Fugacity of equilibrium and transport

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18 december 2018

Three equations is all it takes to understand vapor-liquid equilibrium (VLE) and transport models: *Gas fugacity*, *Liquid fugacity* and the *Filmmodel* of interphase mass exchange.

Equilibrium applies to closed containers, without mass or energy exchange with the outside world. After stirring a while, pressure and temperature of the system content are equalized and equilibrium is achieved. Transport models apply to open systems, where molecules in a liquid evaporate and condense. Fugacity equalization is the driving force of vaporization and condensation in the the fugacity filmmodel.

1. Definitions of fugacity[1]

Fugacity in a vapor phase f_i^G is the partial pressure at system pressure P_{system}[2]:

$$f_i^G = y_i P_{system} \qquad \text{[Pa]}$$

Fugacity of compound i in the Liquid phase uses molefraction x_i in stead of vapor mole fraction y_i. Liquid fugacity also involves pure liquid vapor pressure P^i and the activity coefficient γ_i^L:

$$f_i^L = \gamma_i^L x_i P^i \qquad \text{[Pa]}$$

P^i follows from isothermal Kovats index data[3] and γ_i^L is modeled with an NxN matrix of Wilson binary interaction parameters Λ_{ij} for N component mixtures[4].
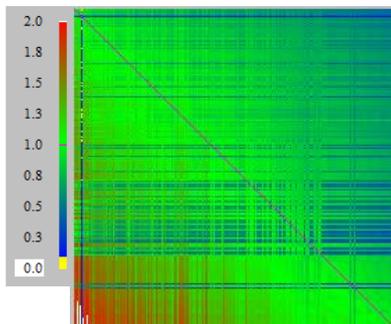
52670 Wilson binary parameters Λ_{ij} of N=230 sample

1.1. Vapor-Liquid Equilibrium by fugacity

At vapor-liquid equilibrium fugacity is equalized:

$$y_i P_{system} = \gamma_i^L x_i P^i \qquad \text{VLE } f_i^G = f_i^L \qquad \text{[Pa]}$$

VLE applies to equilibrium plate separation and phase diagrams. VLE is the driving force of mass transport.

StillPeaks software constructs phase diagrams by solving VLE fugacity for 2 compounds in the binary and normalize to total molefraction one. The marks represent VLE measurements:
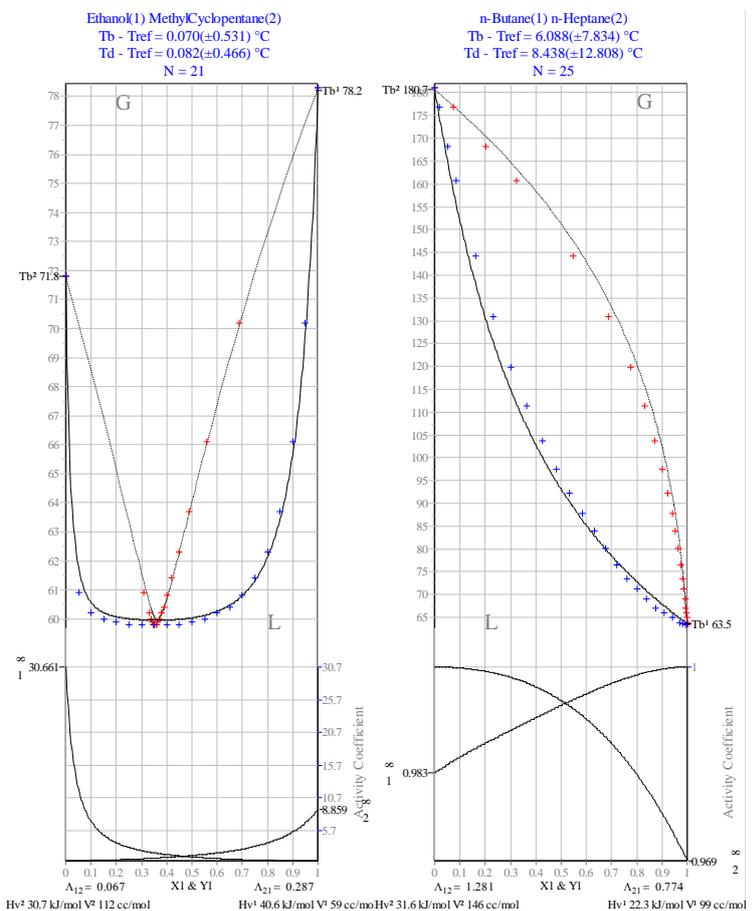
Binary *Txy* diagrams at constant pressure


[1] See chapters 5 and 6 of: Prausnitz et.al.

