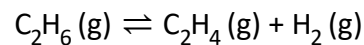


Catalytic Cracking of Ethane

▼ Introduction

Ethylene and hydrogen are generated by a steam cracker using ethane as a feedstock.



The feed is 4 mol of H_2O to 1 mol of ethane, with the cracker operating at 1.01 bar and 1000 K. The products contain CH_4 , C_2H_4 , C_2H_2 , CO_2 , CO , O_2 , H_2 , H_2O , and C_2H_6 in the molar amounts n_1 to n_9 .

	Species	In Feed	In Product
1	CH_4		n_1
2	C_2H_4		n_2
3	C_2H_2		n_3
4	CO_2		n_4
5	CO		n_5
6	O_2		n_6
7	H_2		n_7
8	H_2O	4	n_8
9	C_2H_6	1	n_9

This application calculates the composition of the reaction products by

- calculating the Gibbs energy of formation of the individual species in the products,

employing data from the [ThermophysicalData:-Chemicals](#) package

- constructing a function that describes Gibbs Energy of the products as a function of product composition
- and minimizing the Gibbs Energy of the products, subject to constraints.

```
> restart:
with(ThermophysicalData:-Chemicals):
with(Optimization):

> temp := 1000 * Unit(K):
R      := 8.314 * Unit(J/mol/K):
```

▼ Physical Properties

Enthalpies

```
> h_CH4 := Property("Hmolar", "CH4", temperature =
temp):
h_C     := Property("Hmolar", "C(gr)", temperature =
temp):
h_H2    := Property("Hmolar", "H2", temperature =
temp):
h_H2O   := Property("Hmolar", "H2O", temperature =
temp):
h_O2    := Property("Hmolar", "O2", temperature =
temp):
h_CO    := Property("Hmolar", "CO", temperature =
temp):
h_CO2   := Property("Hmolar", "CO2", temperature =
temp):
h_C2H4  := Property("Hmolar", "C2H4", temperature =
temp):
h_C2H2  := Property("Hmolar", "C2H2,acetylene", temperature =
temp):
h_C2H6  := Property("Hmolar", "C2H6", temperature =
temp):
```

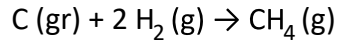
Entropies

```
> s_CH4 := Property("Smolar", "CH4", temperature =
temp):
s_C     := Property("Smolar", "C(gr)", temperature =
temp):
s_H2    := Property("Smolar", "H2", temperature =
temp):
s_H2O   := Property("Smolar", "H2O", temperature =
temp):
s_O2    := Property("Smolar", "O2", temperature =
temp):
s_CO    := Property("Smolar", "CO", temperature =
temp):
s_C     := Property("Smolar", "C(gr)", temperature =
temp):
s_CO2   := Property("Smolar", "CO2", temperature =
temp):
s_C2H4  := Property("Smolar", "C2H4", temperature =
```

```
temp):
s_C2H2 := Property("Smolar", "C2H2,acetylene", temperature =
temp):
s_C2H6 := Property("Smolar", "C2H6", temperature =
temp):
```

▼ Gibbs energy of formation

▼ CH₄



Enthalpy change

$$\begin{aligned} > \text{DeltaH} := 1 * \text{Unit}(\text{mol}) * h_{\text{CH4}} - (1 * \text{Unit}(\text{mol}) * h_{\text{C}} + 2 * \text{Unit}(\text{mol}) * \\ & \quad h_{\text{H2}}) \\ & \qquad \qquad \qquad -89.07 \text{ kJ} \end{aligned} \quad (3.1.1)$$

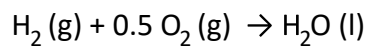
Entropy change

$$\begin{aligned} > \text{DeltaS} := 1 * \text{Unit}(\text{mol}) * s_{\text{CH4}} - (1 * \text{Unit}(\text{mol}) * s_{\text{C}} + 2 * \text{Unit}(\text{mol}) * \\ & \quad s_{\text{H2}}) \\ & \qquad \qquad \qquad -108.55 \frac{\text{J}}{\text{K}} \end{aligned} \quad (3.1.2)$$

Gibbs energy of formation

$$\begin{aligned} > \text{DeltaG}_{\text{CH4}} := \text{DeltaH} - \text{DeltaS} * \text{temp} \\ & \qquad \qquad \qquad 19.49 \text{ kJ} \end{aligned} \quad (3.1.3)$$

▼ H₂O



Enthalpy Change

$$\begin{aligned} > \text{DeltaH} := 1 * \text{Unit}(\text{mol}) * h_{\text{H2O}} - (1 * \text{Unit}(\text{mol}) * h_{\text{H2}} + 0.5 * \text{Unit} \\ & \quad (\text{mol}) * h_{\text{O2}}) \\ & \qquad \qquad \qquad -247.86 \text{ kJ} \end{aligned} \quad (3.2.1)$$

