

Chapter 13

GIBBS ENERGY OF FORMATION

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ABSTRACT

Results for Gibbs energy 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 that are especially applicable for rapid engineering usage with the personal computer or hand calculator. The agreement of correlation and data is quite good.

INTRODUCTION

Gibbs energy of formation is important in the analysis of chemical reactions. Values for individual compounds (reactants and products) are required to determine the change in Gibbs energy for the reaction. This change is significant because of the associated chemical equilibrium for the reaction. If the change in Gibbs energy is negative, the thermodynamics for the reaction are favorable. On the other hand, if the change in Gibbs energy is highly positive, the thermodynamics for the reaction are not favorable.

The chemical equilibrium for a reaction is associated with the change in Gibbs free energy (ΔG_r) for the reaction:

$$\Delta G_{\text{reaction}} = \sum (n\Delta G_f)_{\text{products}} - \sum (n\Delta G_f)_{\text{reactants}} \quad (13-1)$$

1)

The changes in Gibbs energy for a reaction may be used in preliminary work to determine if a reaction is thermodynamically favorable at a given temperature. For thermodynamic equilibrium, the following rough criteria is useful for quick screening of chemical reactions:

$\Delta G_{\text{reaction}} < 0$ kjoule/mol.....reaction favorable

$0 < \Delta G_{\text{reaction}} < 50$ kjoule/mol.....reaction possibly favorable

$\Delta G_{\text{reaction}} > 50$ kjoule/mol.....reaction not favorable

CORRELATION FOR GIBBS ENERGY OF FORMATION

The correlation for Gibbs energy of formation is a series expansion in temperature:

$$\Delta G_f = A + B T + C T^2 \quad (13-2)$$

where

ΔG_f = Gibbs energy of formation of ideal gas, kjoule/mol

A, B, C = regression coefficients for chemical compound

T = temperature, K

The results for Gibbs energy of formation are given in Tables 13-1 and 13-2. 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 (1-37) and inorganics (1-61). 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 Helmholtz and entropy of formation at room temperature (298.15 K). These thermodynamic properties are useful in computing the energy of a chemical explosion.

The thermodynamic equations for computing the energy of a chemical explosion are given by Crowl and Louvar (35). The energy of a chemical explosion involves work of expansion ($dW = PdV$) resulting from the explosion. As the expansion occurs, this energy is transferred from the explosion. At

constant temperature, the change in Helmholtz energy ($dA = -PdV$) is related to such expansion work. Thus, it is convenient to utilize the change in Helmholtz energy to ascertain the energy of an explosion:

$$\text{Explosion Energy}_{\text{limit}} = -\Delta A_{\text{reaction}} \quad (13-3)$$

Since thermal effects and irreversibility are involved in an explosion, this equation represents a limiting or maximum value for the explosion energy.

For an explosion reaction, the change in Helmholtz energy maybe determined from Helmholtz energy of formation for the products and reactants according to equation given below:

$$\Delta A_{\text{reaction}} = \sum (n\Delta A_f)_{\text{products}} - \sum (n\Delta A_f)_{\text{reactants}} \quad (13-4)$$

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 (35), 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 calculated and data values is shown in Figure 14-1 for a representative chemical. The graph discloses favorable agreement of correlation and data.

EXAMPLES

The results can be used to make calculations for Gibbs energy of formation and the change in Gibbs energy for reaction. Examples are given below.

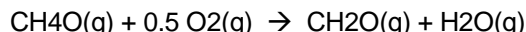
Example 1 Estimate the Gibbs free energy of formation of methane (CH₄) as a low-pressure gas at 500 K.

Correlation constants (A, B, C) for methane from the table are substituted into the equation at a temperature of 500 K:

$$\Delta G_f = -75.262 + 7.5925 \times 10^{-2}(500) + 1.8700 \times 10^{-5}(500^2)$$

$$\Delta G_f = -32.62 \text{ kJoule/mol}$$

Example 2 Calculate the change in Gibbs free energy for the reaction of methanol and oxygen to produce formaldehyde and water at reaction temperature of 600 K:



The change in Gibbs free energy of reaction may be determined from Gibbs free energy of formation for the products and reactants:

$$\Delta G_{\text{reaction}} = \Delta G_{f,\text{CH}_2\text{O}} + \Delta G_{f,\text{H}_2\text{O}} - \Delta G_{f,\text{CH}_4\text{O}} - 0.5 \Delta G_{f,\text{O}_2}$$

Using correlation constants from the table at temperature of 600 K, we obtain:

$$\Delta G_{f,\text{CH}_2\text{O}} = -115.972 + 1.663 \times 10^{-2}(600) + 1.138 \times 10^{-5}(600^2) = -101.90$$

$$\Delta G_{f,\text{H}_2\text{O}} = -241.740 + 4.174 \times 10^{-2}(600) + 7.428 \times 10^{-6}(600^2) = -214.02$$

$$\Delta G_{f,\text{CH}_4\text{O}} = -201.860 + 1.254 \times 10^{-1}(600) + 2.035 \times 10^{-5}(600^2) = -119.28$$

$$\Delta G_{f,\text{O}_2} = 0$$

Substitution of ΔG_f values into the equation for Gibbs free energy of the reaction yields:

$$\Delta G_{\text{reaction}} = -101.9 + (-214.02) - (-119.28) - 0$$

$$\Delta G_{\text{reaction}} = -196.64 \text{ kJoule/mol}$$

Since the change in Gibbs free energy for the reaction is negative, the thermodynamics for the reaction are favorable.

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REFERENCES – ORGANIC COMPOUNDS

1-37. See REFERENCES - ORGANIC COMPOUNDS in Chapter 11 ENTROPY AND ENTROPY OF FORMATION OF GAS

REFERENCES - INORGANIC COMPOUNDS

1-61. See REFERENCES - INORGANIC COMPOUNDS in Chapter 11 ENTROPY AND ENTROPY OF FORMATION OF GAS

