

6.4: The Gibbs-Helmholtz Equation

6.4.0.1: Ideal gas

For a mole of ideal gas we can use the gas law to integrate volume over pressure and we get

$$\Delta G_{molar} = RT \ln \left(\frac{P_2}{P_1} \right)$$

It is customary to identify one of the pressures (P_1) with the *standard state* of **1 bar** and use the plimsoll to indicate the fact that we are referring to a standard state by writing:

$$G_{molar}(P) = G_{molar}^o + RT \ln \left(\frac{P}{1} \right) = G_{molar}^o + RT \ln[P]$$

The fact that we are making the function intensive (per mole) is usually indicated by putting a bar over the G symbol, although this is often omitted for G_{molar}^o

6.4.0.1: Solids

For solids the volume does not change very much with pressure (the *isothermal compressibility* κ is small), so can assume it more or less constant:

$$G(P_{final}) = G(P_{initial}) + \int V dP (\text{from init to final}) \approx G(P_{initial}) + V \int dP (\text{from init to final}) = G(P_{initial}) + V \Delta P$$

6.4.1: The Gibbs-Helmholtz Expression

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

Take the derivative under constant pressure of each side to get

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

We make use of the relationship between C_p and H and C_p and S

$$\left(\frac{\partial G/T}{\partial T} \right)_P = -\frac{H}{T^2} + \frac{C_p}{T} - \frac{C_p}{T} \quad (6.4.1)$$

$$= -\frac{H}{T^2} \quad (6.4.2)$$

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 .

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

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.

6.4.2: Gibbs Energy as a Function of Temperature

If heat capacities are known from 0 K we could determine 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.

$$H(T) = H(0) + \int_0^{T_{fus}} C_p(T)_{solid} dT + \Delta H_{fus} + \int_{T_{fus}}^{T_{boil}} C_p(T)_{liquid} dT + \Delta H_{vap} + etc. \quad (6.4.3)$$

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \Delta S_{fus} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \Delta S_{vap} + etc. \quad (6.4.4)$$

$$= S(0) + \int_0^{T_{fus}} \frac{C_p(T)_{solid}}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{boil}} \frac{C_p(T)_{liquid}}{T} dT + \frac{\Delta H_{vap}}{T_{boil}} + etc. \quad (6.4.5)$$

with $H(T=0)$ = undefined and $S(T=0) = 0$ from the third law of thermodynamics.

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 curves (Equations 6.4.3 and 6.4.5):

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

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

The $H(0)$ problem does not disappear so that once again our curve is subject to an arbitrary offset in the y-direction. The best thing we can do is plot the quantity $G(T) - H(0)$ and leave the offset $H(0)$ undefined.

We have seen above that the derivative of G with temperature is $-S$. As entropy is always positive, this means that the G -curve is always *descending* with temperature. It also means that although the curve is *continuous* even at the phase transitions, the slope of the G curve is not, because the derivative $-S$ makes a jump there. Fig. 22.7 in the book shows an example of such a curve for benzene. Note the kinks in the curve at the mp and the boiling point.

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