Vapor Liquid Equilibrium Calculator: VLECalc **Version 1.3**

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Changes since Version 1.1

- conversion from shareware to freeware

Changes since Version 1.2

- updated documentation to reflect vlecalc.org domain

VLECalc is a program that allows the user to

1) Calculate the system pressure, partial pressures and activity components of a solution at a specified composition and temperature
2) Calculate the boiling point of a specified mixture at a specified pressure
3) Calculate the saturation solubility when dissolving a material above its boiling point in a solvent.
4) Calculate and graph the VLE relationship of a binary mixture
5) Calculate and graph the course of a simple distillation of a multicomponent mixture

The compounds/solvents of interest may be selected from the dataset provided, or be added at the users discretion. The user may select ideal, UNIFAC or NRTL methods for the activity coefficient calculations.

VLECalc assumes that there is only one liquid phase. The results of the calculation do not apply in the case of two or more liquid phases.

VLE Calc requires Microsoft Windows 95 and Microsoft Excel 97.

Licensing and Disclaimer

VLECalc is fully functional and distributed as freeware. No fee may be charged for the use or distribution of this program.

The author will accept no liability for any use of the results provided by this program and cannot guarantee the accuracy or validity of the results. Furthermore, the author will accept no responsibility of the loss of any data or damage of any equipment or systems resulting from the use of the program. Use at your own risk.

1. Vapor Liquid Equilibrium

The condition of thermodynamic equilibrium in a multicomponent two phase (vapor and liquid) system is

$$f_i^V = f_i^L$$

where f is the fugacity of component i in the vapor or liquid phase. To a good approximation, this fundamental relationship can be described by the relationship:

$$y_i P = \gamma_i P_{vi} x_i$$

where y_i and x_i are the mole fractions of component i in the vapor and liquid phases respectively, P is the total system pressure, $P_{vi}(T)$ is the vapor pressure of pure component i at the system temperature T and $\gamma_i(T,\underline{x})$ is the activity coefficient of component i in the liquid phase, which is a function of the composition $\underline{x}$ of all components in the system. The partial pressure of component i in the system is equal to $y_i P$. This equation assumes that the vapor behaves as an ideal mixture and an ideal gas.

Given T and the liquid phase component volumes (L_i = 1 to N), VLECalc estimates the system partial pressures. The relationships between the L_i and the molar composition variables are:

$$v_i = L_i / \Sigma L_i$$

$$x_i = v_i (\rho_i/M_i) / \Sigma v_i (\rho_i/M_i)$$

where v_i is the liquid phase volume fraction, ρ_i is the pure component liquid density and M_i is the molecular weight and the sums are carried out over the N compounds of the system. These relationships neglect volume changes of mixing, liquid phase compressibility and liquid phase thermal expansion of the liquid. A similar relationship is used for the vapor phase mole fractions:

$$y_i = w_i(\rho_i/M_i) / \Sigma w_i (\rho_i/M_i)$$

where w_i is the volume fraction of i in a liquid with a molar composition equal to that of the vapor phase.

VLECalc determines the boiling point of a mixture of liquids at total pressure P by iterating on the system temperature until the estimated sum of partial pressure equals P (within 0.5%).

The saturation point calculation is done isothermally by adjusting the solute/solvent ratio until the estimated system pressure equals the specified value. This calculation requires that the specified system temperature is above the boiling point of the solute species and below that of the solvent. The solvent can can be a mixture.

The Antoine equation is used to estimate the pure component vapor pressures $P_{vi}(T)$:

$$\log_{10} (P_{vi}) = A_i – B_i/(T + C_i)$$

The numerical values of the Antoine parameters A, B, and C depend on the units in which P_v and T are expressed as well as the base of the logarithm. VLECalc uses the Antoine constants with T in Celcius, P_v in mm Hg and the base 10 logarithm.

Generally, a recommended minimum and maximum temperature range is recommended for the Antoine equation of a compound. The user can expect the accuracy of the equation to diminish the further out of the recommended range this equation is used. VLECalc reports these Antoine extrapolations to the user.

Three models for the activity coefficients are available within VLECalc: Ideal, UNIFAC and NRTL.

The ideal model is very simple:

(ideal) $\gamma_i = 1$ $\qquad$ i = 1 to N

The UNIFAC model[i] is a “group contribution” method. Each molecule is taken composite of subgroups; for example, t-butanol is composed of 3 “CH_3” groups, 1 “C” group and 1 “OH” group. There are a finite number (85) such subgroups currently defined. The interactions are defined between molecules at the subgroup level. This precludes the need for molecule/molecule interaction parameters. In essence, the γ_i can be calculated from pure component properties only.

The NRTL[ii] (Non Random Two Liquid) model uses three binary interaction parameters (BIPs) for each binary pair in a multicomponent mixture. There are N(N-1)/2 such molecular binary pairs for an N component system.

Values for the Antoine constants, the UNIFAC group interaction parameters and the NRTL BIPs are available in the literature. DECHEMA has published an extensive set of such information[iii]

2. Distillation

VLECalc can be used to model the progress of a simple "up and over" batch distillation. This calculation assumes no purification "stages" or liquid reflux is occurring during the distillation. It neglects the molar hold-up of the vapor phase in the still. It also assumes that the distillation rate is slow enough so that the distillate composition at any point is that of the vapor in equilibrium with the still pot liquid. It also assumes that a single liquid phase exists during the course of the distillation.

Given a still pot volume V and a distillation rate D:

$$dV/dt = -D$$

and

$$d(v_iV)/dt = -w_iD$$

where v_i is the volume fraction of i in the still pot and w_i is the volume fraction of i in the (instantaneous) distillate. These can be arranged to the Rayleigh equation:

$$dv_i/dr = (w_i - v_i) / (r - 1) \qquad v_i(r=0) = v_{i0} \text{ (known initial still pot volume fractions)}$$

where $r = (V(t=0) – V)/ V(t=0)$.

