

A First Course on Kinetics and Reaction Engineering

Example 3.1

Problem Purpose

This example illustrates the calculation of an equilibrium constant as a function of temperature.

Problem Statement

Methanol can be synthesized in the vapor phase from carbon monoxide and hydrogen according to reaction (1). The heat capacity of a species i , $\hat{C}_{p,i}$, can be calculated using equation (2) where t is equal to the temperature in Kelvin divided by 1000 and A_i through E_i are constants. Values for the constants for species of interest (in the gas phase) are provided in the table below along with values for their standard heats of formation at 298 K, $\Delta H_{f,i}^0(298 \text{ K})$, standard Gibbs free energies of formation, $\Delta G_{f,i}^0(298 \text{ K})$, and standard entropies, S_i^0 . With the constants given below, the resulting heat capacities will have units of $\text{J mol}^{-1} \text{K}^{-1}$. The heats of formation and the free energies are given in the table in kJ mol^{-1} and the standard entropies are in units of $\text{J mol}^{-1} \text{K}^{-1}$. Using the data given in the table below, generate an expression for the equilibrium constant of reaction (1) as a function of temperature and calculate its value at 500, 550 and 600 K.



$$\hat{C}_{p,i} = A_i + B_i t + C_i t^2 + D_i t^3 + \frac{E_i}{t^2} \quad (2)$$

i	CO	CO ₂	H ₂	CH ₃ OH
A_i	25.567590	24.997350	33.107800	21.138073
B_i	6.096130	55.186960	-11.508000	70.878654
C_i	4.054656	-33.691370	11.609300	25.853554
D_i	-2.671301	7.948387	-2.844400	-28.497905
E_i	0.131021	-0.136638	-0.159665	0.0
$\Delta H_{f,i}^0(298 \text{ K})$	-110.53	-393.52	0.0	-201.0
$\Delta G_{f,i}^0(298 \text{ K})$	-137.3689	-394.64777	0.0	-162.6153
S_i^0	197.6482155	213.7689511	130.6656268	239.7234884

Problem Solution

The equilibrium constant at temperature T is found using equation (3).

$$K_1(T) = K_1(298 \text{ K}) \exp \left\{ \int_{298 \text{ K}}^T \frac{\Delta H_1^0(T)}{RT^2} dT \right\} \quad (3)$$

The heat of reaction that appears in equation (3) (in J mol^{-1}) at temperature T is found using equations (4) and (5), following the procedure described in Unit 2. The result is given in equation (6).

$$\Delta H_j^0(298 \text{ K}) = \sum_{i=1}^{N_{\text{species}}} (v_{i,j} \Delta H_{f,i}^0(298 \text{ K})) \quad (4)$$

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{i=1}^{N_{\text{species}}} \left(v_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right) \quad (5)$$

$$\begin{aligned} \Delta H_1^0(T) = & -72632 - 70.645117T + 0.043899T^2 - 4.73234 \times 10^{-7}T^3 \\ & - 5.03445 \times 10^{-9}T^4 - \frac{188309}{T} \end{aligned} \quad (6)$$

The equilibrium constant at 298 K that appears in equation (3) is found using equation (7).

$$K_1(298 \text{ K}) = \exp\left(\frac{-\Delta G_1^0(298 \text{ K})}{R(298 \text{ K})}\right) \quad (7)$$

As discussed in Unit 2, the Gibbs free energy change at 298 K appearing in equation (7) can be found from the Gibbs free energies of formation and the stoichiometric coefficients using equation (8).

$$\begin{aligned} \Delta G_j^0(298 \text{ K}) &= \sum_{i=1}^{N_{\text{species}}} (v_{i,j} \Delta G_{f,i}^0(298 \text{ K})) \\ \Delta G_1^0(298 \text{ K}) &= v_{\text{CO},1} \Delta G_{f,\text{CO}}^0(298 \text{ K}) + v_{\text{H}_2,1} \Delta G_{f,\text{H}_2}^0(298 \text{ K}) \\ &+ v_{\text{CH}_3\text{OH},1} \Delta G_{f,\text{CH}_3\text{OH}}^0(298 \text{ K}) \end{aligned} \quad (8)$$

Substitution of the stoichiometric coefficients and free energies of formation given in the problem statement allows the calculation of the free energy change for the reaction and then the equilibrium constant at 298 K.

$$\Delta G_1^0(298 \text{ K}) = [(-1)(-137.3689) + (-2)(0.0) + (1)(-162.6153)] \text{ kJ mol}^{-1}$$

$$\Delta G_1^0(298 \text{ K}) = -25.2464 \text{ kJ mol}^{-1}$$

$$K_1(298 \text{ K}) = \exp\left(\frac{-(-25.2464)}{(8.3144 \times 10^{-3})(298 \text{ K})}\right)$$

$$K_1(298 \text{ K}) = 26621.8$$

The value of the equilibrium constant at 298 K and the expression for the heat of the reaction as a function of temperature, equation (6) are then substituted into equation (3). After integration and simplification an expression for the equilibrium constant as a function of temperature results, equation (9).

