Chemical Thermodynamics for Process Simulation
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Example 05.17 Henry Constant for Methane in Benzene at 60 °C with the Help of the Soave-Redlich-Kwong Equation of State

problem:

Calculate the Henry constant for methane(1) in benzene(2) at 60 °C with the help of the Soave-Redlich-Kwong equation of state (k_{12} = 0.08*)

*H. Knapp, R. Döring, L. Oellrich, U. Plöcker, J.M. Prausnitz, Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances, DECHEMA Chemistry Data Series, Vol. VI, Frankfurt 1982.

general constants and definitions:

$cm := 0.01m \qquad R_{gas} := 8.31433 \frac{J}{K \cdot mol}$

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

input data

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

Critical data and acentric factor:

$$T_c := \begin{pmatrix} 190.564 \\ 562.014 \end{pmatrix} K \qquad P_c := \begin{pmatrix} 45.992 \\ 49.010 \end{pmatrix} bar \qquad \omega := \begin{pmatrix} 0.0114 \\ 0.2103 \end{pmatrix}$$

Binary parameter k_{SRK}: $\quad k_{SRK} := \begin{pmatrix} 0 & 0.08 \\ 0.08 & 0 \end{pmatrix}$

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

Solution

The Henry constant is defined as the ratio of gas fugacity to its mole fraction in the liquid in the limiting case of a gas partial pressure of zero. As in this case the liquid mole fraction of the gas is also zero, determination of Henry coefficients from experimental data has to use data for non-zero gas partial pressures and involves extrapolation to zero pressure.
In case the phase equilibrium is calculated from an equation of state, values for the fugacity coefficients in the two phases can also be found at zero concentration of a component. For the phase equilibrium it holds that:

$$x_1 \cdot \phi_{L_1} = y_1 \cdot \phi_{V_1} \qquad \text{and} \qquad x_1 = \frac{y_1 \cdot \phi_{V_1}}{\phi_{L_1}} \qquad .1$$

The fugacity of the gas in the vapor phase is calculated as:

$$f_1 = y_1 \cdot \phi_{V_1} \cdot P$$

Using the definition of the Henry constant (for the limiting case of zero gas fugacity):

$$H_{1,2} = \lim_{x_1 \to 0} \frac{f_1}{x_1}$$

At a gas fugacity $f_1 = 0$ it holds that:

$$H_{1,2} = \frac{y_1 \cdot phi_{V_1} \cdot P}{\frac{y_1 \cdot phi_{V_1}}{phi_{L_1}}} \rightarrow H_{1,2} = P \cdot phi_{L_1}$$

In the binary case, the total pressure P is equal to the saturated vapor pressure of the solvent. In order to calculate the Henry constant at a temperature Temp, the phase equilibrium has to be calculated for the following conditions:

$$x := \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad y := \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad P = Ps_2(Temp)$$

In the first step, the equation of state parameters for and between the pure components are calculated from the critical data and the acentric factor at the target temperature of 60°C. The parameters are identical for both phases and do not need to be updated as both phases have the same fixed composition. When calculating Henry coefficients in solvent mixtures, this simplification is in principle not valid, but at low partial pressures of non-associating solvents in the vapor phase, the vapor phase fugacity coefficients can asumed to be unity and for the calculation of the equilibrium pressure, only the fugacity coefficients in the (fixed concentration) liquid phase are required. The number of gases is irrelevant as their concentration in both phases is assumed to be zero.

$$\alpha_{SRK}(Temp) := \left| \begin{array}{l} \text{for } i \in 1..n_{comp} \\ \quad \alpha_{SRK_i} \leftarrow \left[1 + \left[0.48 + 1.574 \cdot \omega_i - 0.176 \cdot (\omega_i)^2 \right] \cdot \left[1 - \left(\frac{Temp}{T_{c_i}} \right)^{0.5} \right] \right]^2 \\ \alpha_{SRK} \end{array} \right.$$

