

4.7: 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

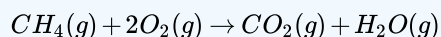
$$\begin{aligned} \int_{T_1}^{T_2} d \left(\frac{\Delta G}{T} \right) &= \Delta H \int_{T_1}^{T_2} d \left(\frac{1}{T} \right) \\ \frac{\Delta G_{T_2}}{T_2} - \frac{\Delta G_{T_1}}{T_1} &= \Delta H \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned} \quad (4.7.1)$$

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

$$\frac{\Delta A_{T_2}}{T_2} - \frac{\Delta A_{T_1}}{T_1} = \Delta U \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4.7.2)$$

✓ Example 4.7.1:

Given the following data at 298 K, calculate ΔG at 500 K for the following reaction:



Compound	ΔG_f° (kJ/mol)	ΔH_f° (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 $\Delta G_{298\text{ K}}$ and can be calculated fairly easily. It will be assumed that ΔH is constant over the temperature range of 298 K – 500 K.

$$\Delta H = (1 \text{ mol})(-393.5 \text{ kJ/mol}) + (2 \text{ mol})(-241.8 \text{ kJ/mol}) - (1 \text{ mol})(-74.5 \text{ kJ/mol}) = -820.6 \text{ kJ}$$

$$\Delta G_{298} = (1 \text{ mol})(-394.4 \text{ kJ/mol}) + (2 \text{ mol})(-228.6 \text{ kJ/mol}) - (1 \text{ mol})(-50.5 \text{ kJ/mol}) = -801.1 \text{ kJ}$$

So using Equation 4.7.1 with the data just calculated gives

$$\begin{aligned} \frac{\Delta G_{500\text{ K}}}{500\text{ K}} - \frac{-801.1 \text{ kJ}}{298\text{ K}} &= (-820.6 \text{ kJ}) \left(\frac{1}{500\text{ K}} - \frac{1}{298\text{ K}} \right) \\ \Delta G_{500\text{ K}} &= -787.9 \text{ kJ} \end{aligned}$$

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!

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