$$K_1(T) = 26621.8 \exp \left\{ \int_{298 \text{ K}}^T \frac{\left[-72632 - 70.645117T + 0.043899T^2 - 4.73234 \times 10^{-7}T^3 \right] - 5.03445 \times 10^{-9}T^4 - \frac{188309}{T}}{RT^2} dT \right\}$$

$$K_1(T) = 26621.8 \exp \left(\begin{array}{l} 17.399 - 8.4967 \ln(T) + 5.2799 \times 10^{-3}T \\ -2.8459 \times 10^{-8}T^2 - 2.0184 \times 10^{-10}T^3 \\ + \frac{8735.7}{T} + \frac{11324}{T^2} \end{array} \right) \quad (9)$$

Evaluation at the three specified temperatures gives the following values for the equilibrium coefficient:

$$K_1(500 \text{ K}) = 6.153 \times 10^{-3}$$

$$K_1(550 \text{ K}) = 7.154 \times 10^{-4}$$

$$K_1(600 \text{ K}) = 1.163 \times 10^{-4}$$

Calculation Details Using MATLAB

It is quite easy to solve the equations encountered in this problem analytically with nothing more than a calculator, but they can equally well be performed numerically. Listing 1 shows the main body of a MATLAB function named Example_3_1 that performs all the calculations. Listing 2 shows two internal functions that are defined within the function Example_3_1. A copy of this file accompanies this solution as Example_3_1.m. The code is relatively straightforward; the only “tricky” part is handling the integral within an integral in the first form of equation (9). In order to do so, it is necessary to define a separate function (named fun in Listing 2) that is equal to the heat of reaction divided by the temperature squared that in turn calls a function (named hr in Listing 2) that calculates the heat of reaction.

Execution of the function using a temperature of 150 °C as the input argument generates the output shown in Listing 3.

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```

% MATLAB file used to solve Example 3.1 from "A First Course on Kinetics
% and Reaction Engineering."
function Example_3_1
    % Data given in the problem statement, converted to units of J, mol and
    % K
    r_gas = 8.3144;
    % stoichiometric coefficients (1 = CO, 2 = H2 and 3 = MeOH)
    nu = [-1
          -2
           1];
    % heats of formation at 298 K
    hf = [-110530
          0
          -201000];
    % free energies of formation at 298 K
    gf = [-137368.9
          0
          -162615.3];
    % heat capacity constants
    A_co = 25.567590;
    A_h2 = 33.1078;
    A_meoh = 21.138073;
    B_co = 6.096130;
    B_h2 = -11.508;
    B_meoh = 70.878654;
    C_co = 4.054656;
    C_h2 = 11.6093;
    C_meoh = 25.853554;
    D_co = -2.671301;
    D_h2 = -2.8444;
    D_meoh = -28.497905;
    E_co = 0.131021;
    E_h2 = -0.159665;
    E_meoh = 0;

    % Expressions for the heat capacities as a cell array of
    % anonymous functions; x is the temperature in K
    Cp = {@(x) (A_co + B_co*x/1000 + C_co*(x/1000).^2 + D_co*(x/1000).^3 +
              E_co./(x/1000).^2);
          @(x) (A_h2 + B_h2*(x/1000) + C_h2*(x/1000).^2 + D_h2*(x/1000).^3 +
              E_h2./(x/1000).^2);
          @(x) (A_meoh + B_meoh*(x/1000) + C_meoh*(x/1000).^2 + D_meoh*(x/1000).^3
              + E_meoh./(x/1000).^2);
          };

    % Calculate the standard heat and free energy of reaction at 298 K
    h_298 = transpose(nu)*hf;
    g_298 = transpose(nu)*gf;

    % Calculate the equilibrium constant at 298 K
    K_298 = exp(-g_298/r_gas/298.);

    % Calculate the equilibrium constant at the three specified
    % temperatures using the two internal functions defined below to
    % calculate the heat of reaction at temperature T and the equilibrium
    % constant at temperature T
    K_500 = K_eq(500)
    K_550 = K_eq(550)
    K_600 = K_eq(600)

```

Listing 1. Main body of a MATLAB function that performs the calculations described in this solution.

```

% Internal function that numerically calculates the heats of reaction
% at temperatures in the vector T
function h_T = hr(T)
    h_T = zeros(1,length(T));
    for j=1:length(T)
        % Sensible heat
        h_s = 0.;
        for i=1:length(nu)
            h_s = h_s + nu(i)*integral(Cp{i},298.,T(j));
        end

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

% Internal function that numerically calculates the equilibrium
% constant at temperature T
function K_T = K_eq(T)
    fun = @(x) (hr(x)/r_gas./x./x);
    integr = integral(fun,298.,T);
    K_T = K_298*exp(integr);
end
end

```

Listing 2. Two internal functions called by the code shown in Listing 1.

```

>> Example_3_1

K_500 =
    0.0062

K_550 =
    7.1537e-04

K_600 =
    1.1631e-04

```

Listing 3. Output generated by the MATLAB function shown in Listing 1.