$$\alpha_{SRK}(Temp) = \begin{pmatrix} 0.704872 \\ 1.403765 \end{pmatrix}$$

$$a_{SRK} := \left| \begin{array}{l} \text{for } i \in 1..n_{comp} \\ \quad a_{SRK_{i,i}} \leftarrow 0.42748 \cdot \frac{R_{gas}^2 \cdot (T_{c_i})^2}{P_{c_i}} \cdot \alpha_{SRK}(Temp)_i \\ \text{for } i \in 1..n_{comp} \\ \quad \text{for } j \in 1..n_{comp} \\ \quad\quad a_{SRK_{i,j}} \leftarrow \sqrt{a_{SRK_{i,i}} \cdot a_{SRK_{j,j}}} \cdot \left(1 - k_{SRK_{i,j}}\right) \\ a_{SRK} \end{array} \right.$$

$$a_{SRK} = \begin{pmatrix} 1.644674 & 6.100492 \\ 6.100492 & 26.73463 \end{pmatrix} \frac{\left(dm^3\right)^2 bar}{mol^2}$$

$$b_{SRK_i} := 0.08664 \cdot \frac{R_{gas} \cdot T_{c_i}}{P_{c_i}}$$

$$b_{SRK} = \begin{pmatrix} 0.029847 \\ 0.082605 \end{pmatrix} \frac{dm^3}{mol}$$

As both phases are pure solvent at a gas partial pressure of zero, the mixture parameters for the phases are equal to the solvent pure component parameters:

$$a_{SRKm} := a_{SRK_{2,2}} \qquad a_{SRKm} = 26.735 \frac{\left(dm^3\right)^2 bar}{mol^2}$$

$$b_{SRKm} := b_{SRK_2} \qquad b_{SRKm} = 82.605 \frac{cm^3}{mol}$$

In the next step, the pure component vapor pressure of the solvent (i.e. the total pressure) has to be determined. For this, the pressure explicit equation of state and functions to solve for the vapor and liquid volume are required:

$$P_{SRK}(v, Temp) := \frac{R_{gas} \cdot Temp}{v - b_{SRKm}} - \frac{a_{SRKm}}{v \cdot \left(v + b_{SRKm}\right)}$$

$$v_L(T, P) := \left| \begin{array}{l} v \leftarrow b_{SRKm} \cdot 1.2 \\ v \leftarrow root\left(P_{SRK}(v, Temp) - P, v\right) \\ v \end{array} \right.$$

$$v_V(T, P) := \left| \begin{array}{l} v \leftarrow \frac{R_{gas} \cdot T}{P} \\ v \leftarrow root\left(P_{SRK}(v, Temp) - P, v\right) \\ v \end{array} \right.$$

With the help of the difference in fugacity coefficients the vapor pressure calculation function will later iterate the vapor pressure. The equation for mixtures is used (App. D, Equ. 0.215) here but a more simple pure component fugacity equation would be sufficient.

$$\mathrm{lnphi}(v, Temp, P, x, i) := \ln\left(\frac{v}{v - b_{SRKm}}\right) - \frac{2 \cdot \sum_j x_j \cdot a_{SRK_{j,i}}}{R_{gas} \cdot Temp \cdot b_{SRKm}} \cdot \ln\left(\frac{v + b_{SRKm}}{v}\right) \ldots$$
$$+ \frac{b_{SRK_i}}{(v - b_{SRKm})} - \ln\left(\frac{P \cdot v}{R_{gas} \cdot Temp}\right) \ldots$$
$$+ \frac{a_{SRKm} \cdot b_{SRK_i}}{R_{gas} \cdot Temp \cdot b_{SRKm}^{2}} \cdot \left(\ln\left(\frac{v + b_{SRKm}}{v}\right) - \frac{b_{SRKm}}{v + b_{SRKm}}\right)$$

For the root function in the vapor pressure function a starting value for the pressure is required. The function employs a simple linear representation of the vapor pressure in the log(P_r) vs. 1/T_r diagram through the critical point and a decadic logarithm of the reduced pressure of -(ω+1) at 1/T_r:

$$Ps(Temp) := \left| \begin{array}{l} P \leftarrow P_{c_2} \cdot 10^{-\left[\frac{\frac{T_{c_2}}{Temp} - 1}{\frac{1}{0.7} - 1} \cdot (\omega_2 + 1)\right]} \\ Ps \leftarrow \mathrm{root}\left(\mathrm{lnphi}\left(v_V(Temp, P), Temp, P, x, 2\right) - \mathrm{lnphi}\left(v_L(Temp, P), Temp, P, x, 2\right), P\right) \\ Ps \end{array} \right.$$

