

CISP

Calculating properties of multi-component mixtures

Mixture software Tutorial

2008

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Introduction

The version 2 of the MIXTURE++ program is intended for estimation of the physical properties of both the pure compounds (mainly gas or liquid) and their mixtures. This is the list of these properties:

- Density

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- Vapor pressure
- Heat of vaporization
- Heat capacity
- Heat conductivity
- Viscosity
- Surface tension

As a rule these properties are functions of temperature, pressure and (in case of mixtures) on the mole fractions of the components. So this is the reason for MIXTURE++ to calculate gas-liquid equilibrium of multi-component system.

It is planned that MIXTURE++ is capable to extract the desired data from at least two databases. The first one is its own database and the second one is DIPPR ® 801 database. As it will be shown below for estimation of some properties it is necessary to know some other data. Therefore the user should be provided with the ability to input them manually, to extract from a database or to use the value that may be estimated by MIXTURE++ itself. The user should be provided also with the possibility to input temperature dependency of a property presented as combination of usual mathematical expressions.

The methods and algorithms listed below were chosen taking in account their applicability to as wide as possible temperature and concentration ranges, their ability to give the least errors and to require as little input parameters as possible.

Mixture Properties

Specific heat of real gases

Method of Lee and Kesler:

$$C_p - C_p^0 = (\Delta C_p)^{(0)} + \omega(\Delta C_p)^{(1)}$$

where C_{p0} – specific heat of ideal gas; ω - Pitzer's acentric factor

The values of $(\Delta C_p)^{(0)}$ and $(\Delta C_p)^{(1)}$ are functions of reduced temperature and pressure and may be found in the tables 5-8 и 5-9 [1].

These tables and the above equation may be used for the gas mixtures too but in this case the reduced temperature, pressure and the mixture constant ω_m should be calculated by use of the following mixing rules:

$$\begin{aligned} T_{cm} &= \frac{1}{V_{cm}^{1/4}} \sum_i \sum_j y_i y_j V_{cij}^{1/4} T_{cij} & T_{cij} &= (T_{ci} T_{cj})^{1/2} k'_{ij} \\ V_{cm} &= \sum_i \sum_j y_i y_j V_{cij} & V_{cij} &= \frac{1}{8} (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \\ \omega_m &= \sum_i y_i \omega_i & P_{cm} &= (0.2905 - 0.085\omega_m) RT_{cm} / V_{cm} \end{aligned}$$

k'_{ij} is a binary parameter that is specific for the method of Lee and Kesler. Its values for some binary mixtures are given in table 4-4 [1]. Besides it for hydrocarbon-hydrocarbon, nitrogen-hydrocarbon, CO₂-hydrocarbon and hydrogen-hydrocarbon systems there are data on the dependency of the value of k'_{ij} upon the relation $T_{ci} V_{ci} / T_{cj} V_{cj}$. These dependencies are shown in Fig. 4-2, 4-3, 4-4 and 4-5 [9-1] and may be converted if necessary from graphical to analytical form.

Density of liquid mixtures

At the moment we are forced to use simple additive estimation. Though maybe after more thorough testing we'll try to use one form of cubic Equation of State (so called Generalized Form Equation of State) that report to give small errors in determination of liquid density. In the worst cases these errors are as small as 10%.

Heat capacity of liquid mixtures

At the moment the pure additive model will be used so neglecting heats of mixing.

Viscosity of liquid mixtures

Method of Teja and Rice

This method is based on the principle of corresponding states.

$$\eta_m = \frac{e^{\ln(\eta\varepsilon)^{(r1)} + [\ln(\eta\varepsilon)^{(r2)} - \ln(\eta\varepsilon)^{(r1)}] \frac{\omega_m - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}}}}{\varepsilon_m};$$

where the superscripts (r1) and (r2) refer to two reference fluids with the known viscosity. It is preferable to choose as such fluids two main components of the given multi-component mixture

ω - Pitzer's acentric factor; η_m – mixture viscosity;

$$\varepsilon = \frac{V_c^{2/3}}{(T_c M)^{1/2}} \text{ - specific for every fluid parameter}$$

$$\varepsilon_m = \frac{V_{cm}^{2/3}}{(T_{cm} M_m)^{1/2}} \text{ - analogous parameter for mixture, where}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij}; \quad T_{cm} = \frac{\sum_i \sum_j x_i x_j T_{cij} V_{cij}}{V_{cm}}; \quad M_m = \sum_i x_i M_i; \quad \omega_m = \sum_i x_i \omega_i$$

$$V_{cij} = \frac{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}{8}; \quad T_{cij} V_{cij} = \psi_{ij} (T_{ci} T_{cj} V_{ci} V_{cj})^{1/2}$$

ψ_{ij} - is an interaction parameter of order unity. There should be possible for user to input it manually, to choose its default value (unity) or calculate from experimental data. It is important to note that for a given mixture at a specified temperature, the viscosity values for the two reference fluids $\eta^{(r1)}$ and $\eta^{(r2)}$ are to be obtained not at T but at temperature equal to $T[(T_c^{(r1)})/T_{cm}]$ for the first and $T[(T_c^{(r2)})/T_{cm}]$ for the second fluid.

For non-polar mixtures, errors average about 1%. For nonpolar-polar and polar-polar mixtures, the average rises to about 2.5%, whereas for mixtures containing water to about 9%.

Viscosity of suspensions

In accordance with the Einstein' Equation viscosity of suspension refers to viscosity of pure liquid as follows:

$$\eta = \eta_0 \frac{1 + \phi/2}{(1 - \phi)^2};$$

where ϕ - volume fraction of the solid phase in suspension.

Viscosity of gas mixtures

For estimation of gas mixture viscosity the same as for pure gas scheme is to be used. The exception is that instead of pure gas constants T_c , P_c and M there are analogous mixture constants that are preliminary calculating in accordance with Lucas mixing rules:

$$T_{cm} = \sum_i y_i T_{ci}; \quad P_{cm} = RT_{cm} \frac{\sum_i y_i Z_{ci}}{\sum_i y_i V_{ci}}; \quad M_m = \sum_i y_i M_i$$

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In addition to them the mixture correction coefficients are calculated as follows:

$$F_{Pi}^0 = \sum y_i F_{Pi}^0 ; F_{Qi}^0 = \left(\sum_i y_i F_{Qi}^0 \right) A ;$$

If subscript H refer to the component with the highest molecular weight and L to the one with the lowest then A is:

$$A = 1 - 0.01 \left(\frac{M_H}{M_L} \right)^{0.87} \quad \text{if } \frac{M_H}{M_L} > 9 \text{ and } 0.05 < y_H < 0.7 ; A = 1 \text{ in all other cases.}$$

Quantum mixture correction coefficient should be calculated only if at least one component of a mixture is He, H₂ or D₂.

So in case of gas mixtures critical volumes and molar fractions of components are to be added to the list of necessary parameters.

Heat conductivity

Heat conductivity of gas mixtures

Heat conductivity of gas mixtures at low pressure

Method of **Wasiljeva-Mason-Saxena-Wilke**

The required input data are:

λ_i - heat conductivity of pure components at low pressure

η_i - viscosity of pure components at low pressure

y_i - mole fraction

M_i - molecular weight

Then $\lambda_m = \frac{\sum_{i=1}^n y_i \lambda_i}{\sum_{j=1}^n y_j \phi_{ij}}$, where λ_m - mixture heat conductivity, and $\phi_{ij} = \frac{\left[1 + (\eta_i/\eta_j)^{1/2} (M_j/M_i)^{1/4} \right]^2}{\left[8(1 + M_i/M_j) \right]^{1/2}}$.