[2] The non-ideal vapor phase also includes the fugacity coefficient φ, which is omitted here for clarity check: Reid Poynting factor on www.

[3] Spieksma (1999) Determination of Vapor Liquid Equilibrium from the Kovats Retention Index on

Dimethylsilicone using theWilson Mixing Model *Journal of High Resolution Chromatography*

[4] Spieksma (1998) Prediction of ASTM Method D86 Distillation of Gasolines and Naphthas according to the Fugacity-Filmmodel from Gas Chromatographic Detailed Hydocarbon Analysis *Journal of Chromatographic Science*

P,T diagrams of nParaffins by Antoine Log(P[mHg])=A-B/(T[°C]+C)
CH4 by Cutler, C2H6 by Loomis, C3..C100 by Kudchadker & Zwolinski API 44
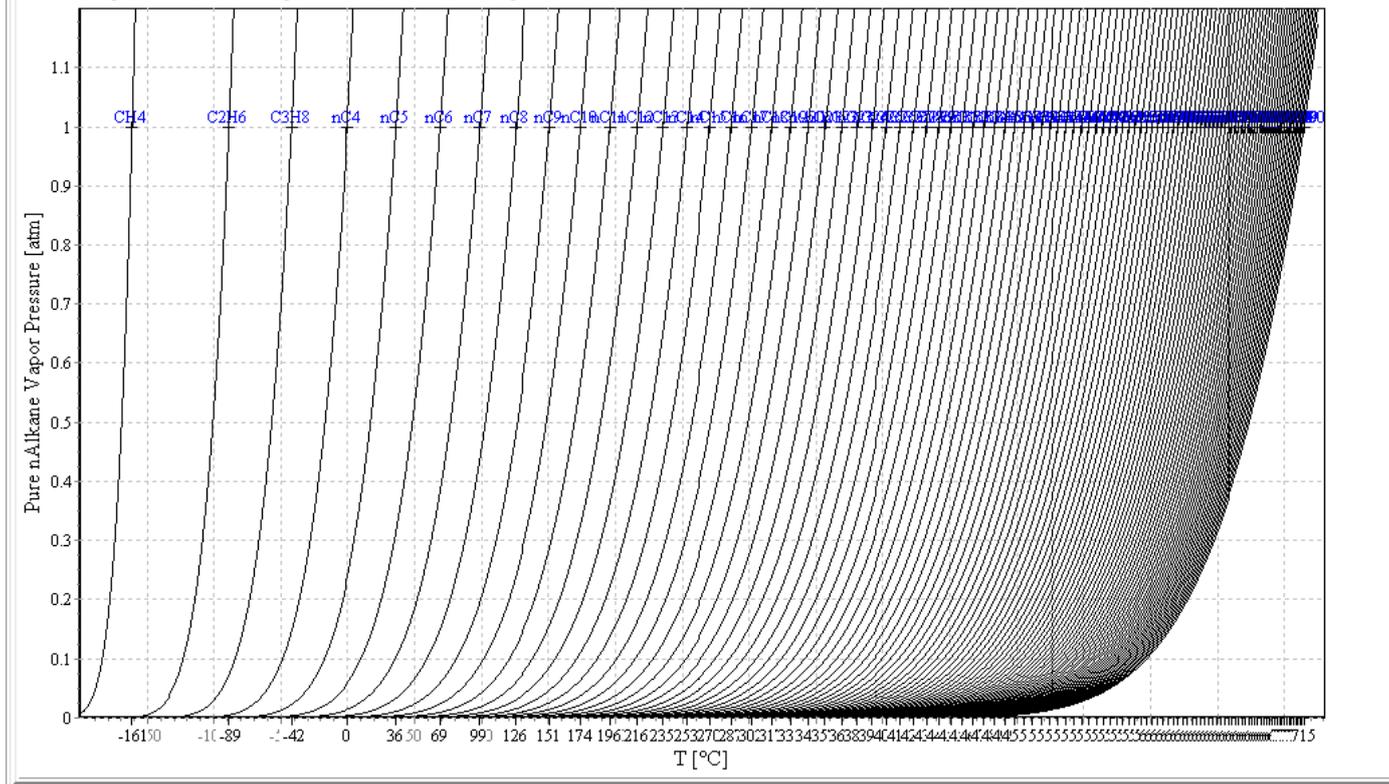
Pure n-Alkane vapor pressures and boiling points