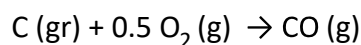
Entropy change

$$\begin{aligned} > \text{DeltaS} := 1 * \text{Unit}(\text{mol}) * s_{\text{H2O}} - (1 * \text{Unit}(\text{mol}) * s_{\text{H2}} + 1/2 * \text{Unit} \\ & \quad (\text{mol}) * s_{\text{O2}}) \\ & \qquad \qquad \qquad -55.27 \frac{\text{J}}{\text{K}} \end{aligned} \quad (3.2.2)$$

Gibbs energy of formation

$$\begin{aligned} > \text{DeltaG}_{\text{H2O}} := \text{DeltaH} - \text{DeltaS} * \text{temp} \\ & \qquad \qquad \qquad -192.58 \text{ kJ} \end{aligned} \quad (3.2.3)$$

▼ CO



Enthalpy change

$$\begin{aligned} > \text{DeltaH} := 1 * \text{Unit}(\text{mol}) * h_{\text{CO}} - (1 * \text{Unit}(\text{mol}) * h_{\text{C}} + 0.5 * \text{Unit}(\text{mol}) * h_{\text{O2}}) \\ & \qquad \qquad \qquad -112.00 \text{ kJ} \end{aligned} \quad (3.3.1)$$

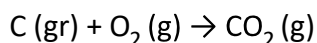
Entropy change

$$\begin{aligned} > \text{DeltaS} := 1 * \text{Unit}(\text{mol}) * s_{\text{CO}} - (1 * \text{Unit}(\text{mol}) * s_{\text{C}} + 0.5 * \text{Unit}(\text{mol}) * s_{\text{O2}}) \\ & \qquad \qquad \qquad 88.29 \frac{\text{J}}{\text{K}} \end{aligned} \quad (3.3.2)$$

Gibbs energy of formation

$$\begin{aligned} > \text{DeltaG}_{\text{CO}} := \text{DeltaH} - \text{DeltaS} * \text{temp} \\ & \qquad \qquad \qquad -200.29 \text{ kJ} \end{aligned} \quad (3.3.3)$$

▼ CO₂



Enthalpy change

$$\begin{aligned} > \text{DeltaH} := 1 * \text{Unit}(\text{mol}) * h_{\text{CO2}} - (1 * \text{Unit}(\text{mol}) * h_{\text{C}} + 1 * \text{Unit}(\text{mol}) * h_{\text{O2}}) \\ & \qquad \qquad \qquad -394.61 \text{ kJ} \end{aligned} \quad (3.4.1)$$

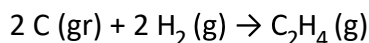
Entropy change

$$\begin{aligned} > \text{DeltaS} := 1 * \text{Unit}(\text{mol}) * s_{\text{CO2}} - (1 * \text{Unit}(\text{mol}) * s_{\text{C}} + 1 * \text{Unit}(\text{mol}) * s_{\text{O2}}) \\ & \qquad \qquad \qquad 1.26 \frac{\text{J}}{\text{K}} \end{aligned} \quad (3.4.2)$$

Gibbs Energy of Formation

$$\begin{aligned} > \text{DeltaG}_{\text{CO2}} := \text{DeltaH} - \text{DeltaS} * \text{temp} \\ & \qquad \qquad \qquad -395.87 \text{ kJ} \end{aligned} \quad (3.4.3)$$

▼ C₂H₄



Enthalpy change

$$\begin{aligned} > \text{DeltaH} := \text{Unit}(\text{mol}) * h_{\text{C2H4}} - (2 * \text{Unit}(\text{mol}) * h_{\text{C}} + 2 * \text{Unit}(\text{mol}) * h_{\text{H2}}) \\ & \qquad \qquad \qquad 38.22 \text{ kJ} \end{aligned} \quad (3.5.1)$$

Entropy change

$$\begin{aligned} > \text{DeltaS} := \text{Unit}(\text{mol}) * s_{\text{C2H4}} - (2 * \text{Unit}(\text{mol}) * s_{\text{C}} + 2 * \text{Unit}(\text{mol}) * s_{\text{H2}}) \\ & \qquad \qquad \qquad -80.93 \frac{\text{J}}{\text{K}} \end{aligned} \quad (3.5.2)$$

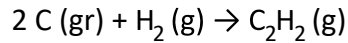
Gibbs energy of formation

$$> \text{DeltaG}_{\text{C2H4}} := \text{DeltaH} - \text{DeltaS} * \text{temp}$$

$$119.15 \text{ kJ}$$

(3.5.3)

