrium free-energy changes are equal; leads to

$$\bar{V}_{\text{int}} dP_{\text{int}} = \bar{V}_{\text{ext}} dP_{\text{ext}}$$

$$dP_{\text{int}} = \frac{\bar{V}_{\text{ext}}}{\bar{V}_{\text{int}}} dP_{\text{ext}} \quad 29$$

Vapor Pressure of Curved Surfaces 2

- Substitute Eq 29 into Eq 28:

$$\frac{\bar{V}_{ext} - \bar{V}_{in}}{\bar{V}_{in}} dP_{ext} = d\left(\frac{2g}{r}\right) \quad 30$$

- But molar volume of gas is much larger than the molar volume of the liquid $\bar{V}_{ext} \gg \bar{V}_{in}$
- Assuming gas behaves ideally, molar volume is

$$\bar{V}_{ext} = \frac{RT}{P_{ext}}$$

- Substitute into Eq 30

$$\begin{aligned} \frac{RT}{P_{ext}} \cdot \frac{dP_{ext}}{\bar{V}_{in}} &= d\left(\frac{2g}{r}\right) \\ \frac{dP_{ext}}{P_{ext}} &= \frac{2g\bar{V}_{in}}{RT} d\left(\frac{1}{r}\right) \end{aligned} \quad 31$$

- Integrate 31 from zero curvature ($r = \infty$, $P = P_o$) to some other surface.

$$\begin{aligned} \int_{P_o}^P \frac{dP_{ext}}{P_{ext}} &= \frac{2g\bar{V}_{in}}{RT} \int_{\infty}^r d\left(\frac{1}{r}\right) \\ \ln\left(\frac{P_r}{P_o}\right) &= \frac{2g\bar{V}_{in}}{RT} \frac{1}{r} \end{aligned} \quad 32$$

- Eq 32 called the **Kelvin equation** gives the relationship between vapor pressure of a spherical particle and its size.
- Vapor pressure increases with decreases in particle size.