1.1. Henry's law by fugacity

Henry's law is the ratio of concentrations in air and water of a compound i in a closed system. Henry's law constant can be derived from VLE $f_i^G = f_i^L$ expressed in concentration[5]:

$$C_i^G = H_i C_i^L \qquad [mol/m^3]$$

With dimensionless Henry's law constant:

$$H_i = \gamma_i^L V^L P^i / RT \qquad \text{HLC} \quad [-]$$

The value of H_i usually rises with temperature because P^i rises exponentially with the T present in the denominator.

1.2 Liquid-liquid equilibrium of bonded polymers

Bonded and cross linked polymers do not dissolve in a pure liquid i phase. Pure liquid i has mole fraction $x_i=1$ and activity coefficient $\gamma_i^L=1$ by definition so pure liquid fugacity is $f^i = P^i$. Polymer networks make room to absorb molecules (swell). Liquid polymer blend at equilibrium with a pure liquid i results in a maximum concentration or solubility:

$$C_i^{Lmax} = S_i^L = 1/\gamma_i^L V^L \qquad \text{LLE } f_i^L = f^i \quad [mol/m^3]$$

The HLC Henry constant has a simple relation with solubility in a liquid polymer:

$$H_i = P^i / RTS_i^L \qquad \text{HLC}_{polymer} \quad [-]$$

1.3 Boiling point and fugacity

The boiling point T_b of multicomponent mixtures is achieved when vapor bubbles form in the liquid because total fugacity exceeds atmospheric pressure. Boiling point can be found by solving:

$$\Sigma f_i^L(T_b) = 101325 \qquad [Pa]$$

In 100 mL of liquid, boiling chips are required for proper BP development without delay.

1.4. Fugacity and chromatography

VLE equations apply to the sub millimeter scale of capillary columns, because the random walk velocity of molecules in liquid and gas phases is fast (cm²/s) compared to for example the film thickness (µm) in capillary GC.

Most studies after the mechanism of GC involve retention volume, a property typical for packed columns. Retention time (t_i) is the result of chromatographic separation by a mobile phase with a residence time of "dead time" t_o in the column.

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[5] Liquid concentration $C_i^L = x_i/V^L = n_i/V_L$ uses liquid phase molar volume that follows from molar mass and density($V^L = M^L/\rho^L$). Gas concentration is $C_i^G = y_i/V^G = n_i/V_G$ and by gas law $V^G = RT/P$.

The capacity factor is the residence time ratio of a compound i in the mobile (t_i^m) and stationary phase (t_i^s) which equals the mol(ecul)ar partition over in the mobile phase (n_i^m) and the stationary phase (n_i^s):

$$(t_i - t_o)/t_o = t_i^s/t_i^m = n_i^s/n_i^m \qquad [-]$$

Phase volume ratio β of stationary phase and mobile phase is:

$$\beta = V_s/V_m \qquad [-]$$

Which follows for capillary GC from diameter (d_c) and film thickness (d_f):

$$\beta = 4d_f/d_c \qquad [-]$$

Henry's law concentration in a liquid is the amount n_i^L of compound i in total volume V_L of liquid:

$$C_i^L = n_i^L/V_L \qquad L\ [mol/m^3]$$

The Henry's law concentration in a gas is the amount in a total gas volume:

$$C_i^G = n_i^G/V_G \qquad G\ [mol/m^3]$$

Combining phase ratio and concentration we see that GC retention is proportional with solubility vapor pressure ratio:

$$(t_i - t_o)/t_o = (C_i^L/C_i^G)\beta = \beta/H_i = \beta RTS_i^L/P^i \qquad [-]$$

Similarly we see LC retention depends on solubility in mobile (S_i^M) and stationary phase (S_i^S):

$$(t_i - t_o)/t_o = (C_i^S/C_i^M)\beta = \beta S_i^S/S_i^M \qquad [-]$$

The mobile phase in LC is not a polymer, so the S_i^M solubility is complicated by solubility of the mobile phase in the pure liquid...