Given the relationship between the w_i and v_i provided by the boiling point calculation, this equation can be integrated. VLECalc use the 4th order Runge-Kutta algorithm for this integration.

3. Installation and Setup

Download and unzip VLECalc.zip in a folder. Then run "Setup" to install in Windows 95 or NT to install in another folder of your choice. All of the necessary DLL and OCX files are packaged in the zip file. The compound specific data – the Antoine constants, UNIFAC subgroup composition, NRTL BIPs – are contained in an Excel 97 file, cmpds.xls. This file may be renamed or relocated as desired. The user may add his/her own data to this file as desired.

[ii] Renon, H., Prausnitz, J.M., *AIChE Journal*, **14**, 135 (1968)

[iii] Gmehling, J. Onken, U., Arlt., W., *Vapor-Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series 1; Frankfurt, (1977).

[i] Fredenslund, Aa., Jones, R.L., Prausnitz, J.M., *AIChE Journal*, **21**, 1086 (1975); Fredenslund, Aa., Gmehling, J., Rasmussen, P., "Vapor-Liquid Equilibria Using UNIFAC", Elsevier, Amsterdam, (1977); Fredenslund, Aa., Gmehling, J., Michelsen, M.L., Rasmussen, P., Prausnitz, J.M., *Ind. Eng. Chem. Process Dev.*, **16**, 450 (1977); Skjold-Jorgensen, S., Kolbe, B., Gmehling, J., Rasmussen, P., *Ind. Eng. Chem. Process Des. Dev.*, **18**, 714 (1979); Gmehling, J., Rasmussen, P., Fredenslund, Aa., *Ind. Eng. Chem. Process Des. Dev.*, **21**, 118 (1982); Macedo, E.A., Weidlich, U., Gmehling, J., Rasmussen, P., *Ind. Eng. Chem. Process Des. Dev.*, **22**, 678 (1983); Tiegs, D., Gmehling, J., Rasmussen, P., Fredenslund, Aa., *Ind. Eng. Chem. Res.*, **26**, 159 (1987)

VLECalc works with Microsoft Excel 97 to provide the interface to the cmpds.xls and to capture the output of the calculations. Microsoft Excel 97 must be installed on the user's computer to successfully load VLECalc. VLECalc will not work with Excel 95.

4. Using the program

The user defines the molecular system to be evaluated with the buttons/combo boxes on the left of the start-up form. The dropdown list in the combo box gives the names of all of the compounds provided in the "Cmpd Data" sheet of the compound database, in the order given in that sheet. This order can be rearranged to meet the user's preference- it does not need to be alphabetical. **DO NOT reorder the columns in any sheet**. **DO NOT rename the sheet tab.**

The OLE automation link to the compound database on this form allows the user to edit the database while running VLECalc. The combo box drop down lists will be updated upon return of control to VLECalc. The "Notes" sheet gives additional information about the use of the compound database.

The user selects the activity coefficient model, the type of calculation desired and presses "Next". This launches the chosen calculation form. The user returns to the startup form by closing the calculation form using the (X) box in the upper right corner.

The "Vapor Pressure" calculation allows the user to define the system L_i and T. The "Boiling Point" calculation allows the user to define the system L_i and P. In each case, the equations defined in section 1 above are calculated.

If the "Capture Calc" box is checked, the results will be captured by Excel. The results are also provided in the "grid" on the form.

The "Saturation" calculation allows the user to define T, P and up to 5 L_i that constitue the "solvent", totaling volume S. T must be below the boiling point of the solvent and above the boiling point of the "solute" at P. The solute species is added gradually to the solvent (at fixed T, P), until the total of the estimated partial pressures equals P.

The "Binary VLE" calculation requires that only two compounds are selected for the system. The user specifies P. VLECalc then performs a series of boiling point calculations and captures the results to the grid and to the graph. By highlighing the X axis or Y axis text box and then clicking on the desired column of the grid, any two the the calculated results can be plotted against each other. A "45 degree" line is plotted if the X vs X box is checked. The notation used:

LVF(i) <=> v_i ; LMF(i) <=> x_i; Gam(i) <=> γ_i; PV(i) <=> P_{vi}; VMF(i) <=> y_i; VVF(i) <=> w_i

The "Distillation" calculation allows the user to define the initial system L_i and P as well as the final volume to which the still pot is taken. After an initial distillation step, the user can add "shots" of solvent to help "chase" out a solvent during a solvent exchange operation. Up to 4 shots can be added.

The user also specifies the step size (in volume units) for the integration as well as the step size that the user wishes to capture the data for the plot/spreadsheet. Usually the data capture step size is larger than the integration step size to keep the volume of output to a managable level.

After running a distillation simulation, the user can graph the resultant volume fractions (of the still pot, the instantaneous distillate and the cummulative disillate) against the cummulative distillate volume by pressing the "Graph" button. These estimates are also captured to Excel if the Capture Data box is checked.

5. Excel Interface

If Excel is not running when VLECalc is started, it will be loaded when a calculation is captured. The user can view the results, save them to disk, plot them in Excel as desired. When the user closes the main form using the (X) box in the upper right corner, the user is prompted to save the captured data in whatever directory the user chooses.

6. Comments

Email: mail@vlecalc.org

Web: http://www.vlecalc.org

VLECalc is programed in Visual Basic 4.0 Standard Edition (32 bit) and uses the Excel 8.0 object library (Excel8.olb). The graphics are provided courtesy of the gslite freeware control version 2.53 published by Bits per Second Ltd. 1996