

CEN 207 Physical Chemistry

Text book:

Atkins' Physical Chemistry, Peter Atkins, Julio de Paula, James Keeler, 11th Edition, Oxford University Press.

Reference books

- . Physical Chemistry, [Robert J. Silbey](#), Robert A. Alberty, [Moungi G. Bawendi](#)
- . Physical Chemistry, Ira N. Levine

The Third Law of thermodynamics

At $T = 0$, all energy of thermal motion has been quenched, and in a perfect crystal all the atoms or ions are in a regular, uniform array. The localization of matter and the absence of thermal motion suggest that such materials also have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because $S = 0$ if there is only one way of arranging the molecules and only one microstate is accessible (the ground state).

The Nernst heat theorem: The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly crystalline.

Combining the First and Second Laws

The fundamental equation:

$$dU = dq + dw \rightarrow \text{for a reversible process; } dU = \overbrace{dq_{rev}}^{TdS} + \overbrace{dw_{rev}}^{-pdV}$$

$dU = TdS - pdV$ The fundamental equation $\rightarrow U = f(S, V)$,

dU can be expressed in terms of changes dS and dV by

$$dU = \overbrace{\left(\frac{\partial U}{\partial S}\right)_V}^T dS + \overbrace{\left(\frac{\partial U}{\partial V}\right)_S}^{-p} dV$$

The slope of plot of U against S at constant V $\left(\frac{\partial U}{\partial S}\right)_V = T$

The slope of plot of U against V at constant S $\left(\frac{\partial U}{\partial V}\right)_S = -p$

Combining the First and Second Laws

Maxwell Relations:

State function	Exact differential	Maxwell relation
U	$dU = TdS - pdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
H	$dH = TdS + Vdp$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
A	$dA = -pdV - SdT$	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
G	$dG = VdP - SdT$	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

The thermodynamic description of mixture

Partial molar property: The easiest partial molar property to visualise is the “partial molar volume”, the contribution that a component of a mixture makes to the volume of a sample.

a) Partial molar volume;

$$V_J = \left(\frac{\partial V}{\partial n_J} \right)_{p,T,\dot{n}}$$

\dot{n} : signifies that the amounts of all other substance present are constant

For a binary mixture (A, B), the total volume of the mixture changes by

$$dV = \overbrace{\left(\frac{\partial V}{\partial n_A} \right)_{p,T,n_B}}^{V_A} dn_A + \overbrace{\left(\frac{\partial V}{\partial n_B} \right)_{p,T,n_A}}^{V_B} dn_B$$

The thermodynamic description of mixture

(according to IUPAC, partial molar property is denoted by \bar{X})

$$dV = V_A dn_A + V_B dn_B$$

Integration of this equation

$$V = \int_0^{n_A} V_A dn_A + \int_0^{n_B} V_B dn_B = V_A \int_0^{n_A} dn_A + V_B \int_0^{n_B} dn_B = V_A n_A + V_B n_B$$