

### 3.12: The Temperature Dependence of $\Delta H$

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  $T_2$

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad (3.12.1)$$

Equation 3.12.1 is often referred to as *Kirchhoff's Law*. If  $C_p$  is independent of temperature, then

$$\Delta H = C_p \Delta T \quad (3.12.2)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral in Equation 3.12.1. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$$C_p(T) = a + bT + \frac{c}{T^2} \quad (3.12.3)$$

After combining Equations 3.12.3 and 3.12.1, the enthalpy change for the temperature change can be found obtained by a simple integration

$$\Delta H = \int_{T_1}^{T_2} \left( a + bT + \frac{c}{T^2} \right) dT \quad (3.12.4)$$

Solving the definite integral yields

$$\Delta H = \left[ aT + \frac{b}{2}T^2 - \frac{c}{T} \right]_{T_1}^{T_2} \quad (3.12.5)$$

$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.12.6)$$

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 3.12.1: Empirical Parameters for the temperature dependence of  $C_p$

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

#### ✓ Example 3.12.1: 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 3.12.1 with a temperature dependence  $C_p$  given by Equation 3.12.3 using the parameters in Table 3.12.1. This results in the integral form (Equation 3.12.6):

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

when substituted with the relevant parameters of Pb(s) from Table 3.12.1

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

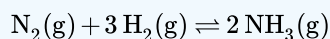
For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

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

### ✓ Example 3.12.2: Enthalpy of Formation

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

**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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