For time saving the next relation may be used: $\phi_{ji} = \frac{\eta_j M_i}{\eta_i M_j} \phi_{ij}$

For mixtures with non-polar components the errors average about 3-4%, if some components are polar then 5-8% as usual.

Heat conductivity of gas mixtures at high pressure

Method of Chung et al:

This method requires performing cumbersome calculation but its easy to program:

$$\begin{aligned} \frac{\varepsilon_i}{k} &= \frac{T_{ci}}{1.2593} & \sigma_i &= 0.809V_{ci}^{1/3} & \sigma_{ii} &= \sigma_i \\ \sigma_{ij} &= (\sigma_i \sigma_j)^{1/2} & \frac{\varepsilon_{ii}}{k} &= \frac{\varepsilon_i}{k} & \frac{\varepsilon_{ij}}{k} &= \left(\frac{\varepsilon_i}{k} \frac{\varepsilon_j}{k} \right)^{1/2} \\ \kappa_{ii} &= \kappa_i & \kappa_{ij} &= (\kappa_i \kappa_j)^{1/2} & \omega_{ii} &= \omega_i \\ \omega_{ij} &= \frac{\omega_i + \omega_j}{2} & M_{ii} &= M_i & M_{ij} &= \frac{2M_i M_j}{M_i + M_j} \\ \sigma_m^3 &= \sum_i \sum_j y_i y_j \sigma_{ij}^3 & \kappa_m &= \sum_i \sum_j y_i y_j \kappa_{ij} & \mu_m^4 &= \sigma_m^3 \sum_i \sum_j \left(\frac{y_i y_j \mu_i^2 \mu_j^2}{\sigma_{ij}^3} \right) \\ \mu_{rm} &= \frac{131.3 \mu_m}{(V_{cm} T_{cm})^{1/2}} & T_m^* &= \frac{T}{\left(\frac{\varepsilon}{k} \right)_m} & \left(\frac{\varepsilon}{k} \right)_m &= \frac{\sum_i \sum_j y_i y_j (\varepsilon_{ij}/k) \sigma_{ij}^3}{\sigma_m^3} \\ M_m &= \left[\frac{\sum_i \sum_j y_i y_j (\varepsilon_{ij}/k) \sigma_{ij}^2 M_{ij}^{1/2}}{(\varepsilon/k)_m \sigma_m^2} \right]^2 & \omega_m &= \frac{\sum_i \sum_j y_i y_j \omega_{ij} \sigma_{ij}^3}{\sigma_m^3} & V_{cm} &= (\sigma_m/0.809)^3 \\ T_{cm} &= 1.2593 \left(\frac{\varepsilon}{k} \right)_m & F_{cm} &= 1 - 0.275 \omega_m + 0.059035 \mu_m^4 + \kappa_m \end{aligned}$$

$$\Omega_v = \left[A(T_m^*)^{-B} \right] + C \left[\exp(-DT_m^*) \right] + E \left[\exp(-FT_m^*) \right]$$

where A=1.16145, B=0.14874, C=0.52487, D= 0.77320, E=2.16178, F=2.43787

$$\eta_m^0 = \frac{26.69 F_{cm} (M_m T)^{1/2}}{\sigma_m^2 \Omega_v} \text{ - viscosity of mixture at low temperature}$$

$$T_{rm} = \frac{T}{T_{cm}}; C_{pm}^0 = \sum_i y_i C_{pi}^0; \alpha_m = \frac{C_{pm}^0 - R}{R} - \frac{3}{2}; \beta_m = 0.7862 - 0.7109 \omega + 1.3168 \omega_m^2; Z = 2.0 + 10.5 T_r^2;$$

$$\Psi = 1 + \alpha_m \left\{ [0.215 + 0.28288 \alpha_m - 1.061 \beta_m + 0.26665 Z] / [0.6366 + \beta_m Z + 1.061 \alpha_m \beta_m] \right\}$$

$$M'_m = \frac{M_m}{1000} \text{ - molecular weight of mixture, kg/mole}$$

$$\lambda_m = \frac{31.2 \eta_m^0 \Psi}{M'_m} \left(G_2^{-1} + B_6 y_m \right) + q B_7 y_m^2 T_{rm}^{1/2} G_2$$

where $q, G_1, G_2, y_m, B_{1..7}$ are to be calculated the same way as in method of Chung for heat conductivity of pure gases at high pressure with using of the proper mixture values of $V_m, \omega_m, \mu_{rm}, \kappa_m$.

It's clear that mixture molar volume is an input parameter too and it should be preliminary calculated as discussed above.

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The errors for non-polar gases are about 5%. Its applicability for polar mixtures is questionable.

Heat conductivity of liquid mixtures

Method of Li:

$$\lambda_m = \sum_{i=1}^n \sum_{j=1}^n \phi_i \phi_j \lambda_{ij} \quad \text{where} \quad \lambda_{ij} = 2(\lambda_i^{-1} + \lambda_j^{-1})^{-1}; \quad \phi_i = \frac{x_i V_i}{\sum_{j=1}^n x_j V_j}$$

where λ_i , x_i , V_i are the heat conductivity of pure component, its mole fraction in the mixture and its molar volume. For mixtures not containing water the molar volumes of pure components at specified temperature may be substituted with critical molar volumes.

Diffusion coefficients

Diffusion coefficients in binary gas mixtures

At medium pressures **Method of Fuller** is recommended:

$$D_{AB} = \frac{0.00143 T^{1.75}}{PM_{AB}^{1/2} \left[(\sum_v)_A^{1/3} + (\sum_v)_B^{1/3} \right]^2};$$

where D_{AB} – binary diffusion coefficient, cm²/sec; T – temperature, K

P – pressure, bar; $M_{AB} = 2[(1/M_A) + (1/M_B)]^{-1}$

M_A and M_B – molecular weights of components A and B, g/mole;

$(\sum_v)_A$ and $(\sum_v)_B$ - are the sums of atomic and structural volumes that are given in the next Table:

Atomic and structural increment of diffusion volumes			
C	15.9	F	14.7
H	2.31	Cl	21.0
O	6.11	Br	21.9
N	4.54	I	29.8
Aromatic ring	-18.3	S	22.9
Heterocyclic ring	-18.3		

For some simple molecules the diffusion volumes are given in the next Table:

Diffusion volumes of simple molecules			
He	2.67	CO	18.0
Ne	5.98	CO ₂	26.9
Ar	16.2	N ₂ O	35.9
Kr	24.5	NH ₃	20.7
Xe	32.7	H ₂ O	13.1
H ₂	6.12	SF ₆	71.3
D ₂	6.84	Cl ₂	38.4
N ₂	18.5	Br ₂	69.0
O ₂	16.3	SO ₂	41.8
Air	19.7		

The errors average about 4%. The range of applicability is up to 10-15 bar.

If the pressure is greater then **Correlation of Takahashi** should be used:

There it is assumed that

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$$\frac{D_{AB}P}{(D_{AB}P)^+} = f(T_r, P_r);$$

where pseudo-critical values T_c and P_c for calculation of T_r and P_r are to be calculated as follows:

$$T_c = y_A T_{cA} + y_B T_{cB}; \quad P_c = y_A P_{cA} + y_B P_{cB}$$

The function $f(T_r, P_r)$ is shown in Fig. 11-3 [9-1]. For purpose of computer calculation this figure should be transformed into a table. The Table of such type is using, for example, in the method of Lee and Kesler.