$P := Ps(Temp)$ $\qquad P = 0.516\,atm$

Verifying the equilibrium condition for this pressure leads to a sufficiently small deviation:

$$\mathrm{lnphi}\left(v_V(Temp, P), Temp, P, x, 2\right) - \mathrm{lnphi}\left(v_L(Temp, P), Temp, P, x, 2\right) = 1.118 \times 10^{-4}$$

At this pressure the fugacity coefficient of the gas in the liquid is:

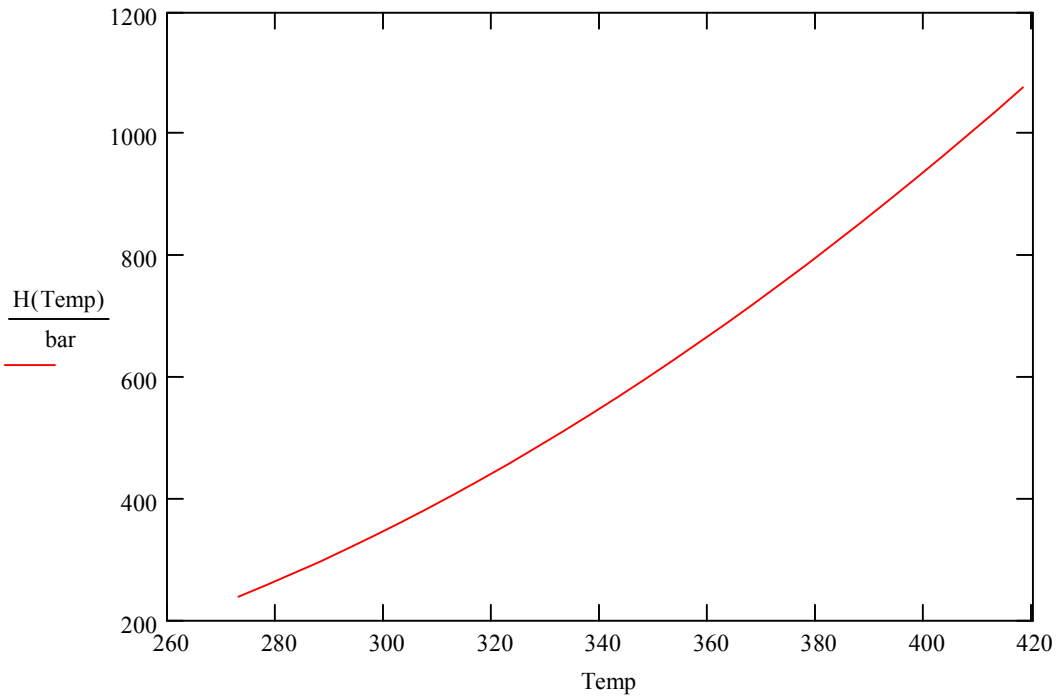
$$phi_{L_1} := \exp\left(\mathrm{lnphi}\left(v_L(Temp, P), Temp, Ps(Temp), x, 1\right)\right) \qquad phi_{L_1} = 978.73$$

and the Henry coefficient of methane in benzene is:

$$H_{21} := phi_{L_1} \cdot P \qquad H_{21} = 511.62\,bar$$

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. It should be noted that the result is not purely predictive, as a binary parameter k_{ij} has been used that was probably obtained from VLE data over the whole concentration range. Thus the calculation represents an extrapolation to the behavior at infinite dilution.

Using the functions defined above, the Henry coefficient can now be plotted as function of temperature:

$$H(Temp) := \exp\left(lnphi\left(v_L(Temp, P), Temp, Ps(Temp), x, 1\right)\right) \cdot Ps(Temp)$$

$$Temp := 273.15, 278.15 .. 473.15$$