Catalytic Cracking of Ethane

Introduction

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

$$C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)$$

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

CH_4

C (gr) + 2 H_2 (g) → CH_4 (g)

Enthalpy change

```
> DeltaH := 1*Unit(mol)*h_CH4 - (1*Unit(mol)*h_C + 2*Unit(mol)*
  h_H2)
```

$$-89.07\ \text{kJ} \qquad \textbf{(3.1.1)}$$

Entropy change

```
> DeltaS := 1*Unit(mol)*s_CH4 - (1*Unit(mol)*s_C + 2*Unit(mol)*
  s_H2)
```

$$-108.55\ \frac{\text{J}}{\text{K}} \qquad \textbf{(3.1.2)}$$

Gibbs energy of formation

```
> DeltaG_CH4 := DeltaH - DeltaS*temp
```

$$19.49\ \text{kJ} \qquad \textbf{(3.1.3)}$$

H_2O

H_2 (g) + 0.5 O_2 (g) → H_2O (l)

Enthalpy Change

```
> DeltaH := 1*Unit(mol)*h_H2O - (1*Unit(mol)*h_H2 + 0.5*Unit
  (mol)*h_O2)
```

$$-247.86\ \text{kJ} \qquad \textbf{(3.2.1)}$$

Entropy change

```
> DeltaS := 1*Unit(mol)*s_H2O - (1*Unit(mol)*s_H2 + 1/2*Unit
  (mol)*s_O2)
```

$$-55.27\ \frac{\text{J}}{\text{K}} \qquad \textbf{(3.2.2)}$$

Gibbs energy of formation

```
> DeltaG_H2O := DeltaH - DeltaS*temp
```

$$-192.58\ \text{kJ} \qquad \textbf{(3.2.3)}$$

CO

C (gr) + 0.5 O_2 (g) → CO (g)

Enthalpy change

```
> DeltaH := 1*Unit(mol)*h_CO - (1*Unit(mol)*h_C + 0.5*Unit(mol)
  *h_O2)
```

$$-112.00\ \text{kJ} \qquad \textbf{(3.3.1)}$$

Entropy change

```
> DeltaS := 1*Unit(mol)*s_CO - (1*Unit(mol)*s_C + 0.5*Unit(mol)
  *s_O2)
```

$$88.29\ \frac{\text{J}}{\text{K}} \qquad \textbf{(3.3.2)}$$

Gibbs energy of formation

```
> DeltaG_CO := DeltaH - DeltaS*temp
```

$$-200.29\ \text{kJ} \qquad \textbf{(3.3.3)}$$

CO_2

C (gr) + O_2 (g) → CO_2 (g)

Enthalpy change

```
> DeltaH := 1*Unit(mol)*h_CO2 - (1*Unit(mol)*h_C + 1*Unit(mol)*
  h_O2)
```

$$-394.61\ \text{kJ} \qquad \textbf{(3.4.1)}$$

Entropy change

```
> DeltaS := 1*Unit(mol)*s_CO2 - (1*Unit(mol)*s_C + 1*Unit(mol)*
  s_O2)
```

$$1.26\ \frac{\text{J}}{\text{K}} \qquad \textbf{(3.4.2)}$$

Gibbs Energy of Formation

```
> DeltaG_CO2 := DeltaH - DeltaS*temp
```

$$-395.87\ \text{kJ} \qquad \textbf{(3.4.3)}$$

C_2H_4

2 C (gr) + 2 H_2 (g) → C_2H_4 (g)

Enthalpy change

```
> DeltaH := Unit(mol)*h_C2H4 - (2*Unit(mol)*h_C + 2*Unit(mol)*
  h_H2)
```

$$38.22\ \text{kJ} \qquad \textbf{(3.5.1)}$$

Entropy change

```
> DeltaS := Unit(mol)*s_C2H4 - (2*Unit(mol)*s_C + 2*Unit(mol)*
  s_H2)
```

$$-80.93\ \frac{\text{J}}{\text{K}} \qquad \textbf{(3.5.2)}$$

Gibbs energy of formation

```
> DeltaG_C2H4 := DeltaH - DeltaS*temp
```

119.15 kJ (3.5.3)

C_2H_2

2 C (gr) + H_2 (g) → C_2H_2 (g)

Enthalpy change

```
> DeltaH := Unit(mol)*h_C2H2 - (2*Unit(mol)*h_C + 1*Unit(mol)*
  h_H2)
```

224.98 kJ (3.6.1)

Entropy change

```
> DeltaS := Unit(mol)*s_C2H2 - (2*Unit(mol)*s_C + 1*Unit(mol)*
  s_H2)
```

$53.80 \frac{J}{K}$ (3.6.2)

Gibbs energy of formation

```
> DeltaG_C2H2 := DeltaH - DeltaS*temp
```

171.18 kJ (3.6.3)

C_2H_6

2 C (gr) + 3 H_2 (g) → C_2H_6 (g)

Enthalpy change

```
> DeltaH := Unit(mol)*h_C2H6 - (2*Unit(mol)*h_C + 3*Unit(mol)*
  h_H2)
```

-105.04 kJ (3.7.1)

Entropy change

```
> DeltaS := Unit(mol)*s_C2H6 - (2*Unit(mol)*s_C + 3*Unit(mol)*
  s_H2)
```

$-215.88 \frac{J}{K}$ (3.7.2)

Gibbs energy of formation

```
> DeltaG_C2H6 := DeltaH - DeltaS*temp
```

110.83 kJ (3.7.3)

H_2

```
> DeltaG_H2:= 0:
```

O_2

```
> DeltaG_O2:= 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]
```

$$[n1 = 6.75 \times 10^{-2}\ \text{mol}, n2 = 9.13 \times 10^{-8}\ \text{mol}, n3 = 2.77 \times 10^{-10}\ \text{mol}, n4 = 5.57 \times 10^{-1}\ \text{mol}, n5 = 1.38 \times 10^{0}\ \text{mol}, n6 = 0.00 \times 10^{0}, n7 = 5.35 \times 10^{0}\ \text{mol}, n8 = 1.51 \times 10^{0}\ \text{mol}, n9 = 1.50 \times 10^{-7}\ \text{mol}] \quad (6.1)$$