Diffusion coefficients in liquid mixture

Binary diffusion coefficients at infinite dilution

The solution of A in B is considered to be infinitely diluted up to concentration of A equal to 10%.

For estimation of diffusion coefficient D_{AB}^0

Modified method of Tyn and Calus can be used:

$$D_{AB}^0 = 8.93 \times 10^{-8} \frac{V_B^{0.267}}{V_A^{0.433}} \frac{T}{\eta_B} \left(\frac{\sigma_B}{\sigma_A} \right)^{0.15};$$

where D_{AB}^0 - diffusion coefficient of component A in a solute B, cm^2/sec

V_A, V_B - molar volumes of A and B at their normal boiling temperatures, cm^3/mole

η_B - viscosity of a solute B, centipoise

σ_A, σ_B - surface tensions of A and B at their normal boiling temperatures, dyn/cm

The required surface tensions may be estimated as follows:

$$\sigma = P_c^{2/3} T_c^{1/3} (0.132 \alpha_c - 0.278) (1 - T_{br})^{11/9}$$

$$\text{where } P_c \text{ in bars, } T_b \text{ and } T_c \text{ in Kelvin, } T_{br} = T_b/T_c \text{ and } \alpha_c = 0.9076 \left[1 + \frac{T_{br} \ln(P_c/1.013)}{1 - T_{br}} \right]$$

Errors are within 10-15% as a rule.

The method is not valid (like all others) if viscosity of a solute is greater than 30 centipoises.

Dependency of binary diffusion coefficients upon concentration

If the concentration of a component is greater than 20%

Corralation of Vignes should be applied:

$$D_{AB} = \left[(D_{AB}^0)^{x_B} (D_{BA}^0)^{x_A} \right] \alpha;$$

where α - coefficient of thermodynamic correction; $\alpha = \left[\left(\frac{\partial \ln a}{\partial \ln x} \right) \right]_{P,T}$; a - activity coefficient

Due to Gibbs-Duhem equation it doesn't matter what a component to use for calculation. The result will be the same.

Dependency of binary diffusion coefficients upon pressure

For we assume the viscosity of component at specified pressure to be estimated preliminary then pressure correction may be applied to diffusion coefficient:

$$\left(D_{AB}^0 \right)_P = \frac{\left(D_{AB}^0 \right)_{\text{low}} \eta_{\text{Blow}}}{\eta_{BP}}$$

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Diffusion in multi-component liquid systems

It seems there is no simple and convenient way for estimation of flux of any component in multi-component liquid mixture. The only possibility is to estimate the diffusion of a solute that diffuses through a homogeneous solution of mixed solvents.

Perkins and Geankoplis had suggested

$$D_{Am}^0 = \frac{\sum_{\substack{j=1 \\ j \neq A}}^n x_j D_{Aj}^0 \eta_j^{0.8}}{\eta_m^{0.8}};$$

where D_{Am}^0 - effective diffusion coefficient for a dilute solute A into mixture, cm³/sec

D_{Aj}^0 - infinite dilution binary coefficient of solute A into the solvent j, cm³/sec

η_m - mixture viscosity, cP

η_j - pure component viscosity, cP

x_j - mole fraction of j.

When tested with data for eight ternary systems, errors were normally less than 20%, except for cases involving CO₂. For CO₂ as a solute diffusing into mixed solvents **Takahashi** et al recommend:

$$D^0(\text{CO}_2 - m) \left(\frac{\eta_m}{V_m} \right)^{1/3} = \sum x_j D^0_{(\text{CO}_2-j)} \left(\frac{\eta_j}{V_j} \right)$$

,where V_m and V_j - molar volumes in cm³/mole if a mixture and solute respectively.

This equation gives errors less than 4% as a rule.

Surface tension of liquid mixtures

Method of Macleod and Sugden for mixtures:

$$\delta_m^{1/4} = \sum_{i=1}^n [P_i] (\rho_{Lm} x_i - \rho_{Vm} y_i);$$

where σ_m - surface tension of mixture, dyn/cm; $[P_i]$ - parachor of component (i);

x_i, y_i - mole fractions of (i) in liquid and gas phases;

ρ_{Lm}, ρ_{Vm} - liquid and gas density, mole/cm³

Parachor of pure component in case it wasn't determined by group contribution method may be calculated as follows:

$$[P] = \frac{\sigma^{1/4}}{(\rho_L - \rho_v)}, \text{ where all the values refer to the pure component.}$$

Substances Properties

Constant properties

The following constant substance properties can be estimated:

- critical pressure;
- critical temperature;
- normal boiling temperature;
- critical compressibility;
- critical molar volume;
- Pitzer's acentric factor;
- enthalpy of ideal gas formation.

All of them, except enthalpy of ideal gas formation, are estimated by special method developed by Dr. S.L. Dobychn. For estimating properties by this method one has to describe substance chemical structure and specify some additional information about substance type (e.g. whether it is acid or alcohol), if required. This method is also used to estimate vapor pressure of pure liquid. Results of estimating by using this method for substances of different types can be seen in the following table:

	Pc	Tc	Tb	Zc	Vc	ω
o-Xylene	2.6%	0.63%	0.60%	0%	0.81%	3.2%
Acetophenone	2.3%	4.7%	4.3%	2.4%	3.6%	1.1%
Acetophenone (with T _b)*	2.3%	0.34%	-	2.4%	3.6%	1.1%
1-Butanol	2.4%	1.2%	0.92%	3.5%	2.9%	0.34%
Ethyl Fluoride	0.76%	1.7%	2.2%	1.9%	6.1%	13%
o-Dichlorobenzene	0.34%	2.7%	1.2%	4.5%	0.28%	30%

*) There are two results for Acetophenone because for some substances error in normal boiling temperature is quite big so it's better to input it manually, if possible.

As for enthalpy of ideal gas formation, it is estimated by Joback method, which is described in "Specific heat of Ideal gas" chapter.

Specific heat of Ideal gas

Up to nowadays for estimation of ideal gas heat capacities Joback's method is extensively used and gives rather good results. It also allows to estimate enthalpy of ideal gas formation.