Gas chromatography is not just based on solubility like liquid chromatography, so LC uses solvent gradients and GC uses temperature programs.

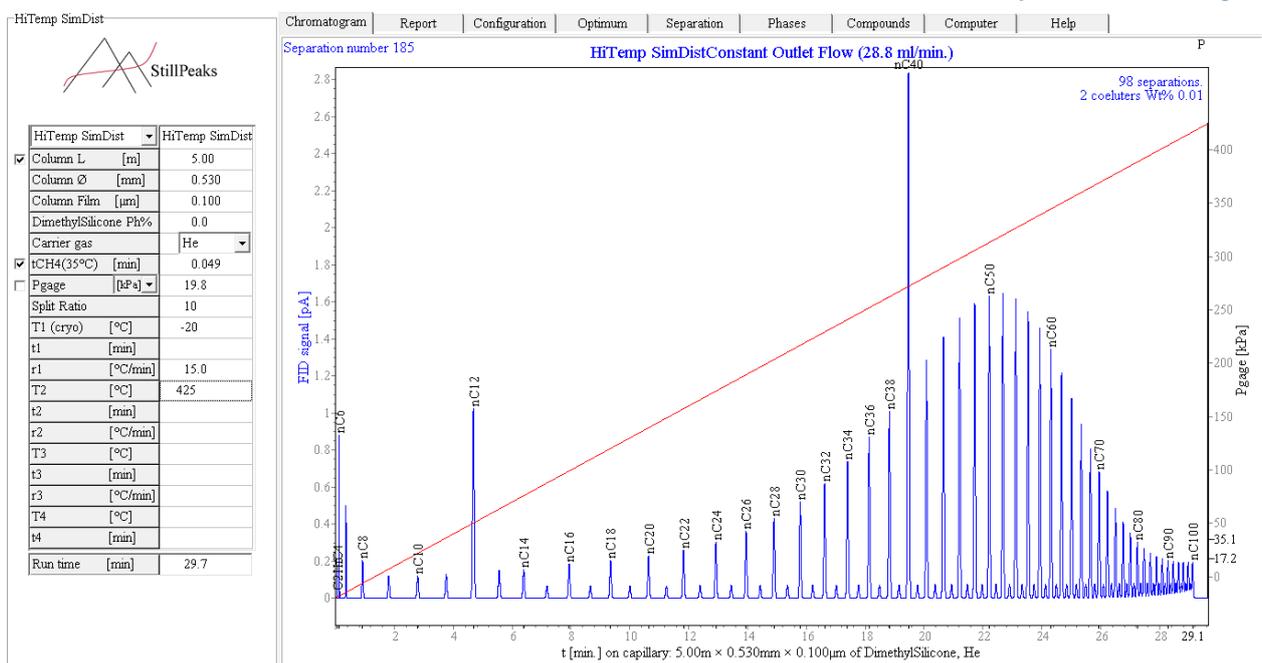Kwantes and Rijders (1958) derived a similar GC equation:

$$(t_i - t_o)/t_o = \beta RT/(\gamma_i^L V^L P^i) \qquad [-]$$

Which was a dead end because cross linked and bonded polymer stationary phases have $V^L \rightarrow \infty$ and $t_i = t_o$ is predicted.

