

# A First Course on Kinetics and Reaction Engineering

## Example 2.1

### Problem Purpose

This problem illustrates how to calculate a heat of reaction using standard heat of formation data.

### Problem Statement

Calculate the standard heat of reaction at 150 °C for the oxidative dehydrogenation of ethane to ethylene, reaction (1). In doing so, use tabulated values of the standard heat of formation at 298 K.



### 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 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 formation, and accordingly, equation (3) will be used.

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

Standard heats of formation 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 Felder and Rousseau's text [1].

Table 1. Standard heats of formation from Felder and Rousseau [1].

Species, $i$	$\Delta H_{f,i}^0$ (298 K) (kJ/mol)
C <sub>2</sub> H <sub>6</sub>	-84.67
O <sub>2</sub>	0
C <sub>2</sub> H <sub>4</sub>	52.28
H <sub>2</sub> O (g)	-241.83

Table 2. Specific molar heat capacities from Felder and Rousseau [1].

Heat Capacity (kJ mol <sup>-1</sup> K <sup>-1</sup> ), $\hat{C}_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3$ , $T$ in °C				
Species, $i$	$a_i$	$b_i$	$c_i$	$d_i$
C <sub>2</sub> H <sub>6</sub>	49.37	13.92 x 10 <sup>-2</sup>	-5.816 x 10 <sup>-5</sup>	7.28 x 10 <sup>-9</sup>
O <sub>2</sub>	29.1	1.158 x 10 <sup>-2</sup>	-0.6076 x 10 <sup>-5</sup>	1.311 x 10 <sup>-9</sup>
C <sub>2</sub> H <sub>4</sub>	40.75	11.47 x 10 <sup>-2</sup>	-6.891 x 10 <sup>-5</sup>	17.66 x 10 <sup>-9</sup>
H <sub>2</sub> O (g)	33.46	0.688 x 10 <sup>-2</sup>	0.7604 x 10 <sup>-5</sup>	-3.593 x 10 <sup>-9</sup>

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

$$\Delta H_1^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,1} \Delta H_{f,i}^0(298 \text{ K})$$

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

$$\Delta H_1^0(298 \text{ K}) = (-2)(-84.67 \text{ kJ mol}^{-1}) + (-1)(0 \text{ kJ mol}^{-1}) \\ + (2)(52.28 \text{ kJ mol}^{-1}) + (2)(-241.83 \text{ kJ mol}^{-1})$$

$$\Delta H_1^0(298 \text{ K}) = -209.76 \text{ kJ mol}^{-1}$$

Since the heat capacity data from Felder and Rousseau require  $T$  in °C, equation (2) must be modified slightly to calculate  $\Delta H_1^0(T)$ . Specifically, the limits of integration must be changed. Also, since the heat capacities are in Joules, the heat of reaction at 298 K must be converted from kJ mol<sup>-1</sup> to J mol<sup>-1</sup>.

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{\substack{i=\text{all} \\ \text{species}}} \left( \nu_{i,j} \int_{25}^T \hat{C}_{p,i} dT \right)$$

$$\begin{aligned} \Delta H_1^0(T) = \Delta H_1^0(298 \text{ K}) &+ \left( \nu_{C_2H_6,1} \int_{25}^T \hat{C}_{p,C_2H_6} dT \right) + \left( \nu_{O_2,1} \int_{25}^T \hat{C}_{p,O_2} dT \right) \\ &+ \left( \nu_{C_2H_4,1} \int_{25}^T \hat{C}_{p,C_2H_4} dT \right) + \left( \nu_{H_2O,1} \int_{25}^T \hat{C}_{p,H_2O} dT \right) \end{aligned}$$

$$\begin{aligned} \Delta H_1^0(T) = -209.76 \text{ kJ mol}^{-1} &\left( \frac{1000 \text{ J}}{\text{kJ}} \right) \\ &+ (-2) \int_{25}^T (49.37 + 13.92 \times 10^{-2} T - 5.816 \times 10^{-5} T^2 + 7.28 \times 10^{-9} T^3) dT \\ &+ (-1) \int_{25}^T (29.1 + 1.158 \times 10^{-2} T - 0.6076 \times 10^{-5} T^2 + 1.311 \times 10^{-9} T^3) dT \\ &+ (2) \int_{25}^T (40.75 + 11.47 \times 10^{-2} T - 6.891 \times 10^{-5} T^2 + 17.66 \times 10^{-9} T^3) dT \\ &+ (2) \int_{25}^T (33.46 + 0.688 \times 10^{-2} T + 0.7604 \times 10^{-5} T^2 - 3.593 \times 10^{-9} T^3) dT \end{aligned}$$

$$\Delta H_1^0(150 \text{ }^\circ\text{C}) = -207700 \text{ J mol}^{-1} = -207.7 \text{ kJ mol}^{-1}$$

### Calculation Details Using MATLAB

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\_1 that performs all the calculations. A copy of this file accompanies this solution as Example\_2\_1.m. It must be invoked with the temperature in °C as its only argument. The code is relatively straightforward. One point to note is that the heat capacities must be defined using a dummy variable in place of the temperature.

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_1(T)
% index key: 1 = ethane, 2 = oxygen, 3 = ethylene, 4 = water
% T in degrees C

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

% Expressions for the heat capacities in J/mol-C as cell array
of
% anonymous functions; x is the temperature in degrees C
Cp = {@(x) (49.37 + 13.92e-2*x - 5.816e-5*x.^2 + 7.28e-9*x.^3);
      @(x) (29.1 + 1.158e-2*x - 0.6076e-5*x.^2 + 1.311e-9*x.^3);
      @(x) (40.75 + 11.47e-2*x - 6.891e-5*x.^2 + 17.66e-9*x.^3);
      @(x) (33.46 + 0.688e-2*x + 0.7604e-5*x.^2 - 3.593e-9*x.^3);
      };

% Standard heats of formation at 298 K in kJ/mol
hf = [-84.67
      0
      52.28
      -241.83];

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

% Sensible heat
h_s = 0.;
for i=1:length(nu)
    h_s = h_s + nu(i)*integral(Cp{i},25.,T);
end

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

end % of Example_2_1
```

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

```
>> Example_2_1(150)
ans =
-2.0770e+05
```

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

### Reference Cited

1. R. M. Felder and R. W. Rousseau, "Elementary Principles of Chemical Processes," 2<sup>nd</sup> ed. 1986, New York: John Wiley & Sons.