Joback's method:

$$C_p^0 = \left(\sum_j n_j \Delta_a - 37.93 \right) + \left(\sum_j n_j \Delta_b + 0.210 \right) T + \left(\sum_j n_j \Delta_c - 3.91 \times 10^{-4} \right) T^2 + \left(\sum_j n_j \Delta_d + 2.06 \times 10^{-7} \right) T^3;$$

$$H_{form} = \sum_j n_j \Delta_H + 6.829 \times 10^7;$$

where n_j is the number of j-type group in the molecule and Δ is the corresponding group contributions whose values are shown in the following table:

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	Δ values, J/mol K				
	Δ_a	Δ_b	Δ_c	Δ_d	Δ_H
Non-ring increments					
-CH ₃	1.95E+1	-8.08E-3	1.53E-4	-9.67E-8	-7.645E+7
>CH ₂	-9.09E-1	9.50E-2	-5.44E-5	1.19E-8	-2.064E+7
>CH-	-2.30E+1	2.04E-1	-2.65E-4	1.20E-7	2.989E+7
>C<	-6.62E+1	4.27E-1	-6.41E-4	3.01E-7	8.223E+7
=CH ₂	2.36E+1	-3.81E-2	1.72E-4	-1.03E-7	-9.63E+6
=CH-	-8.00	1.05E-1	-9.63E-5	3.56E-8	3.797E+7
=C<	-2.81E+1	2.08E-1	-3.06E-4	1.46E-7	8.399E+7
=C=	2.74E+1	-5.57E-2	1.01E-4	-5.02E-8	1.4214E+8
≡CH	2.45E+1	-2.71E-2	1.11E-4	-6.78E-8	7.93E+7
≡C-	7.87	2.01E-2	-8.33E-6	1.39E-9	1.1551E+8
Ring increments					
-CH ₂ -	-6.03	8.54 E-2	-8.00 E-6	-1.80 E-8	-2.68E+7
>CH-	-2.05E+1	1.62 E-1	-1.60 E-4	6.24 E-8	8.67E+6
>C<	-9.09E+1	5.57 E-1	-9.00 E-4	4.69 E-7	7.972E+7
=CH-	-2.14	5.74 E-2	-1.64 E-6	-1.59 E-8	2.09E+6
=C<	-8.25	1.01 E-1	-1.42 E-4	6.78 E-8	4.643E+7
Halogen increments					
-F	2.65E+1	-9.13E-2	1.91E-4	-1.03E-7	-2.5192E+8
-Cl	3.33E+1	-9.63E-2	1.87E-4	-9.96E-8	-7.155E+7
-Br	2.86E+1	-6.49E-2	1.36E-4	-7.45E-8	-2.948E+7
-I	3.21E+1	-6.41E-2	1.26E-4	-6.87E-8	2.106E+7
Oxygen increments					
-OH (alcohol)	2.57E+1	-6.91E-2	1.77E-4	-9.88E-8	-2.0804E+8
-OH (phenol)	-2.81	1.11E-1	-1.16E-4	4.94E-8	-2.2165E+8
-O- (nonring)	2.55E+1	-6.32E-2	1.11E-4	-5.48E-8	-1.3222E+8
-O- (ring)	1.22E+1	-1.26E-2	6.03E-5	-3.86E-8	-1.3816E+8
>C=O (nonring)	6.45	6.70E-2	-3.57E-5	2.86E-9	-1.3322E+8
>C=O (ring)	3.04E+1	-8.29E-2	2.36E-4	-1.31E-7	-1.645E+8
O=CH- (aldehyde)	3.09E+1	-3.36E-2	1.60E-4	-9.88E-8	-1.6203E+8
-COOH (acid)	2.41E+1	4.27E-2	8.04E-5	-6.87E-8	-4.2672E+8
-COO- (ester)	2.45E+1	4.02E-2	4.02E-5	-4.52E-8	-3.3792E+8
=O (except as above)	6.82	1.96E-2	1.27E-5	-1.78E-8	-2.4761E+8
Nitrogen increments					
-NH ₂	2.69E+1	-4.12E-2	1.64E-4	-9.76E-8	-2.202E+7
>NH (nonring)	-1.21	7.62E-2	-4.86E-5	1.05E-8	5.347E+7
>NH (ring)	1.18E+1	-2.30E-2	1.07E-4	-6.28E-8	3.165E+7
>N- (nonring)	-3.11E+1	2.27E-1	-3.20E-4	1.46E-7	1.2334E+8
>N- (ring)	-	-	-	-	2.361E+7
-N= (nonring)	8.83	-3.84E-3	4.35E-5	-2.60E-8	5.552E+7
-N= (ring)	5.69	-4.12E-3	1.28E-4	-8.88E-8	9.37E+7
-CN	3.65E+1	-7.33E-2	1.84E-4	-1.03E-7	8.843E+7
-NO ₂	2.59E+1	-3.74E-3	1.29E-4	-8.88E-8	-6.657E+7
Sulfur increments					
-SH	3.53E+1	-7.58E-2	1.85E-4	-1.03E-7	-1.733E+7
-S- (nonring)	1.96E+1	-5.61E-3	4.02E-5	-2.76E-8	4.187E+7
-S- (ring)	1.67E+1	4.81E-3	2.77E-5	-2.11E-8	3.91E+7

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Results of estimation for different substances:

	C_p^0		H_{form}
	$\epsilon_{average}$	ϵ_{max}	ϵ
o-Xylene	0.46%	1.12%	13%
Acetophenone	8.02%	15.3%	2.5%
Acetophenone (with T_b)	8.02%	15.3%	2.5%
1-Butanol	0.85%	2.69%	1.2%
Ethyl Fluoride	0.41%	1.12%	6.3%
o-Dichlorobenzene	2.15%	3.17%	13%

Vapor pressure of pure liquid

For estimation of vapor pressure of pure liquids we recommend to use

The Equation of Gomez and Todos:

$$\ln P_{vpr} = \beta \left[\frac{1}{T_r^m} - 1 \right] + \gamma [T_r^7 - 1]$$

All the liquids are considered to belong to one of three classes: non-polar (organic and non-organic), polar and those that have hydrogen bonds. Procedures for determining m , β and γ are unique for every class.

Non-polar:

$$\beta = -4.26700 - \frac{221.79}{h^{2.5} \exp(0.0384h^{2.5})} + \frac{3.8126}{\exp(2272.44/h^3)} + \Delta^* ; m = 0.78425 \exp(0.089315h) - \frac{8.5217}{\exp(0.74826h)} ;$$

where: $h = T_{br} \frac{\ln(P_c/1.01325)}{1 - T_{br}}$; $\Delta^* = 0$ with the exception of He (0.41815), H₂ (0.19904), Ne (0.02319); γ is

calculated from the equation $\gamma = ah + b\beta$ where $a = \frac{1 - 1/T_{br}}{T_{br}^7 - 1}$; $b = \frac{1 - 1/T_{br}^m}{T_{br}^7 - 1}$

Polar (with the exception of water and alcohols)

$$m = 0.466T_c^{0.166} ; \gamma = 0.08594 \exp(7.462 \times 10^{-4} T_c)$$

For water and alcohols

$$m = 0.0052M^{0.29} T_c^{0.72} ; \gamma = \frac{2.464}{M} \exp(9.8 \times 10^{-6} M T_c)$$

In the last two cases β is calculated from $\beta = \frac{\gamma}{b} - \frac{ah}{b}$, where a , b and h are calculated like in case of non-polar liquids.

However, in Mixture the special unique method is used (see "Constant properties" chapter). Results of estimation using this method for different substances can be seen in the following table:

	$\epsilon_{average}$	ϵ_{max}
o-Xylene	6.17%	7.34%
Acetophenone	50.8%	63.0%
Acetophenone (with T_b)	2.01%	2.84%
1-Butanol	8.72%	12.1%
Ethyl Fluoride	20.0%	26.4%
o-Dichlorobenzene	15.8%	19.3%

Heat of vaporization.

In accordance with the Clausius-Clayperon equation:

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$$\Delta H_v = T \Delta V_v \frac{dP_v}{dT}$$

In case of pure liquids for calculation of pressure derivative upon temperature some correlation equation (that is used in DIPPR database or Gomez-Todos equation) may be used, and for calculation of ΔV_v - methods of Lee-Kesler and Rackett.

In case of liquid mixtures all the desired values may be calculated by use of Equation of State. And then the solution will be intrinsically non-contradictory.

