

19.13: The Temperature Dependence of ΔH

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$$dH = C_p dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (19.13.1)$$

Equation 19.13.1 is often referred to as *Kirchhoff's Law*. If C_p is independent of temperature, then

$$\Delta H = C_p \Delta T \quad (19.13.2)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 19.13.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \quad (19.13.3)$$

After combining Equations 19.13.3 and 19.13.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) dT \quad (19.13.4)$$

Solving the definite integral yields

$$\Delta H = \left[aT + \frac{b}{2}T^2 - \frac{c}{T} \right]_{T_1}^{T_2} \quad (19.13.5)$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (19.13.6)$$

This expression can then be used with experimentally determined values of a , b , and c , some of which are shown in the following table.

Table 19.13.1: *Empirical Parameters for the temperature dependence of C_p*

Substance	a (J mol ⁻¹ K ⁻¹)	b (J mol ⁻¹ K ⁻²)	c (J mol ⁻¹ K)
C(gr)	16.86	4.77 x 10 ⁻³	-8.54 x 10 ⁵
CO ₂ (g)	44.22	8.79 x 10 ⁻³	-8.62 x 10 ⁵
H ₂ O(l)	75.29	0	0
N ₂ (g)	28.58	3.77 x 10 ⁻³	-5.0 x 10 ⁴
Pb(s)	22.13	1.172 x 10 ⁻²	9.6 x 10 ⁴

✓ Example 19.13.1: Heating Lead

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution

The enthalpy change is given by Equation 19.13.1 with a temperature dependence C_p given by Equation 19.13.3 using the parameters in Table 19.13.1. This results in the integral form (Equation 19.13.6):

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

when substituted with the relevant parameters of Pb(s) from Table 19.13.1

$$\begin{aligned}\Delta H &= (22.14 \frac{J}{mol K})(353 K - 273 K) \\ &\quad + \frac{1.172 \times 10^{-2} \frac{J}{mol K^2}}{2} ((353 K)^2 - (273 K)^2) \\ &\quad - 9.6 \times 10^4 \frac{J K}{mol} \left(\frac{1}{(353 K)} - \frac{1}{(273 K)} \right) \\ \Delta H &= 1770.4 \frac{J}{mol} + 295.5 \frac{J}{mol} + 470.5 \frac{J}{mol} \\ &= 2534.4 \frac{J}{mol}\end{aligned}$$

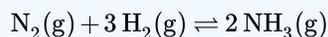
For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{rxn}(T_2) = \Delta H_{rxn}(T_1) + \int_{T_1}^{T_2} \Delta C_p \Delta T$$

✓ Example 19.13.2: Enthalpy of Formation

The enthalpy of formation of $\text{NH}_3(\text{g})$ is -46.11 kJ/mol at 25°C . Calculate the enthalpy of formation at 100°C .

Solution



with $\Delta H(298 \text{ K}) = -46.11 \text{ kJ/mol}$

Compound	C_p ($\text{J mol}^{-1} \text{K}^{-1}$)
$\text{N}_2(\text{g})$	29.12
$\text{H}_2(\text{g})$	28.82
$\text{NH}_3(\text{g})$	35.06

$$\begin{aligned}\Delta H(373 \text{ K}) &= \Delta H(298 \text{ K}) + \Delta C_p \Delta T \\ &= -46110 + \frac{J}{mol} \left[2 \left(35.06 \frac{J}{mol K} \right) - \left(29.12 \frac{J}{mol K} \right) - 3 \left(28.82 \frac{J}{mol K} \right) \right] (373 \text{ K} - 298 \text{ K}) \\ &= -49.5 \frac{kJ}{mol}\end{aligned}$$

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