

Chapter 12

ENTHALPY OF FORMATION

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ABSTRACT

Results for enthalpy of formation are presented for major organic and inorganic chemicals. The major chemicals include many compound types. The results are provided in easy-to-use tabulations which are especially applicable for rapid engineering usage with the personal computer or hand calculator. The agreement of correlation and data is quite good.

INTRODUCTION

Enthalpy of formation for individual compounds in chemical reactions is required to determine the heat of reaction, $\Delta H_{\text{reaction}}$ and associated heating and cooling requirements:

$$\Delta H_{\text{reaction}} = \sum (n\Delta H_f)_{\text{products}} - \sum (n\Delta H_f)_{\text{reactants}} \quad (12-1)$$

If $\Delta H_{\text{reaction}} < 0$, then the chemical reaction is exothermic and cooling is needed to maintain reaction temperature. If $\Delta H_{\text{reaction}} > 0$, the reaction is endothermic and heating is required to conduct the chemical reaction. Since the heat effects of a reaction may be determined from the enthalpy of formation for individual compounds, results for enthalpy of formation are presented in this article for major chemicals.

CORRELATION FOR ENTHALPY OF FORMATION

The correlation for enthalpy of formation of the ideal gas is a series expansion in temperature:

$$\Delta H_f = A + B T + C T^2 \quad (12-2)$$

where ΔH_f = enthalpy of formation of ideal gas, kJoule/mol
A, B, C = regression coefficient for chemical compound
T = temperature, K

The results for enthalpy of formation are given in Tables 12-1 and 12-2. The tabulations are arranged by chemical formula to provide ease of use in quickly locating data. A wide variety of substances are covered.

In preparing the compilation, a literature search was conducted to identify data source publications for organics (1-40) and inorganics (1-60). The publications were screened for appropriate data. The compilation resulted from the screening.

For organics, the range for application is denoted by the respective minimum and maximum temperatures (TMIN and TMAX). In the absence of data, values at 298.15 K were extended to higher temperatures by integration of the appropriate thermodynamic equations involving heat capacities. The numerous data points were processed with a generalized least-square computer program for minimizing the deviation. The spot values at room temperature (298.15 K) are the actual data. The spot values at elevated temperature (500 K) are calculated from the correlation. Since water and hydrogen chloride are of major industrial importance, regression coefficients are provided for these compounds at the end of the table.

For inorganics, results are also given for internal energy of formation and entropy at room temperature (298.15 K). These thermodynamic properties are useful in computing the energy of a chemical explosion. As given by Crowl and Louvar (20), the equations for a chemical explosion involve the change in Helmholtz free energy which may be calculated from data for internal energy of formation and entropy:

$$\text{Explosion Energy}_{\text{limit}} = -\Delta A_{\text{reaction}} \quad (12-3)$$

$$\Delta A_{\text{reaction}} = \Delta U_{\text{reaction}} - T \Delta S_{\text{reaction}} \quad (12-4)$$

$$\Delta U_{\text{reaction}} = \sum (n\Delta U_f)_{\text{products}} - \sum (n\Delta U_f)_{\text{reactants}} \quad (12-5)$$

$$\Delta S_{\text{reaction}} = \sum (nS)_{\text{products}} - \sum (nS)_{\text{reactants}} - R \ln \sum (x_i \ln x_i)_{\text{products}} \quad (12-6)$$

The last term ($R \ln \sum x_i$) in the above equation represents the entropy of mixing. The R is the universal gas constant.

The actual energy release in a chemical explosion will be less than the limiting value given by the change in Helmholtz energy because of thermal effects and irreversibility. In an example in Crowl and Louvar (20), 12% of the limiting value is suggested for a vapor cloud explosion in a partially confined area (ethylene explosion in a ditch). For vapor cloud explosion in an unconfined area, 2% of the limiting value is suggested by the same authors.

A comparison of correlation and data is shown in Figure 12-1 for a representative chemical. The graph discloses favorable agreement of correlation and data.

EXAMPLES

The correlation results can be used to make calculations for enthalpy of formation and heat of reaction. Examples are given below.

Example 1 Let us estimate the enthalpy of formation of methane (CH_4) as a low-pressure gas at 500 K.

We obtain correlation constants (A , B , C) for methane from the table and substitute them into the equation at a temperature of 500 K to get:

$$\Delta H_f = -63.425 - 4.336 \times 10^{-2}(500) + 1.722 \times 10^{-5}(500^2)$$

$$\Delta H_f = -80.80 \text{ kJoule/mol}$$

Example 2 Calculate the heat of reaction for the dehydrogenation of 1-butene (C_4H_8) to 1,3 butadiene (C_4H_6) at a reaction temperature of 900 K:



The heat of reaction may be determined from enthalpy of formation at 900 K for the products and reactants:

$$\Delta H_{\text{reaction}} = \Delta H_{f,\text{C}_4\text{H}_6} + \Delta H_{f,\text{H}_2} - \Delta H_{f,\text{C}_4\text{H}_8}$$

Using coefficients for 1-butene and 1,3-butadiene from the table and the equation for enthalpy of formation, we obtain:

$$\Delta H_{f,\text{C}_4\text{H}_8} = 21.822 - 8.546 \times 10^{-2}(900) + 3.89 \times 10^{-5}(900^2) = -23.58$$

$$\Delta H_{f,\text{H}_2} = 0$$

$$\Delta H_{f,\text{C}_4\text{H}_6} = 123.286 - 5.123 \times 10^{-2}(900) + 2.319 \times 10^{-5}(900^2) = 95.97$$

Substitution of ΔH_f values at 900 K into the equation for heat of reaction yields:

$$\Delta H_{\text{reaction}} = 95.97 + 0 - (-23.58)$$

$$\Delta H_{\text{reaction}} = 119.55 \text{ kJoule/mol}$$

Since $\Delta H_{\text{reaction}} > 0$, the reaction is endothermic and would require heating to maintain the reaction temperature.

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