Results of estimation for different substances:

	$\epsilon_{average}$	ϵ_{max}
o-Xylene	3.57%	8.49%
Acetophenone	8.14%	21.5%
Acetophenone (with T_b)	2.18%	14.4%
1-Butanol	4.44%	23.7%
Ethyl Fluoride	1.49%	5.41%
o-Dichlorobenzene	3.76%	14.0%

Density of pure liquids

Modified method of Rackett:

$$\frac{M}{\rho} = \frac{R \cdot T_c}{P_c} \cdot Z_{RA}^{(1+(1-Tr)^{2/7})};$$

where M is a molar weight in grams, R – gas constant (82,06), T_c – critical temperature in Kelvins, P_c – critical pressure in bars, T_r – reduced temperature (T/T_c), Z_{RA} – constant specific for liquid that should be taken from table 3.10 [1]. As a result the density will be received in g/cm³. In case of unknown Z_{RA} its value may be estimated as follows:

$$Z_{RA} = 0.29056 - 0.08775 \cdot w;$$

where w – Pitzer's acentric factor.

If one experimental density is available that is density of liquid at the reduced temperature T_r , then the following form of Rackett's equation may be recommended:

$$\frac{M}{\rho} = \frac{M}{\rho_R} Z_{RA}^{\phi}, \text{ where } \phi = (1 - T_r)^{2/7} - (1 - T_r^R)^{2/7}$$

The calculation leads to unsatisfactory result in critical point where instead of Z_{RA} one should use Z_c .

So calculated it'll be density at the pressure of saturated vapors at the given temperature. To receive the density at higher pressures the method of Hankinson, Brobst and Thomson may be used:

$$\frac{M}{\rho} = \frac{M}{\rho_s} \left(1 - c \ln \frac{\beta + P}{\beta + P_{vp}} \right);$$

where ρ_s – density at the pressure of saturated vapors and P_{vp} , β and c should be calculated as follows:

$$\beta/P_c = -1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3},$$

$$e = \exp(f + g\omega_{SRK} + h\omega_{SRK}^2) \text{ and } c = j + k\omega_{SRK}.$$

Here ω_{SRK} is the constant specific for liquid; it may be found in Table 3-10 [1]. If it is unknown it may be replaced simply by Pitzer's acentric factor ω .

The constants from a to k are:

$$a = -9.070217 \quad d = -135.1102 \quad g = 0.250047 \quad j = 0.0861488$$

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b = 62.45326

f = 4.79594

h = 1.14188

k = 0.0344483

Results of estimation for different substances:

	$\epsilon_{average}$	ϵ_{max}
o-Xylene	3.71%	5.50%
Acetophenone	6.13%	12.6%
Acetophenone (with T_b)	7.23%	7.72%
1-Butanol	15.0%	19.2%
Ethyl Fluoride	8.50%	13.8%
o-Dichlorobenzene	6.30%	9.28%

Heat capacity of pure liquids

As an input parameter we should know ideal gas heat capacity that may be estimated as discussed above or in case of availability of the proper coefficients in any accessible database may be calculated at any given temperature.

In previous version of program Mixture for liquid heat capacity estimation method of Lee and Kesler was used. But this method is applicable mainly to hydrocarbons and with some restrictions to not very polar liquids.

Now we recommend using the combination of two methods:

Method of Rowlinson and Bondi:

$$\frac{C_{pL} - C_p^0}{R} = 1.45 + 0.45(1 - T_r)^{-1} + 0.25w \left[17.11 + 25.2(1 - T_r)^{1/3} T_r^{-1} + 1.742(1 - T_r)^{-1} \right]$$

$$\frac{C_{pL} - C_{\sigma L}}{R} = \exp(20.1T_r - 17.9); \quad \frac{C_{\sigma L} - C_{satL}}{R} = \exp(8.655T_r - 8.385)$$

Errors are generally less than 5% at the temperatures up to $0.99T_r$. Below $T_r \sim 0.8$ C_{pL} , $C_{\sigma L}$ and C_{satL} may be considered to be the same number. It is not applicable for alcohols at temperatures below $0.75T_r$. In this case and when Pitzer's acentric factor or critical temperature is unknown it is recommended to use The Method of Missenard.

It's a group contribution method. It may be used at temperatures below $0.75T_r$ giving the errors less than 5%. As mentioned above at these temperatures the values of C_{pL} , $C_{\sigma L}$, C_{satL} coincide. Group's increments are listed in Table 5-11 [1].

Results of estimation for different substances:

	Method	$\epsilon_{average}$	ϵ_{max}
o-Xylene	Rowlinson and Bondi	2.60%	3.93%
Acetophenone	Missenard	7.11%	10.7%
Acetophenone (with T_b)	Missenard	7.49%	10.7%
1-Butanol	Missenard	8.25%	19.2%
Ethyl Fluoride	Rowlinson and Bondi	3.86%	5.28%
o-Dichlorobenzene	Rowlinson and Bondi	7.93%	13.9%

Viscosity of pure liquids

Viscosity of pure liquids at high temperatures

For estimation of viscosity of pure liquids at temperatures above $T_r \sim 0,7$ it is recommended to use

Method of Letsou and Stiel:

$$\eta_{SL} = \frac{(\eta_L \xi)^{(0)} + \omega(\eta_L \xi)^{(1)}}{\xi};$$

where

$$(\eta_L \xi)^{(0)} = 10^{-3}(2.648 - 3.725T_r + 1.309T_r^2); (\eta_L \xi)^{(1)} = 10^{-3}(7.425 - 13.39T_r + 5.933T_r^2)$$

$$\xi = 0.176 \left(\frac{T_c}{M^3 P_c^4} \right)^{1/6}.$$

Here T_r is reduced temperature, M – molecular weight, T_c и P_c – critical temperature and pressure, ω - Pitzer's acentric factor. The result will be in centipoises.

Viscosity of pure liquids at low temperature

For estimation of viscosity of pure liquids at temperatures below $T_r \sim 0,7$ one of the following two methods should be used:

Method of Orrick and Erbar

$$\eta_L = \frac{e^{\left(A + \frac{B}{T} \right)}}{\rho_L M};$$

where η_L - viscosity of liquid in centipoises; ρ_L - density of liquid at 20°C, g/cm³; M – molecular weight; T – temperature, K.

For liquids with normal boiling temperature below 20°C it is necessary nevertheless to use the density at 20°C (assuming that liquid is at higher than normal pressure). In case of liquid has melting temperature above 20°C than the density at melting temperature should be used.

So it's useful to mention that:

1. In case of manual input of liquid density, the user should be informed about these circumstances.
2. If it'll be requested to use the estimated density than the melting temperature should be available.

The group contributions are shown in the next Table.

Method of **Orrick and Erbar** is applicable to nitrogen and sulfur containing substances. It gives an average error ~ 15%.

