Graphical determination of the approximate values of parameters in the Wilson equation for a binary solution

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A diagram allowing to determine the values of the parameters Λ_{12} and Λ_{21} in the Wilson equation on the basis of the limiting activity coefficients of the components of a binary solution at $\Delta G^{\mathrm{E}}>0$ is presented.

В работе приводится диаграмма для определения значений параметров Λ_{12} и Λ_{21} уравнения Вильсона на основании значений предельных коэффициентов активности составляющих двойного раствора при $\Delta G^{\mathrm{E}}>0$.

The calculation of parameters of the Wilson equation [1] from the equilibrium liquid—vapour data is usually performed by the least-squares method. The procedure and calculation programmes are described in detail in [2]. The numerical solution of a system of normal equations necessitates the initial estimate of parameters of the Wilson equation. If this estimate is far from being right, some difficulties may arise in the convergence of calculation or the calculation necessitates a considerable number of iterations, which is tedious especially if a less efficient machine-computing technique is used.

The limiting activity coefficients provide a good basis for the initial estimate of parameters of the Wilson equation for binary systems. Their approximate value may be calculated in a relatively simple way (we presuppose an ideal vapour phase) either from the isothermal P—x data [3]

$$\gamma_1^{\infty}=\frac{P_2^0}{P_1^0}\left[1+\frac{1}{P_2^0}\lim_{x_1\to 0}\left(\frac{\partial P}{\partial x_1}\right)_T\right] \qquad (1)$$

or from the y—x (isobaric or isothermal) data [4]

$$\gamma_1^{\infty}=\frac{P_2^0}{P_1^0}\lim_{x_1\to 0}\left(\frac{\partial y_1}{\partial x_1}\right)_{P(T)} \qquad (2)$$

(The relationships for the calculation of γ_2^{∞} are to be obtained by replacing indices 1 and 2 with each other.) The values of the limit of the partial derivations in eqns (*1*) and (*2*) are to be determined in the simplest way graphically from the P—x or y—x curves.

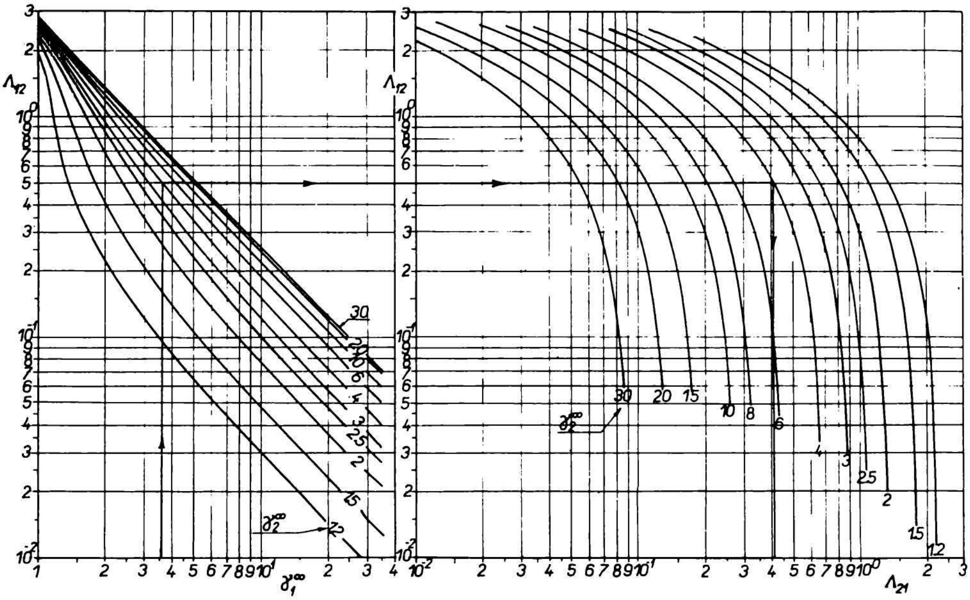

Fig. 1. Diagram for the calculation of the parameters Λ_{12} and Λ_{21} of the Wilson equation from the known values of limiting activity coefficients.

The dependence of the parameter Λ_{12} of the Wilson equation on the limiting activity coefficients may be expressed by the following equation [5]

$$\ln \Lambda_{12} = -\ln \gamma_1^{\infty} + 1 - \frac{1}{\gamma_2^{\infty}} \exp\,(1 - \Lambda_{12}) \tag{3}$$

while Λ_{21} is to be calculated from equation

$$\Lambda_{21} = \frac{1}{\gamma_2^{\infty}} \exp\,(1 - \Lambda_{12}). \tag{4}$$

Equations (*3*) and (*4*) make it possible to calculate Λ_{12} and Λ_{21} unambiguously for the solutions with a positive value of ΔG^{E} [5]. On the basis of eqns (*3*) and (*4*) we have constructed a diagram (Fig. 1) for these solutions which allows to determine the parameters of the Wilson equation from the known values of the limiting activity coefficients. An example of the practical use is drawn in the diagram. For $\gamma_1^{\infty} = 3.5$ and $\gamma_2^{\infty} = 4$ it is to be obtained $\Lambda_{12} = 0.5$ and $\Lambda_{21} = 0.41$.

Symbols

P	vapour pressure of solution
P_1^0, P_2^0	vapour pressure of pure components

y_1	mole fraction of component 1 in vapour phase
x_1	mole fraction of component 1 in liquid phase
Λ_{12}, Λ_{21}	parameters of the Wilson equation
γ_1^{∞}, γ_2^{∞}	limiting activity coefficients of components 1 and 2

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