▼ C₂H₂



Enthalpy change

$$> \text{DeltaH} := \text{Unit(mol)} * h_{\text{C}_2\text{H}_2} - (2 * \text{Unit(mol)} * h_{\text{C}} + 1 * \text{Unit(mol)} * h_{\text{H}_2})$$

$$224.98 \text{ kJ}$$

(3.6.1)

Entropy change

$$> \text{DeltaS} := \text{Unit(mol)} * s_{\text{C}_2\text{H}_2} - (2 * \text{Unit(mol)} * s_{\text{C}} + 1 * \text{Unit(mol)} * s_{\text{H}_2})$$

$$53.80 \frac{\text{J}}{\text{K}}$$

(3.6.2)

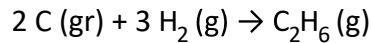
Gibbs energy of formation

$$> \text{DeltaG}_{\text{C}_2\text{H}_2} := \text{DeltaH} - \text{DeltaS} * \text{temp}$$

$$171.18 \text{ kJ}$$

(3.6.3)

▼ C₂H₆



Enthalpy change

$$> \text{DeltaH} := \text{Unit(mol)} * h_{\text{C}_2\text{H}_6} - (2 * \text{Unit(mol)} * h_{\text{C}} + 3 * \text{Unit(mol)} * h_{\text{H}_2})$$

$$-105.04 \text{ kJ}$$

(3.7.1)

Entropy change

$$> \text{DeltaS} := \text{Unit(mol)} * s_{\text{C}_2\text{H}_6} - (2 * \text{Unit(mol)} * s_{\text{C}} + 3 * \text{Unit(mol)} * s_{\text{H}_2})$$

$$-215.88 \frac{\text{J}}{\text{K}}$$

(3.7.2)

Gibbs energy of formation

$$> \text{DeltaG}_{\text{C}_2\text{H}_6} := \text{DeltaH} - \text{DeltaS} * \text{temp}$$

$$110.83 \text{ kJ}$$

(3.7.3)

▼ H₂

$$> \text{DeltaG}_{\text{H}_2} := 0:$$

▼ O₂

$$> \text{DeltaG}_{\text{O}_2} := 0:$$

▼ Constraints

A mole balance on the carbon, hydrogen and oxygen gives these constraints

Carbon	$n_1 + 2 n_2 + 2 n_3 + n_4 + n_5 + 2 n_9 = 2$
Hydrogen	$4 n_1 + 4 n_2 + 2 n_3 + 2 n_7 + 2 n_8 + 6 n_9 = 14$
Oxygen	$2 n_4 + n_5 + 2 n_6 + n_8 = 4$

```
> cons :=
    n1 + 2*n2 + 2*n3 + n4 + n5 + 2*n9 = 2 * Unit(mol)
    ,4*n1 + 4*n2 + 2*n3 + 2*n7 + 2*n8 + 6*n9 = 14 * Unit(mol)
    ,2*n4 + n5 + 2*n6 + n8 = 4 * Unit(mol):
```

▼ Gibbs Energy of the Products

Collect the Gibbs Energy of all species in a list

```
> DeltaG := [DeltaG_CH4, DeltaG_C2H4, DeltaG_C2H2, DeltaG_CO2,
    DeltaG_CO, DeltaG_O2, DeltaG_H2, DeltaG_H2O, DeltaG_C2H6] /~
    Unit(mol):
```

Total Gibbs Energy of the products

```
> Gt := n -> add(n[i] * DeltaG[i], i=1..9) + R * temp * add(n[i]
    * ln((n[i] + 1e-10*Unit(mol))/ add(n[i], i=1..9))), i=1..9):
```

▼ Optimization

```
> Digits := 20:
> composition := Minimize(Gt([n1, n2, n3, n4, n5, n6, n7, n8, n9]
    ), {cons}, initialpoint = [n1 = 1 * Unit(mol), n2 = 1 * Unit
    (mol), n3 = 1 * Unit(mol), n4 = 1 * Unit(mol), n5 = 1 * Unit
    (mol), n6 = 1 * Unit(mol), n7 = 1 * Unit(mol), n8 = 1 * Unit
    (mol), n9 = 1 * Unit(mol)], assume = nonnegative, iterationlimit
    = 300):
```

Hence the product composition is

```
> composition[2]
[ n1 = 6.75 × 10-2 mol, n2 = 9.13 × 10-8 mol, n3 = 2.77 × 10-10 mol, n4 = 5.57 × 10-1 mol, n5
    = 1.38 × 100 mol, n6 = 0.00 × 100, n7 = 5.35 × 100 mol, n8 = 1.51 × 100 mol, n9 = 1.50
    × 10-7 mol ] (6.1)
```