6.6: Temperature Dependence of A and G

In differential form, the free energy functions can be expressed as

$$dA = -pdV - SdT$$

and

$$dG = -Vdp - SdT$$

So by inspection, it is easy to see that

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

and

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

And so, it should be fairly straightforward to determine how each changes with changing temperature:

$$\Delta A = -\int_{T_1}^{T_2} \left(\frac{\partial A}{\partial T}\right)_V dT = -\int_{T_1}^{T_2} S\,dT$$

and

$$\Delta G = -\int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_p dT = -\int_{T_1}^{T_2} S\,dT$$

But the temperature dependence of the entropy needed to be known in order to evaluate the integral. A convenient work-around can be obtained starting from the definitions of the free energy functions.

$$A = U - TS$$

and

$$G = H - TS$$

Dividing by T yields

$$\frac{A}{T} = \frac{U}{T} - S$$

and

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

Now differentiating each expression with respect to T at constant V or p respectively yields

$$\left(\frac{\partial \left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

and

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

Or differentiating with respect to $1/T$ provides a simpler form that is mathematically equivalent:

$$\left(\frac{\partial \left(\frac{A}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_V = U$$

and

$$\left(\frac{\partial \left(\frac{G}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_p = H$$

Focusing on the second expression (since all of the arguments apply to the first as well), we see a system that can be integrated. Multiplying both sides by $d(1/T)$ yields:

$$d \left(\frac{G}{T} \right) = H d \left(\frac{1}{T} \right)$$

Or for finite changes ΔG and ΔH:

$$d \left(\frac{\Delta G}{T} \right) = \Delta H d \left(\frac{1}{T} \right)$$

and integration, assuming the *enthalpy change is constant over the temperature* interval yields
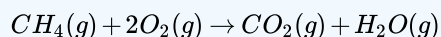
$$\int_{T_1}^{T_2} d \left(\frac{\Delta G}{T} \right) = \Delta H \int_{T_1}^{T_2} d \left(\frac{1}{T} \right)$$

$$\frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} = \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{6.6.1}$$

Equation ??? is the **Gibbs-Helmholtz equation** and can be used to determine how ΔG changes with changing temperature. The equivalent equation for the Helmholtz function is

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \tag{6.6.2}$$

> ✔ Example 6.6.1:
>
> Given the following data at 298 K, calculate ΔG at 500 K for the following reaction:
>
> $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(g)$$
>
> | Compound | ΔG_f^o (kJ/mol) | ΔH_f^o (kJ.mol) |
> |:---:|:---:|:---:|
> | CH$_4$(g) | -50.5 | -74.6 |
> | CO$_2$(g) | -394.4 | -393.5 |
> | H$_2$O(g) | -228.6 | -241.8 |
>
> **Solution**
> ΔH and $\Delta G_{298\,K}$ and can be calculated fairly easily. It will be assumed that ΔH is constant over the temperature range of 298 K – 500 K.
>
> $$\Delta H = (1\,mol)(-393.5\,kJ/mol) + (2\,mol)(-241.8\,kJ/mol) - (1\,mol)(-74.5\,kJ/mol) = -820.6\,kJ$$
>
> $$\Delta G_{298} = (1\,mol)(-394.4\,kJ/mol) + (2\,mol)(-228,6\,kJ/mol) - (1\,mol)(-50.5\,kJ/mol) = -801.1\,kJ$$
>
> So using Equation 6.6.1 with the data just calculated gives
>
> $$\frac{\Delta G_{500\,K}}{500\,K} - \frac{-801.1\,kJ}{298\,K} = (-820.6\,kJ) \left(\frac{1}{500\,K} - \frac{1}{298\,K} \right)$$

$$\Delta G_{500\ K} = -787.9\ kJ$$

Note: ΔG became a little bit less negative at the higher temperature, which is to be expected for a reaction which is exothermic. An increase in temperature should tend to make the reaction less favorable to the formation of products, which is exactly what is seen in this case!