Example 05.18 Henry Constant for Methane in Benzene at 60 °C Using the Method of Prausnitz and Shair

problem:

Estimate the Henry constant of methane(1) in benzene(2) at 60 °C using the method of Prausnitz and Shair.

general constants and definitions:

$cm := 0.01m \quad R_{gas} := 8.31433 \frac{J}{K \cdot mol} \quad g := 0.001kg$

$kPa := 1000Pa \quad bar := 10^5 Pa \quad dm := 0.1m \quad mmHg := \frac{1}{760} atm$

input data

$n_{comp} := 2 \quad i := 1 .. n_{comp} \quad j := 1 .. n_{comp}$

Required parameters for methane from Table 5.15::

Hypothetical liquid molar volume: $v_{gas} := 52 \cdot 10^{-6} \frac{m^3}{mol}$

Solubility parameter: $\delta_{gas} := 11622 \left(\frac{J}{m^3}\right)^{\frac{1}{2}}$

Critical data: $T_{c_gas} := 190.4K$

$P_{c_gas} := 46bar$

Temperature: $Temp := (60 + 273.15)K$

Antoine constants of benzene:

$Ant := (6.87987 \quad 1196.76 \quad 219.161)$

Antoine function for vapor pressure calculation:

$$Ps(Temp, i) := 10^{\left(Ant_{i,1} - \frac{Ant_{i,2}}{\frac{Temp}{K} - 273.15 + Ant_{i,3}}\right)} mmHg$$

Liquid density of benzene (see App. A):

$T_c := 562.014K \qquad \theta(Temp) := 1 - \frac{Temp}{T_c}$

$$\rho_{solvent}(T) := \left[306.28 + \left(502.4341 \cdot \theta(T)^{0.35} + 531.5958 \cdot \theta(T)^{\frac{2}{3}} - 663.9853 \cdot \theta(T) + 469.5977 \cdot \theta(T)^{\frac{4}{3}}\right)\right] \frac{kg}{m^3}$$

$$\rho_{solvent}(Temp) = 836.567\ kg\ m^{-3}$$

Molecular weight of benzene: $M_{w_solvent} := 78.114 \frac{g}{mol}$

Solution

Prausnitz and Shair (J. M. Prausnitz, F. H. Shair:: AIChE J. **7**, 682 (1961)) described the standard fugacity of a gas using the equation:

$$\ln\left(\frac{f^{\circ}_{gas}}{P_{c_gas}}\right) = 7.81 - \frac{8.06}{T_{r_gas}} - 2.94 \cdot \ln\left(T_{r_gas}\right)$$

with: $T_{r_gas}(Temp) := \frac{Temp}{T_{c_gas}}$

Rearranging leads to:

$$f^{\circ}_{gas}(Temp) := \exp\left(\left(7.81 - \frac{8.06}{T_{r_gas}(Temp)} - 2.94 \cdot \ln\left(T_{r_gas}(Temp)\right)\right)\right) \cdot P_{c_gas}$$

$$f^{\circ}_{gas}(Temp) = 218.636\ bar$$

The Henry coefficient can be calculated via the expression:

$$H = \lim_{x \to 0} \frac{x \cdot \gamma \cdot f^{\circ}}{x} = \gamma_{inf_dil} \cdot f^{\circ}$$

In the Prausnitz-Shair method, the activity coefficient of the gas at infinite dilution is calculated using the Hildebrand regular solution theory. This requires the knowledge of the solvation parameter δ of the solvent, which can be calculated from the heat of vaporization and the liquid molar volume of the solvent:

The heat of vaporization can be calculated from the slope of the vapor pressure equation using Clausius-Clapeyron (Equ. 2.82). The change in compressibility factor upon vaporization is assumed to be one (ideal vapor phase and neglectable liquid volume). This simplification should introduce an error of less than 1%.

$$\Delta z_{vap} := 1$$

$$\Delta h_{vap_solvent}(Temp) := -\left(R_{gas} \cdot \Delta z_{vap} \cdot \frac{\ln\left(\frac{Ps(Temp + .01 \cdot K, 1)}{bar}\right) - \ln\left(\frac{Ps(Temp - .01 \cdot K, 1)}{bar}\right)}{\frac{1}{Temp + .01K} - \frac{1}{Temp - 0.01K}}\right)$$

$$\Delta h_{vap_solvent}(Temp) = 32630 \frac{J}{mol}$$

$$v_{solvent}(Temp) := \frac{M_{w_solvent}}{\rho_{solvent}(Temp)}$$

$$\delta_{solvent}(Temp) := \left(\frac{\Delta h_{vap_solvent}(Temp) - R_{gas} \cdot Temp}{v_{solvent}(Temp)} \right)^{.5}$$

$$\delta_{solvent}(Temp) = 17883 \left(\frac{J}{m^3} \right)^{0.5}$$

$$\gamma_{inf_dil}(Temp) := \exp\left[\frac{v_{gas}}{R_{gas} \cdot Temp} \cdot \left(\delta_{gas} - \delta_{solvent}(Temp)\right)^2 \right]$$

$$\gamma_{inf_dil}(Temp) = 2.087$$

Now the Henry coefficient of methane in Benzene at 60°C can be calculated:

$$H(Temp) := \gamma_{inf_dil}(Temp) \cdot f^{\circ}_{gas}(Temp)$$

$$H(Temp) = 456\,bar$$

The experimental value is approx. 513 bar [J. Horiuti, Sci. Papers Inst. Phys. Chem. Res. (Japan) **17** (341), 125-256 (1931)]. Although rather old, the experimental value is in good agreement with other data at different temperatures.

The above function for the calculation of the Henry coefficient can also be used at other temperatures.