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Group	A	B
Carbon atoms*	$-(6.95+0.21n)$	$275+99n$
$\begin{array}{c} \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	-0.15	35
$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{R} \\ \\ \text{R} \end{array}$	-1.20	400
Double bond	0.24	-90
Five-membered ring	0.10	32
Six-membered ring	-0.45	250
Aromatic ring	0	20
Ortho substitution	-0.12	100
Meta substitution	0.05	-34
Para substitution	-0.01	-5
Chlorine	-0.61	220
Bromine	-1.25	365
Iodine	-1.75	400
-OH	-3.00	1600
-COO-	-1	420
-O-	-0.38	140
$\begin{array}{c} \\ -\text{C}=\text{O} \end{array}$	-0.50	350
-COOH	-0.90	770

Method of Przedzdecki and Sridhar

$$\eta_L = \frac{V_0}{E(V - V_0)};$$

where η_L - viscosity of liquid in centipoises; V – molar volume of liquid at current temperature, cm^3/mole . The parameters E and V_0 are defined as follows:

$$E = -1.12 + \frac{V_c}{12.94 + 0.10M - 0.23P_c + 0.0424T_f - 11.58(T_f/T_c)}$$

$$V_0 = 0.0085\omega T_c - 2.02 + \frac{V_m}{0.342(T_f/T_c) + 0.894};$$

where:

T_c – critical temperature, K

P_c – critical pressure, bar

V_c – critical molar volume, cm^3/mole

M – molecular weight, g/mole

T_f – freezing (melting) temperature, K

ω - Pitzer's acentric factor

V_m – molar volume at freezing temperature

So there are three cases:

1. V_m and V are known and the user inputs them manually

3. Their values are calculating from estimated density and molecular weight: $V = \frac{M}{\rho}$

4. One experimental value of molar volume or density is available at any temperature (not so far from the current). Then if to designate them as T^R and V^R the molar volume at the current and freezing temperatures may be calculated as follows:

*excluding the atoms that are parts of other groups

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$$V(T) = \frac{f(T)}{f(T^R)} V^R;$$

where:

$$f(T) = H_1(1 - \omega H_2); \quad H_1 = 0.33593 - 0.33953T_r + 1.51941T_r^2 - 2.02512T_r^3 + 1.11422T_r^4;$$

$$H_2 = 0.29607 - 0.09045T_r - 0.04842T_r^2$$

This method should not be used for alcohols. For other compounds the errors varies widely and, except for a few materials, the technique underestimate the liquid viscosity. It not recommended for using near melting point (below $T_r \sim 0.55$).

Results of estimation for different substances:

	Method	$\epsilon_{\text{average}}$	ϵ_{max}
o-Xylene	Przedzecki and Sridhar	3.64%	7.27%
Acetophenone	Przedzecki and Sridhar	19.1%	27.1%
Acetophenone (with T_b)	Przedzecki and Sridhar	7.09%	15.3%
1-Butanol	Orrick and Erbar	6.25%	25.0%
Ethyl Fluoride	Przedzecki and Sridhar	11.8%	23.0%
o-Dichlorobenzene	Przedzecki and Sridhar	5.27%	14.9%

Dependency of viscosity of pure liquid upon pressure

In the above-discussed ways of liquid viscosity estimation all the final viscosity are at the pressure of saturated vapors. To obtain viscosity at any higher pressure Lucas has suggested to use the following equation:

$$\frac{\eta}{\eta_{SL}} = \frac{1 + D(\Delta P_r / 2.118)^A}{1 + C\omega\Delta P_r};$$

where η - viscosity at the specified pressure; η_{SL} - viscosity of saturated liquid at vapor pressure

$$\Delta P_r = (P - P_{vp}) / P_c$$

ω - Pitzer's acentric factor

$$A = 0.9991 - \left[4.674 \times 10^{-4} / (1.0523T_r^{-0.03877} - 1.0513) \right]$$

$$D = \left[0.3257 / (1.0039 - T_r^{2.573})^{0.2906} \right] - 0.2086$$

$$C = -0.07921 + 2.1616T_r - 13.4040T_r^2 + 44.1706T_r^3 - 84.829T_r^4 + 96.1209T_r^5 + 96.1209T_r^6 - 59.8127T_r^7$$

Viscosity of pure gases

Method of Lucas

Input parameters:

M - molecular weight, g/mole

P_c - critical pressure, bar

μ - dipole moment, debye

P - pressure, bar

T_c - critical temperature, K

Z_c - critical coefficient of compressibility

T - temperature of gas, K

If value of dipole moment is not available it should be taken as unity.

If the gas under consideration is the quantum one then it is the specific case so among input parameters should be the parameter that will specify whether the gas is:

1. Helium

2. Hydrogen

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3. Deuterium

4. Other

Then multi-stage calculation follows:

$$\mu_r = 52.46 \frac{\mu^2 P_c}{T_c^2} \text{ - reduced dipole moment}$$

Its value defines the parameter F_P^0 :

$$\text{For } 0 \leq \mu_r < 0.022 \quad F_P^0 = 1$$

$$\text{For } 0.022 \leq \mu_r < 0.075 \quad F_P^0 = 1 + 30.55(0.292 - Z_c)^{1.72}$$

$$\text{For } 0.075 \leq \mu_r \quad F_P^0 = 1 + 30.55(0.292 - Z_c)^{1.72} [0.96 + 0.1(T_r - 0.7)]$$

where T_r – reduced temperature.

Quantum parameter F_Q^0 differs from unity for quantum gases He, H₂ or D₂ only:

$$F_Q^0 = 1.22 Q^{0.15} \left(1 + 0.00385 [(T_r - 12)^2]^{1/M} \text{sign}(T_r - 12) \right);$$

where $Q = 1.38$ (He), $Q = 0.76$ (H₂), $Q = 0.52$ (D₂)

Then:

$$Z_1 = \left[0.807 T_r^{0.618} - 0.357 \exp(-0.449 T_r) + 0.340 \exp(-4.058 T_r) + 0.018 \right] F_P^0 F_Q^0$$

Then the value of T_r defines the parameter Z_2 :

$$\text{For } T_r \leq 1.0 \quad Z_2 = 0.600 + 0.760 P_r^\alpha + (6.990 P_r^\beta - 0.6)(1 - T_r);$$

where $\alpha = 3.262 + 14.98 P_r^{5.508}$, $\beta = 1.390 + 5.746 P_r$.

Here and below P_r – reduced pressure.

$$\text{For } T_r > 1.0 \text{ (practically without any limitation)} \quad Z_2 = Z_1 \left[1 + \frac{a P_r^e}{b P_r^f + (1 + c P_r^d)^{-1}} \right];$$

where

$$a = \frac{a_1}{T_r} \exp(a_2 T_r^\gamma); \quad b = a(b_1 T_r - b_2); \quad c = \frac{c_1}{T_r} \exp(c_2 T_r^\delta); \quad d = \frac{d_1}{T_r} \exp(d_2 T_r^\epsilon); \quad e = 1.3088, \quad f = f_1 \exp(f_2 T_r^\zeta)$$

and

$$a_1 = 1.245e-03$$

$$b_1 = 1.6553$$

$$c_1 = 0.4489$$

$$d_1 = 1.7368$$

$$f_1 = 0.9425$$

$$a_2 = 5.1726$$

$$b_2 = 1.2723$$

$$c_2 = 3.0578$$

$$d_2 = 2.2310$$

$$f_2 = -0.1853$$

$$\gamma = -0.3286$$

$$\delta = -37.7332$$

$$\epsilon = -7.6351$$

$$\zeta = 0.4489$$

After calculation of Z_1 and Z_2 parameter Y is defining as $Y = \frac{Z_2}{Z_1}$ and then correction coefficients F_P and F_Q

should be calculated

$$F_P = \frac{1 + (F_P^0 - 1) Y^{-3}}{F_P^0}; \quad F_Q = \frac{1 + (F_Q^0 - 1) [Y^{-1} - (0.007)(\ln Y)^4]}{F_Q^0}$$

Then coefficient ξ is being calculated:

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$$\xi = 0.176 \left(\frac{T_c}{M^3 P_c^4} \right)^{1/6}$$

And finally $\eta = \frac{Z_2 F_p F_Q}{\xi}$; where η - viscosity in micropoises.