Prediction of polymer solubility is work in progress.
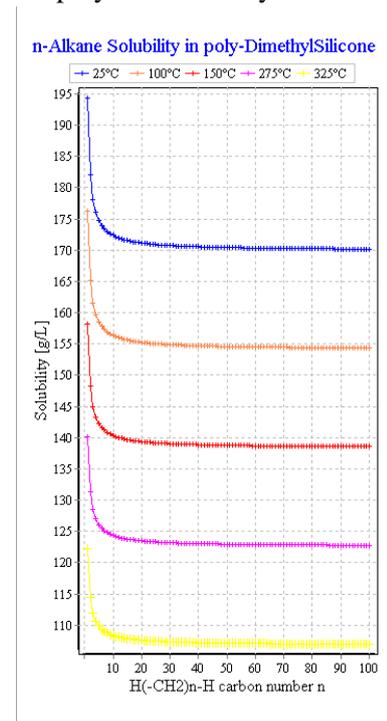
Chromatogram with CH4 to nC100 retention times calculated from solubility and the *P,T* diagram.

2. Fugacity-Filmmodel of mass transfer

Fluid phase systems are encountered in environmental chemistry (fate of persistent organic pollutants) and technical chemistry (distillation and extraction plates). The fugacity-film model assumes liquid and gas phases are well-stirred and that resistance to vaporization is located in the interphase boundary layer. The molar flux J_i^L of compound i through interphase area A is:

$$J_i^L = \kappa_i(f_i^L - f_i^G) \qquad [\text{mol/m}^2\text{/s}]$$

Equilibrium evaporation flux J_i^L is zero because $f_i^G = f_i^L$. Maximum evaporation flux is achieved from a liquid exposed to fresh air with $f_i^G = 0$. Transfer rate κ_i is based on diffusion rate D_i^L [m²/s], film thickness δ_L [m] and the product of gas constant and temperature RT [J/mol]:

$$\kappa_i = D_i^L / \delta_L RT \qquad [\text{mol/N/s}]$$

Fugacity accounts for the Newtons of driving force. Thin films δ_L and fast D_i^L increase evaporation rate. Evidently, elevated temperature T decreases transfer rate, which is compensated by the increase of D_i^L with T. Based on these model equations, the ASTM method D86 distillation is predicted from Detailed Hydrocarbon Analysis[4]. Now the mathematic modeling of equilibrium and transport are given, the physical property values need to be solved. StillPeaks software combines this behind a user friendly Graphical User Interface.

References

This publication ties together separation science over a wide time span. The science of Solid-Vapor-Liquid equilibria (Henry 1800), Properties of Binary and Multicomponent Mixtures (>1900) of Molecules (Stokes-Einstein 1904) and the Pure Liquids (van der Waals 1998) can be formulated with fugacity (Lewis 1924 Shiu & McKay 1984) and the filmmodel (Whitman 1927) to obtain the fugacity-filmmodel (1998 Spieksma).

Fugacity-Filmmodel of evaporation:
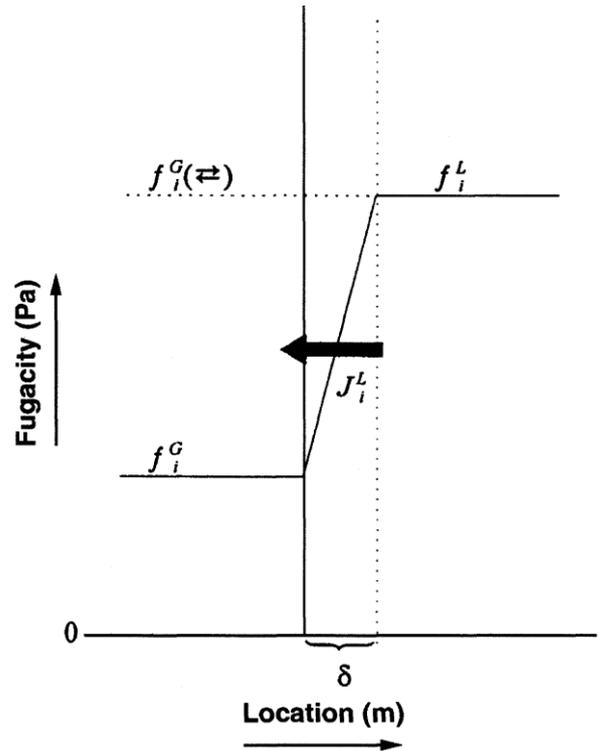
Concentration based driving forces jump at the LG interphase following Henry's law.

Calculation of ASTM D86 dewpoints compared to physical data (crosses):