

## 4.4: Calculations of Enthalpies of Reaction at $T \neq 298$ K

Standard enthalpies of formation are usually reported at room temperature ( $T = 298$  K), but enthalpies of formation at any temperature  $T'$  can be calculated from the values at 298 K using eqs. (2.4) and (3.13):

$$\begin{aligned} dH &= C_P dT \rightarrow \int_{H_{T=298}^\ominus}^{H_{T'}^\ominus} dH = \int_{T=298}^{T'} C_P dT \\ H_{T'}^\ominus - H_{T=298}^\ominus &= \int_{T=298}^{T'} C_P dT \\ H_{T'}^\ominus &= H_{T=298}^\ominus + \int_{T=298}^{T'} C_P dT, \end{aligned} \quad (4.9)$$

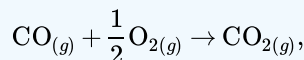
which, in conjunction with Hess's Law (Equation ???), results in:

$$\Delta_{\text{rxn}} H_{T'}^\ominus = \Delta_{\text{rxn}} H_{T=298}^\ominus + \int_{T=298}^{T'} \Delta C_P dT, \quad (4.10)$$

with  $\Delta C_P = \sum_i \nu_i C_{P,i}$ .

### ? Exercise 4.4.2

Calculate  $\Delta_{\text{rxn}} H$  of the following reaction at 398 K, knowing that  $\Delta_{\text{rxn}} H^\ominus$  at 298 K is -283.0 kJ/mol, and the following  $C_P$  values:  $\text{CO}_{(g)} = 29$  J/(mol K),  $\text{O}_{2(g)} = 30$  J/(mol K),  $\text{CO}_{2(g)} = 38$  J/(mol K):



#### Answer

Using Equation 4.10 we obtain:

$$\Delta_{\text{rxn}} H^{398} = \overbrace{-283.0}^{\Delta_{\text{rxn}} H^\ominus} + \int_{298}^{398} \left( \overbrace{38}^{C_P^{\text{CO}_2}} - \overbrace{29}^{C_P^{\text{CO}}} - \frac{1}{2} \overbrace{30}^{C_P^{\text{O}_2}} \right) \times 10^{-3} dT,$$

which, assuming that the heat capacities does not depend on the temperature, becomes:

$$\begin{aligned} \Delta_{\text{rxn}} H^{398} &= -283.0 + \left( 38 - 29 - \frac{1}{2} 30 \right) \times 10^{-3} (398 - 298) \\ &= -283.6 \text{ kJ/mol.} \end{aligned}$$

As we notice from this result, a difference in temperature of 100 K translates into a change in  $\Delta_{\text{rxn}} H^\ominus$  of this reaction of only 0.6 kJ/mol. This is a trend that is often observed, and values of  $\Delta_{\text{rxn}} H$  are very weakly dependent on changes in temperature for most chemical reactions. This numerical result can also be compared with the amount that is experimentally measured for  $\Delta_{\text{rxn}} H^{398}$  of this reaction, which is -283.67 kJ/mol. This comparison strongly supports the assumption that we used to solve the integral in Equation 4.10, confirming that the heat capacities are mostly independent of temperature.

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