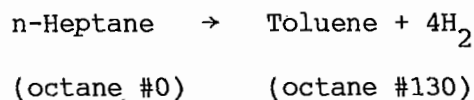


SolutionIntroduction

Catalytic Reforming is an important process in the manufacture of automotive gasoline. In this process, the octane number of light naphthas (which contain primarily paraffins) is increased by reaction at moderate temperatures and pressures. Typically, octane numbers may be boosted from 60 to 100 in a catalytic reforming operation.

We will focus on one of the many reactions which occurs in a reformer:



Pressure, temperature, and hydrogen/hydrocarbon ratio are very important in the reforming operation. Temperatures greater than about 400°C are required to make the reaction favorable. High pressure and high hydrogen/hydrocarbon ratios are desirable from a catalytic standpoint because the catalyst remains free of carbon deposits at high hydrogen partial pressures, but this obviously has a negative effect on the thermodynamic favorability of the reaction. Usually, the temperature is boosted to about 500°C to compensate. Typically hydrogen to hydrocarbons ratios of about 4 enter the catalytic reformer and the operating pressure is about 10 atmospheres.

An excellent (and practical) test of your abilities as expert thermodynamicists would be to determine the composition and dew point of a reaction product from a reformer assuming that reaction equilibrium was achieved in the reactor. However, because of time constraints, we will have to limit the scope of calculations, and make various approximations as we proceed.

Problems

I. 30 points

Compute the fugacity coefficients of n-heptane and hydrogen for a 1 part n-heptane (1)/4 parts hydrogen (3), at 500°C and 10 atmospheres of pressure. You may use the ideal gas law for up to 20% credit, the Lewis Fugacity Rule for up to 75% credit, the generalized correlations for a binary mixture for up to 100% credit, or Van Der Waals equation for a binary mixture for up to 100% credit.

II. 35 points

Compute the pressure at which liquid would start to form (the dew point pressure) and the composition of the liquid for a gaseous mixture of 0.040 mole% heptane (1), 0.160 mole% toluene (2), and 0.800 mole% hydrogen (3) at 200°C. Assume:

1. Hydrogen is insoluble in the liquid (mole fraction zero).
2. The standard state fugacities of toluene and n-hexane are equal to their vapor pressures at 200°C (Poynting correction and  $\phi_i^S$  are 1).
3. The fugacity coefficients for heptane, toluene, and hydrogen are all one.

You may use Raoult's Law for up to 20% credit or the Van Laar Correlation for up to 100% credit.

III. 35 points

Compute the maximum pressure in the reactor if we are to achieve at least 80% conversion of n-heptane at 500°C. Entering the reactor is a mixture of 1 mole n-heptane (1), 4 moles of  $H_2$  (3), and no toluene (2). Assume that the fugacity coefficients of n-heptane, toluene, and hydrogen are all one.

Data

|                                        | Heptane (1) | Toluene (2) | H <sub>2</sub> (3) |
|----------------------------------------|-------------|-------------|--------------------|
| T <sub>C</sub> (°K)                    | 540.2       | 591.7       | 33.2               |
| P <sub>C</sub> (atm)                   | 27.0        | 40.6        | 12.8               |
| v <sub>C</sub> (cm <sup>3</sup> /mole) | 432.0       | 316.0       | 65.0               |
| z <sub>C</sub>                         | 0.263       | 0.264       | 0.305              |
| ω                                      | 0.351       | 0.257       | 0.0                |

Heat Capacity Constants

|                      |         |         |      |
|----------------------|---------|---------|------|
| α                    | 7.094   | 0.576   | 6.52 |
| β × 10 <sup>3</sup>  | 123.447 | 93.493  | 0.78 |
| γ × 10 <sup>6</sup>  | -38.719 | -31.227 | 0    |
| ζ × 10 <sup>-5</sup> | 0       | 0       | 0.12 |

Antoine Constants

|   |          |          |   |
|---|----------|----------|---|
| A | 6.89386  | 6.95087  | - |
| B | 1264.370 | 1342.310 | - |
| C | 216.640  | 219.187  | - |

|                                |        |       |   |
|--------------------------------|--------|-------|---|
| ΔH <sub>f,298</sub> (cal/mole) | -44885 | 11950 | 0 |
| ΔG <sub>f,298</sub> (cal/mole) | 1920   | 29228 | 0 |

Heat Capacity Equation:

$$C_p = (\text{cal/mole}^\circ\text{K}) = \alpha + \beta T (^\circ\text{K}) + \gamma T^2 (^\circ\text{K}) + \zeta/T^2 (^\circ\text{K})$$

Antoine Equation:

$$\log_{10} P_i^S (\text{torr}) = A - B/[T(^\circ\text{C}) + C]$$

Van Laar Equation, Heptane (1)/Toluene (2) Binary Mixture:

$$\ln \gamma_1 = A \left( \frac{Bx_2}{Ax_1 + Bx_2} \right)^2 \quad A = 0.3037$$

$$\ln \gamma_2 = B \left( \frac{Ax_1}{Ax_1 + Bx_2} \right)^2 \quad B = 0.2651$$