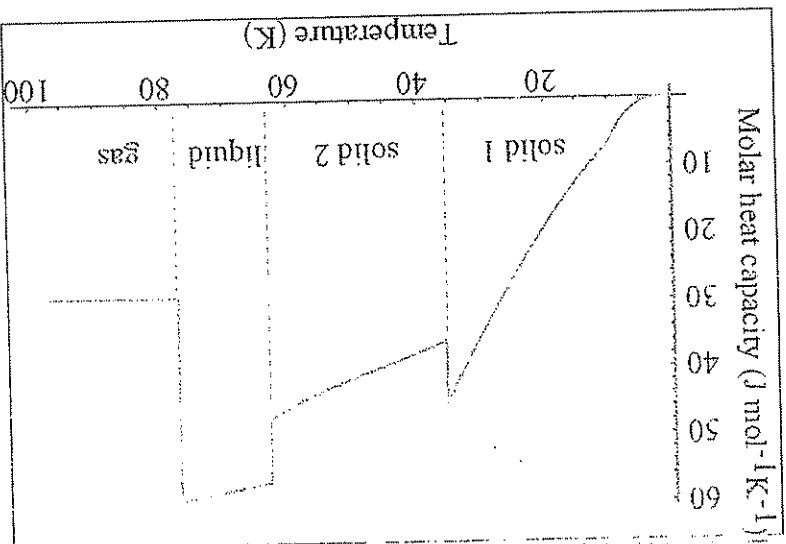


Absolute Entropies and the Third Law of

Thermodynamics

$$S_m(T) = S_m(0K) + \int_0^T \frac{C_{p,m}^{solid}}{T'} dT' + \frac{\Delta H_{fusion}}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}^{liquid}}{T'} dT' + \frac{\Delta H_{vaporization}}{T_b} + \int_{T_b}^T \frac{C_{p,m}^{gas}}{T'} dT'$$



Gibbs free energy at function of T.

If heat capacities are know from 0K we could -as we have seen- determine

http://wikis.lib.mcsu.edu/index.php/CH_431/Lecture_11

both enthalpy and entropy by integration:

$$S(T) = S(0) + \int_0^T \frac{C_p}{T'} dT'$$

$$H(T) = H(0) + \int_0^T C_p dT'$$

As we have seen we must be careful at phase transitions such as melting or vaporization. At these points the curves are *discontinuous* and the derivative C_p is undefined.

$$\begin{aligned} H(T) &= H(0) + \int_0^{T_{melt}} C_p(T)_{solid} dT + \Delta_{fusion} H + \int_{T_{melt}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta_{vap} H + etc. \\ S(T) &= S(0) + \int_0^{T_{melt}} \frac{C_p(T)_{solid}}{T'} dT + \Delta_{fusion} S + \int_{T_{melt}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T'} dT + \Delta_{vap} S + etc \\ S(T) &= S(0) + \int_0^{T_{melt}} \frac{C_p(T)_{solid}}{T'} dT + \frac{\Delta_{fusion} H}{T} + \int_{T_{melt}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T'} dT + \frac{\Delta_{vap} H}{T} + etc \\ H(0) &= \text{undefined} \\ S(0) &= 0 \text{ (third law)} \end{aligned}$$

We also discussed the fact that the third law allows us to define $S(0)$ as zero in most cases. For the enthalpy we cannot do that so that our curve is with respect to an undefined zero point. We really should plot $H(T) - H(0)$ and leave $H(0)$ undefined.

Because the Gibbs free energy $G = H - TS$ we can also construct a curve for G as a function of temperature, simply by combining the H and the S curve:

$$G(T) = H(T) - TS(T)$$

Interestingly, if we do so, the discontinuities at the phase transition points will drop out for G because at these points $\Delta_{fus} H = T_{fus} \Delta_{fus} S$.

G is always continuous

The Gibbs-Helmholtz expression

$$\frac{G}{T} = \frac{H}{T} - S$$

$$\left(\frac{\partial G/T}{\partial T} \right)_P = -\frac{H}{T^2} + \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P - \left(\frac{\partial S}{\partial T} \right)_P$$

$$\left(\frac{\partial G/T}{\partial T} \right)_P = -\frac{H}{T^2} + \frac{C_P}{T} - \frac{C_P}{T}$$

$$\left(\frac{\partial G/T}{\partial T} \right)_P = -\frac{H}{T^2}$$

$$\left(\frac{\partial \Delta G/T}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$

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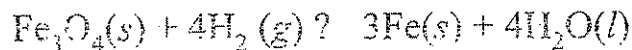
For step 3 we made use of the relationship between C_p and H and C_p and S

We said before that S is a first order derivative of G . As you can see from this derivation the enthalpy H is also a first order derivative, albeit not of G itself but of G/T .

The last step in the derivation simply takes the step before twice -say for the G and H at the begin and end of a *process*- and subtracts the two identical equations leading to a Δ symbol. In this differential form the Gibbs-Helmholtz equation can be applied to any process.

Entropy Changes in Chemical Reactions

$$\Delta S_R^\circ = \sum_i \nu_i S_i^\circ$$



$$\Delta S_{298.15}^\circ = 3S_{298.15}^\circ(\text{Fe}, s) + 4S_{298.15}^\circ(\text{H}_2\text{O}, l) - S_{298.15}^\circ(\text{Fe}_3\text{O}_4, s) - 4S_{298.15}^\circ(\text{H}_2, g)$$

To calculate reaction entropy at T other than standard, use

$$\Delta S_T^\circ = \Delta S_{298.15}^\circ + \int_{298.15}^T \frac{\Delta C_P^\circ}{T'} dT'$$