

A First Course on Kinetics and Reaction Engineering

Example 2.2

Problem Purpose

This problem illustrates how to calculate a heat of reaction using standard heat of combustion data. It also shows one way to handle the situation where one of the reagents undergoes a phase transition somewhere in the interval between 298 K and the temperature of interest.

Problem Statement

Generate an expression for the standard heat of the oxidative dehydrogenation of ethane to ethylene, reaction (1), as a function of temperature. Use that expression to calculate the standard heat of the reaction at 150 °C. In doing so, use tabulated standard heats of combustion at 298 K, and use heat capacity data from a different source than was used in Example 2.1.



Problem Solution

The heat of reaction at any temperature other than 298 K is usually calculated using equation (2) which assumes there are no phase changes for any of the species in the temperature range between 298 K and the desired temperature, T .

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{\substack{i=\text{all} \\ \text{species}}} \left(v_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right) \quad (2)$$

The stoichiometric coefficients are taken from the balanced equation for the reaction, keeping the sign convention in mind. The necessary heat capacities can be found in any number of places including thermodynamics handbooks and textbooks. They are often provided in the form of polynomial equations in T .

The standard heat of reaction at 298 K can be computed using either heats of formation or heats of combustion. Here the problem instructs us to use heats of combustion, and accordingly, equation (3) will be used.

$$\Delta H_j^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} (-\Delta H_{c,i}^0(298 \text{ K})) \quad (3)$$

Standard heats of combustion at 298 K can be found in thermodynamics handbooks and also in some textbooks. For present purposes, the data in Tables 1 and 2 were found in the text by Smith and Van Ness [1], and they correspond to combustion where the products are liquid H_2O and gaseous CO_2 . Noting that the product of reaction (1) is gaseous H_2O , the standard heat of vaporization will be needed, and Smith and Van Ness give a value of $10,519 \text{ cal mol}^{-1}$ for the standard heat of vaporization of liquid

water. The negative of this value is entered in Table 1 since that is the heat released when gaseous water is transformed to the standard state of liquid water.

Table 1. Standard heats of combustion from Smith and Van Ness [1].

Species, i	$\Delta H_{c,i}^0$ (298 K) (cal/mol)
C ₂ H ₆	-372,820
O ₂	0
C ₂ H ₄	-337,230
H ₂ O (g)	-10,519

Table 2. Specific molar heat capacities from Smith and Van Ness [1].

Heat Capacity (cal mol ⁻¹ K ⁻¹), $\hat{C}_{p,i} = \alpha_i + \beta_i T + \gamma_i T^2$, T in K			
Species, i	α_i	β_i	γ_i
C ₂ H ₆	2.247	38.201 x 10 ⁻³	-11.049 x 10 ⁻⁶
O ₂	6.148	3.102 x 10 ⁻³	-0.923 x 10 ⁻⁶
C ₂ H ₄	2.830	28.601 x 10 ⁻³	-8.726 x 10 ⁻⁶
H ₂ O (g)	7.256	2.298 x 10 ⁻³	0.283 x 10 ⁻⁶

Using the data in Table 1, equation (3) is used to find the standard heat of reaction (1) at 298 K.

$$\Delta H_j^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} (-\Delta H_{c,i}^0(298 \text{ K}))$$

$$\Delta H_1^0(298 \text{ K}) = -v_{\text{C}_2\text{H}_6,1} \Delta H_{c,\text{C}_2\text{H}_6}^0(298 \text{ K}) - v_{\text{O}_2,1} \Delta H_{c,\text{O}_2}^0(298 \text{ K}) \\ - v_{\text{C}_2\text{H}_4,1} \Delta H_{c,\text{C}_2\text{H}_4}^0(298 \text{ K}) - v_{\text{H}_2\text{O},1} \Delta H_{c,\text{H}_2\text{O}}^0(298 \text{ K})$$

$$\Delta H_1^0(298 \text{ K}) = -(-2)(-372,820 \text{ cal mol}^{-1}) - (-1)(0 \text{ cal mol}^{-1}) \\ - (2)(-337,230 \text{ cal mol}^{-1}) - (2)(-10,519 \text{ cal mol}^{-1})$$

$$\Delta H_1^0(298 \text{ K}) = -50,142 \text{ cal mol}^{-1}$$

The heat of reaction is then found by substitution in equation (2). Note that by adding in the latent heat of vaporization of water above, the heat of reaction at 298 K that we found is for the production of

gas phase water. As a result, we only need to heat the water from 298 K to the final temperature, and so we can use equation (2) directly. If we hadn't added that heat of vaporization, our standard heat at 298 K would be for the reaction producing liquid water. In that case, we would have needed to modify equation (2) appropriately. As it is, we need to use a fictitious heat capacity for water vapor, because at temperatures below 100 °C water is actually a liquid. The heat capacity being used here for water vapor can be applied at temperatures where water is actually a liquid, that is, the heat capacity we are using is a fictitious heat capacity.