As a rule average errors are about 5% at any temperature and pressure.

Results of estimation for different substances:

	$\epsilon_{average}$	ϵ_{max}
o-Xylene	3.14%	6.78%
Acetophenone	3.28%	4.60%
Acetophenone (with T_b)	1.63%	3.99%
1-Butanol	2.83%	2.92%
Ethyl Fluoride	1.61%	2.98%
o-Dichlorobenzene	3.40%	11.8%

Heat conductivity

Heat conductivity of pure gases

Heat conductivity of pure gases at low pressure

Method of Chung et al:

$$\lambda = \frac{3.75 \Psi \eta R}{M};$$

where λ - heat conductivity, wt/(m·K); M – molecular weight, kg/mole
 η - gas viscosity at low pressure, N·sec/m² (it is Z1 defined earlier)
R – gas constant, 8.314 J/(mole·K)

$$\Psi = 1 + \alpha \left\{ [0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z] / [0.6366 + \beta Z + 1.061\alpha\beta] \right\}; \quad \alpha = \left(\frac{C_p^0 - R}{R} \right) - \frac{3}{2}$$

$$\beta = 0.7862 - 0.7109\omega + 1.3168\omega^2 \quad \text{- for non-polar gases; } \beta = 0,758 \quad \text{- for polar; } Z = 2.0 + 10.5T_r^2$$

The errors average about 5% for non-polar and about 10-15% for polar. It is applicable in pressure range from 10⁻³ up to 10 bar.

Results of estimation for different substances:

	$\epsilon_{average}$	ϵ_{max}
o-Xylene	7.69%	22.4%
Acetophenone	11.1%	12.9%
Acetophenone (with T_b)	5.59%	6.77%
1-Butanol	14.2%	22.5%
Ethyl Fluoride*	-	-
o-Dichlorobenzene	7.39%	17.8%

*) No experimental data for this compound

Heat conductivity of pure gases at high pressure

If the pressure exceeds 10 bar then

Method of Chung for high pressures is recommended:

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$$\lambda = \frac{31.2\eta^0\Psi}{M} (G_2^{-1} + B_6y) + qB_7y^2T_r^{1/2}G_2;$$

where λ - heat conductivity, Wt/(m·K); M – molecular weight, kg/mole
 η - gas viscosity at low pressure, N·sec/m² (coincide with Z1 discussed above but needs to change the units); Ψ - should be calculated as in case of low pressure

$$q = 3.586 \times 10^{-3} (T_c/M)^{1/2} / V_c^{2/3}; V_c - \text{critical volume, cm}^3/\text{mole};$$

T_c – critical temperature, K; T_r – reduced temperature, T/T_c

$$y = \frac{V_c}{6V}; G_1 = \frac{1-0.5y}{(1-y)^3}; G_2 = \frac{(B_1/y)[1 - \exp(-B_4y)] + B_2G_1 \exp(B_5y) + B_3G_1}{B_1B_4 + B_2 + B_3}$$

Coefficients from B₁ to B₂ are the functions of Pitzer's acentric factor, reduced dipole moment

$$\mu_r = 131.3 \frac{\mu}{(V_c T_c)^{1/2}} \text{ and association factor } k;$$

$$B_i = a_i + b_i\omega + c_i\mu_r^4 + d_i k;$$

coefficients a_i, b_i, c_i and d_i are given in the next Table:

i	a _i	b _i	c _i	d _i
1	2.4166 E+0	7.4824 E-1	-9.1858 E-1	1.2172 E+2
2	-5.0924 E-1	-1.5094 E+0	-4.9991 E+1	6.9983 E+1
3	6.6107 E+0	5.6207 E+0	6.4760 E+1	2.7039 E+1
4	1.4543 E+1	-8.9139 E+0	-5.6379 E+0	7.4344 E+1
5	7.9274 E-1	8.2019 E-1	-6.9369 E-1	6.3173 E+0
6	-5.8634 E+0	1.2801 E+1	9.5893 E+0	6.5529 E+1
7	9.1089 E+1	1.2811 E+2	-5.4217 E+1	5.2381 E+2

Factor k is zero for non-polar and slightly polar gases. Its values for some polar components are given in the next Table:

Compound	k
Methanol	0.215
Ethanol	0.175
n-Propanol	0.143
i-Propanol	0.143
n-Butanol	0.132
i-Butanol	0.132

Compound	k
n-Pentanol	0.122
n-Hexanol	0.114
n-Heptanol	0.109
Acetic Acid	0.0916
Water	0.076

It seems that user must have possibility to input k manually using the above Table as a reference.

For alcohols (including polyatomic) k may be calculated as follows:

$$k = 0.0682 + \frac{0.2767 \cdot 17 \cdot (\text{number of -OH groups})}{M};$$

where M – molecular weight.

For not very polar compounds the errors average about 5-8%.

Heat conductivity of pure liquids

Method of **Sato and Riedel**:

$$\lambda_L = \frac{(1.11/M^{1/2}) [3 + 20(1 - T_{br})^{2/3}]}{3 + 20(1 - T_{br})^{2/3}}$$

where T_{br} – reduced boiling temperature. As usual the errors don't exceed 15%. For non-polar compounds at reduced temperatures greater than 0.8 the scheme of calculation for pure gases should be used.

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Then if the specified pressure is greater than vapor pressure and is > 60 bar the pressure correction should be applied in accordance with

Method of Missenard:

$$\lambda_L(P_r) = \lambda_L(\text{low pressure}) \left(1 + QP_r^{0.7}\right);$$

where the values of parameter Q are given in the next Table:

Tr	Reduced pressure					
	1	5	10	50	100	200
0.8	0.036	0.038	0.038	0.038	0.038	0.038
0.7	0.018	0.025	0.027	0.031	0.032	0.032
0.6	0.015	0.020	0.022	0.024	0.025	0.025
0.5	0.012	0.0165	0.017	0.019	0.020	0.020

Results of estimation for different substances:

	Method	$\epsilon_{\text{average}}$	ϵ_{max}
o-Xylene	Sato and Riedel	3.10%	3.71%
Acetophenone	Sato and Riedel	12.2%	17.4%
Acetophenone (with T_b)	Sato and Riedel	9.02%	12.2%
1-Butanol	Sato and Riedel	9.73%	5.14%
Ethyl Fluoride	Sato and Riedel	10.3%	11.5%
o-Dichlorobenzene	Sato and Riedel	2.65%	2.35%

Surface tension of pure liquids

To estimate surface tension of pure liquids with the exception of strongly associative ones (i.e. acetic acid, formamide) **Method of Hakim et al** may be recommended:

$$\sigma = P_c^{2/3} T_c^{1/3} Q_p \left(\frac{1 - T_r}{0.4} \right)^m;$$

where σ - surface tension, dyn/cm; P_c – critical pressure, bar; T_c – critical temperature, K;

$$Q_p = 0.1560 + 0.365w - 1.754X - 13.57X^2 - 0.506w^2 + 1.287wX;$$

$$m = 1.210 + 0.538w - 14.61X - 32.07X^2 - 1.656w^2 + 22.03wX;$$

$$X = \log P_{\text{vpr}}(0.6) + 1.70w + 1.552$$

ω – Pitzer's acentric factor.

