

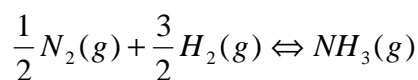
### Worked exercise Topic 4

Use the data presented in the following table to determine the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the chemical synthesis of one mol of ammonia from nitrogen and hydrogen at 298 K and 500 K.

	$\Delta H^\circ_{298}(\text{kcal/mol})$	$\Delta S^\circ_{298\text{K}}(\text{cal/mol}\cdot\text{K})$	$C_p(\text{cal/mol}\cdot\text{K})$
$\text{N}_2$	0.0	45.767	6.52
$\text{H}_2$	0.0	31.211	6.94
$\text{NH}_3$	-11.04	46.010	6.19

**Solution:**

The reaction is as follows



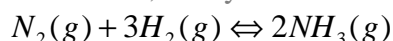
The data provided in the Table corresponds to the enthalpy and entropy of formation along with the constant pressure heat capacity. This last one must be an average value in the temperature range 298 K – 500 K.

Let us calculate firstly the thermodynamic functions at 298 K.

The reaction enthalpy of ammonia at 298 K for the reaction written above coincides with the enthalpy of formation given in the Table because in both cases 1 mol of ammonia is formed. Therefore:

$$\Delta H^\circ_{298} = -11040 \text{ cal.}$$

Sometimes, the synthesis of ammonia is written in an alternative way:



In this case, two moles of ammonia are formed so the reaction enthalpy must be  $\Delta H^\circ_{298} = -11040 \times 2 = -22080 \text{ cal.}$

To calculate the reaction entropy we must recall transparency 26.

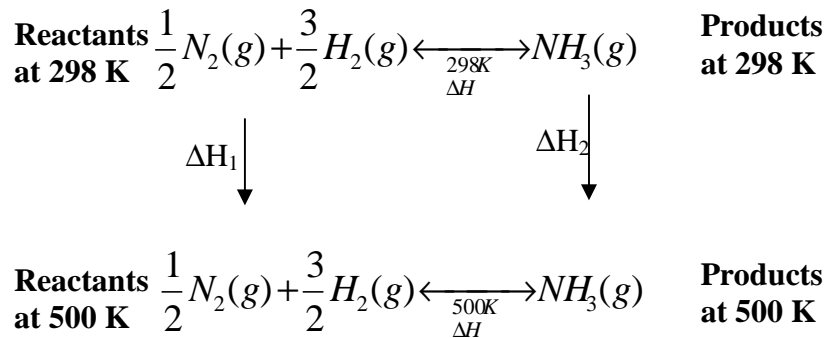
$$\Delta S^\circ_R = \Delta S^\circ_f(\text{NH}_3) - \frac{1}{2}\Delta S^\circ_f(\text{N}_2) - \frac{3}{2}\Delta S^\circ_f(\text{H}_2) = -23.69 \text{ cal / K}$$

For an equilibrium reaction the free energy change is given by (recall transparency 31)

$$\begin{aligned} \Delta G^\circ_{\text{reaction}} &= [\Delta H^\circ_f(\text{NH}_3) - T\Delta S^\circ_{\text{NH}_3}] - \left[ \frac{1}{2}(\Delta H^\circ_f(\text{N}_2) - T\Delta S^\circ_{\text{N}_2}) + \frac{3}{2}(\Delta H^\circ_f(\text{H}_2) - T\Delta S^\circ_{\text{H}_2}) \right] = \\ &= \Delta H^\circ_f(\text{NH}_3) - \frac{1}{2}\Delta H^\circ_f(\text{N}_2) - \frac{3}{2}\Delta H^\circ_f(\text{H}_2) - T[\Delta S^\circ_{\text{NH}_3} - \frac{1}{2}\Delta S^\circ_{\text{N}_2} - \frac{3}{2}\Delta S^\circ_{\text{H}_2}] = \Delta H^\circ_R - T\Delta S^\circ = \\ &= -11040 - 298 \times (-23.69) = -3977 \text{ cal} \end{aligned}$$

Now we will calculate thermodynamic properties at 500 K

We can draw the following overall scheme for the enthalpy.



We need to go from Reactants at 298 K to Products at 500 K. Let us calculate the reaction enthalpy change at 500 K.

We can establish the following equation.

$$\Delta H_1 + \Delta H_R^{500} = \Delta H_R^{298} + \Delta H_2 \quad \Delta H_R^{500} = \Delta H_R^{298} + \Delta H_2 - \Delta H_1$$

And recalling transparency 22

$$\Delta H_1 = \int_{T_1=298}^{T_1=500} \frac{1}{2} C_P(N_2) dT + \int_{T_1=298}^{T_1=500} \frac{3}{2} C_P(H_2) dT = 2761 \text{ cal}$$

$$\Delta H_1 = \int_{T_1=298}^{T_1=500} 1 C_P(NH_3) dT = 1250 \text{ cal}$$

$$\Delta H_R^{500} = -12551 \text{ cal}$$

Now we will proceed with the calculation of the entropy change at 500 K

$$\Delta S_R^{500} = \Delta S_f^{500}(NH_3) - \frac{1}{2} \Delta S_f^{500}(N_2) - \frac{3}{2} \Delta S_f^{500}(H_2)$$

We need to calculate the entropies of formation of both the reactants and the product at 500 K. Recalling transparencies 26 and 27 for a constant pressure process:

$$\Delta S_f^{500}(N_2) = \Delta S^{298}(N_2) + \int_{T_1=298}^{T_1=500} \frac{C_P(N_2) dT}{T} = C_P(N_2) \ln \frac{500}{298} = 49.1 \text{ cal / mol} \cdot K$$

$$\Delta S_f^{500}(NH_3) = \Delta S^{298}(NH_3) + \int_{T_1=298}^{T_1=500} \frac{C_P(NH_3) dT}{T} = C_P(NH_3) \ln \frac{500}{298} = 49.2 \text{ cal / mol} \cdot K$$

$$\Delta S_f^{500}(H_2) = \Delta S^{298}(H_2) + \int_{T_1=298}^{T_1=500} \frac{C_P(H_2) dT}{T} = C_P(H_2) \ln \frac{500}{298} = 34.8 \text{ cal / mol} \cdot K$$

$$\Delta S_R^{500} = 49.2 - \frac{3}{2} 34.8 - \frac{1}{2} 49.1 = -27.6 \text{ cal / K}$$

Finally we need to calculate reaction free energy change at 500 K

$$\Delta G_{reaction}^{500} = \Delta H_R^{500} - T\Delta S_R^{500} = -12551 - 500 \times (-27.6) = 1230 \text{ cal}$$

Note that at 500 K, the reaction free energy change is positive while at lower temperatures it was negative.