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{\substack{i=\text{all} \\ \text{species}}} \left(\nu_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right)$$

$$\begin{aligned} \Delta H_1^0(T) = \Delta H_1^0(298 \text{ K}) &+ \left(\nu_{\text{C}_2\text{H}_6,1} \int_{298}^T \hat{C}_{p,\text{C}_2\text{H}_6} dT \right) + \left(\nu_{\text{O}_2,1} \int_{298}^T \hat{C}_{p,\text{O}_2} dT \right) \\ &+ \left(\nu_{\text{C}_2\text{H}_4,1} \int_{298}^T \hat{C}_{p,\text{C}_2\text{H}_4} dT \right) + \left(\nu_{\text{H}_2\text{O},1} \int_{298}^T \hat{C}_{p,\text{H}_2\text{O}} dT \right) \end{aligned}$$

$$\begin{aligned} \Delta H_1^0(T) = -50,142 \text{ cal mol}^{-1} \\ &+ (-2) \int_{298}^T (2.247 + 38.201 \times 10^{-3} T - 11.049 \times 10^{-6} T^2) dT \\ &+ (-1) \int_{298}^T (6.148 + 3.102 \times 10^{-3} T - 0.923 \times 10^{-6} T^2) dT \\ &+ (2) \int_{298}^T (2.830 + 28.601 \times 10^{-3} T - 8.726 \times 10^{-6} T^2) dT \\ &+ (2) \int_{298}^T (7.256 + 2.298 \times 10^{-3} T + 0.283 \times 10^{-6} T^2) dT \end{aligned}$$

$$\Delta H_1^0(T) = (-52,250 + 9.53T - 8.853 \times 10^{-3} T^2 + 2.045 \times 10^{-6} T^3) \text{ cal mol}^{-1}$$

This is the desired expression for the heat of reaction as a function of temperature. Substitution of $T = 150 \text{ }^\circ\text{C}$ (423 K) shows that the heat of reaction is $-49,650 \text{ cal mol}^{-1}$ at 150°C .

Let's return to the standard heat of reaction at 298 K and suppose we hadn't included the heat of vaporization of water. In that case, we would have needed to modify equation (2) to account for the phase change upon heating from 298 K to the temperature T . Only the term accounting for the sensible heat of water would need to be modified. If we assume that T is greater than $100 \text{ }^\circ\text{C}$ (373 K), then one way to

modify equation (2) would be to replace the term $\left(\nu_{\text{H}_2\text{O},1} \int_{298}^T \hat{C}_{p,\text{H}_2\text{O}} dT \right)$ with three terms corresponding to

heating liquid water from 298 K to 373 K (its normal boiling point), the latent heat of vaporization at the normal boiling point and the heating of the resulting water vapor from 373 K to the temperature T :

$$v_{H_2O,l} \left(\int_{298}^{373K} \hat{C}_{p,H_2O(l)} dT + \Delta H_{vap,H_2O}^0(373\text{ K}) + \int_{373K}^T \hat{C}_{p,H_2O(v)} dT \right)$$

Calculation Details Using MATLAB

As was the case for Example 2.1, the calculations described in this solution are quite easy to perform manually, but they can equally well be performed numerically. Listing 1 shows a MATLAB function named `Example_2_2` that performs all the calculations. A copy of this file accompanies this solution as `Example_2_2.m`. It must be invoked with the temperature in °C as its only argument. The code is relatively straightforward and similar to the code used for the calculations in Example 2.1.

Execution of the function using a temperature of 150 °C as the input argument generates the output shown in Listing 2.

```
function h_T = Example_2_2(T)
% index key: 1 = ethane, 2 = oxygen, 3 = ethylene, 4 = water
% T in K

% Stoichiometric coefficients
nu = [-2
      -1
       2
       2];

% Expressions for the heat capacities in cal/mol-K as cell array
of
% anonymous functions; x is the temperature in K
Cp = {@(x) (2.247 + 38.201e-3*x - 11.049e-6*x.^2);
      @(x) (6.148 + 3.102e-3*x - 0.923e-6*x.^2);
      @(x) (2.830 + 28.601e-3*x - 8.726e-6*x.^2);
      @(x) (7.256 + 2.298e-3*x + 0.283e-6*x.^2);
      };

% Standard heats of combustion at 298 K in cal/mol; products are
CO2(g)
% and H2O (l)
hc = [-372820.
      0
      -337230.
      -10519.];

% Standard heat of reaction at 298 K in kcal/mol
h_298 = -transpose(nu)*hc/1000;

% Sensible heat in cal/mol
h_s = 0.;
for i=1:length(nu)
    h_s = h_s + nu(i)*integral(Cp{i},298.,T);
end

% Standard heat of reaction at T in kcal/mol
h_T = h_298 + h_s/1000.;

end % of Example_2_2
```

Listing 1. MATLAB function that performs the calculations described in this solution.

```
>> Example_2_2(150)
ans =
-51.0127
```

Listing 2. Output generated by the MATLAB function shown in Listing 1.

Reference Cited

1. Smith, J.M. and H.C.V. Ness, *Introduction to Chemical Engineering Thermodynamics*. 2nd Ed. ed. 1959, New York: McGraw-Hill.