Method gives errors of about 5% both fo polar and non-polar liquids.

In case of strongly associative liquids at temperatures less then normal boiling the errors may reach 30-50% and for them **Method of Macleod, Sugden and Quale** may be used:

$$\sigma = \{[P](\rho_L - \rho_v)\}^4$$

where [P] – temperature-independent parameter parachor. Its value may be estimated by using group contribution method using group increments represented in Table 11-3 [1].

Results of estimation for different substances:

	Method	$\epsilon_{\text{average}}$	ϵ_{max}
o-Xylene	Hakim et al.	2.75%	16.1%
Acetophenone	Hakim et al.	21.7%	50.9%
Acetophenone (with T_b)	Hakim et al.	7.87%	20.2%
1-Butanol	Hakim et al.	4.58%	4.72%
Ethyl Fluoride	Hakim et al.	13.7%	34.0%

	Method	$\epsilon_{\text{average}}$	ϵ_{max}
o-Dichlorobenzene	Hakim et al.	4.52%	22.4%

Gas-Liquid Equilibrium in multi-component systems

Calculation based on Equations Of State

For estimation of gas-liquid equilibrium of multi-component systems in a wide range of temperature and pressure one of the cubic equation of state (EOS) is recommended to use:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + uV + wb^2}$$

where a, b, u and w for pure components for different EOS are:

Equation	u	w	b	a
Redlich-Kwong	1	0	$\frac{0.08664RT_c}{P_c}$	$\frac{0.42748R^2T_c^{2.5}}{P_c T^{1/2}}$
Soave	1	0	$\frac{0.08664RT_c}{P_c}$	$\frac{0.42748R^2T_c^2}{P_c} \left[1 + f_\omega \left(1 - T_r^{1/2}\right)\right]^2$ where $f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$
Peng-Robinson	2	-1	$\frac{0.07780RT_c}{P_c}$	$\frac{0.42748R^2T_c^2}{P_c} \left[1 + f_\omega \left(1 - T_r^{1/2}\right)\right]^2$ where $f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$

where ω -Pitzer's acentric factor.

The alternative form of EOS is:

$$Z^3 - (1 + B^* - uB^*)Z^2 + (A^* + wB^{*2} - uB^* - uB^{*2})Z - A^*B^* - wB^{*2} - wB^{*3}$$

where Z – compressibility; $A^* = \frac{aP}{R^2T^2}$; $B^* = \frac{bP}{RT}$

So for the given temperature and pressure cubic EOS may be easily and analytically solved with respect to Z. If EOS has the only real solution it indicates that at the given temperature and pressure the specified substance can exist only in gas phase. If there are three real roots then minimal found compressibility refers to liquid phase and maximum – to gas phase.

In case of multi-component systems there is a problem with determining the suitable mixing parameters a_m and b_m . To obtain them various mixing rules were proposed. One them is as follows:

$$a_m = \sum_i \sum_j y_i y_j (a_i a_j)^{1/2} (1 - k_{ij}); \quad b_m = \sum_i y_i b_i$$

where k_{ij} – binary interaction coefficient. For some binary systems its values are given in Table 4-2 [1]. Much more completed lists can be found in the literature.

For hydrocarbon-hydrocarbon pairs it may be taken as zero.

The problem of calculating phase equilibrium of multi-component gas-liquid system may be formulated as follows: at the given temperature and specified mole fractions of components in liquid phase it's necessary to find pressure and mole fractions in gas phase. The list of unknown variables is as follows:

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Z^V, Z^L	compressibility of gas and liquid phases
P	pressure
$y_1, y_2 \dots y_{n-1}$	mole fractions of n-1 components in gas phase, the mole fraction of the last component is obviously equal to unity minus sum of all other mole fractions.

Obviously there are n+2 unknown variables, where n – number of components.

It is known that multi-component systems is in equilibrium when the fugacities of every component in gas and in liquid phase coincide:

$$f_{iV} = f_{iL}$$

If to introduce the fugacity coefficient as:

$$\phi_i^{V,L} = \frac{f_i^{V,L}}{y_i^{V,L} P}$$

then the condition of equilibrium will be:

$$\frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V}$$

where x_i and y_i – mole fraction of component (i) in liquid and gas phase respectfully.

There are n such equations. In addition there are two equations of state – one for gas phase and other one for liquid. So in all there are n+2 equations for n+2 unknown variables, and so there must be unique solution of the above formulated problem.

Here it is the analytical expression for fugacity coefficients for any cubic EOS:

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B^*) + \frac{A^*}{B^* \sqrt{u^2 - 4w}} \left(\frac{b_i}{b} - \delta_i \right) \ln \frac{2Z + B^* (u + \sqrt{u^2 - 4w})}{2Z + B^* (u - \sqrt{u^2 - 4w})};$$

$$\text{where } \frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum_j y_j T_{cj}/P_{cj}}; \delta_i = \frac{2a_i^{1/2}}{a} \sum_j x_j a_j^{1/2} (1 - \bar{k}_{ij});$$

x_i and Z – mole fraction of component (i) and compressibility in the phase of interest.

The algorithm of finding the solution of the described system of equations is presented in detail in [2] and it had been already realized as a subroutine written in Delphi Pascal language.

As to the value of \bar{k}_{ij} , there should be possible for a user to input them manually, to maintain the database of them and to evaluate their value from experimental data.

Calculation based on Modified UNIFAC method

For calculation of gas-liquid equilibrium at moderate temperatures (at least when there are no any supercritical component in the system) the method of modified UNIFAC can be successfully used in the activity coefficient model. Anyway there are some mixing rules for cubic equations of state where the excess energy of Gibbs (that may be calculated from activity coefficient) is used. We plan to thoroughly evaluate their possibilities so the realization of UNIFAC calculations has some reasons.

To calculate the activity coefficients by modified UNIFAC method they consider having to parts - combinatorial (C) and residual (R):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

The combinatorial is calculated as follows:

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$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i} \right) \right);$$

where $V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}$; $V_i = \frac{r_i}{\sum_j x_j r_j}$; $r_i = \sum v_k^{(i)} R_k$; $F_i = \frac{q_i}{\sum_j x_j q_j}$; $q_i = \sum v_k^{(i)} Q_k$.

Here x_i - volume fraction of component (i) in liquid phase,

$v_k^{(i)}$ - number of group (k) in molecule (i),

Q_k - relative van der Waals surface of subgroup (k)

R_k - relative van der Waals volume of subgroup (k)

The residual activity coefficient is calculating as follows:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)})$$

, where $\ln \Gamma_k = Q_k \left(1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right)$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; \quad X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j}; \quad \Psi_{nm} = \exp \left(- \frac{a_{nm} + b_{nm} T + c_{nm} T^2}{T} \right)$$

$\ln \Gamma_k^{(i)}$ should be calculated in the same way but for pure component (i).

References

1. Reid, Prausnitz, Poling., 1987. The Properties of Gases and Liquids. McGraw-Hill, Fourth Edition.
2. Hasan Orbey, Stanley I. Sandler, 1998, Modeling Vapor-Liquid Equilibria. Cubic Equations of State and Their Mixing Rules. Cambridge University Press.