

that 1-octanethiol has the same reactivity as α -toluenethiol. The observed second-order dependence suggests that reaction (2) is rate-determining and this would be expected since the half-life for reaction (1) at 100° is 3.1 min³. However, further work on this aspect of the problem is desirable before any definite mechanistic conclusions can be made. The present results are consistent with the recent observation that stable nitroxide radicals are capable of abstracting hydrogen atoms from thiols⁴.

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A New Method for the Precise Determination of the Excess Gibbs Function of a Liquid Mixture

WE propose a new experimental method for the determination of the excess Gibbs function, G^E , of a mixture of two liquids of comparable volatility.

For a liquid mixture at given temperature containing mole fraction x of the second component, G^E is determined by the relations:

$$G^E(x)/RT = (1-x) \ln \left\{ (1-y)p\delta_1/(1-x)p_1^0 \right\} + x \ln \left\{ yp\delta_2/xp_2^0 \right\} \quad (1)$$

$$\partial \{G^E(x)/RT\} / \partial x = \ln \left\{ (1-y)\delta_1xp_2^0/yp\delta_2(1-x)p_1^0 \right\} \quad (2)$$

where y is the mole fraction of the second component in the vapour phase in equilibrium with the liquid, p , p_1^0 and p_2^0 are the vapour pressures of the mixture and of the two pure components, and δ_1 and δ_2 are abbreviations for factors¹ which take account among other things of the imperfection of the vapour phase but which we shall assume to be known from independent measurements and shall not need to discuss further here.

In the most usual experimental method¹ G^E is calculated according to equation (1) from values of p , x and y measured by use of a re-circulating still. Only two of these three quantities are actually necessary in view of the further relation (2). The extra information can be used² to test the results for thermodynamic consistency, a procedure which is especially desirable because of the difficulties associated with bringing a re-circulating still to a steady state which differs insignificantly from equilibrium, and of the difficulties associated with the analysis of the samples of liquid and (condensed) vapour taken from the still. It is notoriously time-consuming and tedious to make precise measurements with a re-circulating still. The only advantage of the method is the elementary nature of the calculation of G^E directly from equation (1).

More recently G^E has been calculated according to equations (1) and (2) from less-tedious measurements, made under equilibrium conditions in a static vapour pressure apparatus, of p and x only³, or of p and y only⁴. The calculation of G^E is much more complicated⁵, but can nowadays easily be carried out with a computer⁶. The calculation is usually made by assuming that G^E can be expressed by m terms of such an expansion as:

$$G^E = x(1-x) \sum_{i=1}^m A_i(1-2x)^i \quad (3)$$

On using equation (3) to eliminate G^E from (1) and (2) we then have 2 equations in the $(1+m)$ unknowns y or x ,

and A_1, \dots, A_m . A number n of measurements of p and x , or of p and y , at different compositions then gives $2n$ equations in $(n+m)$ unknowns, which can be solved if $n \geq m$. The number m of parameters needed in equation (3) is at the most 4 and is often only 1 or 2. By far the greatest experimental difficulty in the method is the precise measurement of the composition x or y .

In our method no precise measurement of any composition is needed. Instead, we propose to measure the bubble-point pressure p^b , and the dew-point pressure p^d , of a mixture of given, but only roughly known, overall composition. We then have a set of equations (1) to (3) with:

$$x = x^b, y = y^b, \text{ and } p = p^b \quad (4)$$

and another set with:

$$x = x^d, y = y^d, \text{ and } p = p^d \quad (5)$$

together with the equation:

$$x^b = y^d \quad (6)$$

which expresses the fact that the liquid phase at the bubble point has the same composition as the vapour phase at the dew point. On using equation (3) to eliminate G^E these become 5 equations in the $(4+m)$ unknowns x^b, y^b, x^d, y^d , and A_1, \dots, A_m . A number n of measurements of p^b and p^d at different compositions then gives $5n$ equations in $(4n+m)$ unknowns, which can be solved if $n \geq m$. We have written a computer programme to solve such a set of $5n$ equations for $n \geq m$ and have tried it out on sets of values of p^b and p^d interpolated from published measurements of p , x and y obtained by use of re-circulating stills. In particular we have successfully tested the programme on results¹⁰ for $\text{CCl}_4 + \text{CHCl}_3$ (small deviations from Raoult's law; $m=1$) and on results⁶ for $\text{CCl}_4 + \text{CH}_3\text{CN}$ (large deviations with azeotropy; $m=4$). Even in the worst example we studied ($m=4, n=4$) trial values of the x 's and y 's within about ± 0.01 of the correct values were sufficiently close to ensure convergence, provided that the chosen compositions were not too close to that of the azeotrope. Experimentally it is easy to make up a mixture so that $x^b (=y^d)$ is known to this accuracy. Trial values of x^d and y^b can then be read from a rough plot.

We are building an apparatus for the measurement of bubble-point and dew-point pressures of mixtures of $\text{C}(\text{CH}_3)_4 + \text{Si}(\text{CH}_3)_4$ at a series of roughly known overall compositions, and expect to be able to use the results to determine values of the parameters A_1, \dots, A_m , and hence of G^E , as precisely as could be done by any of the older methods, and much more quickly.

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Effect of Adsorbed Olefines on the Oxidation of Aluminium Films

THE presence of adsorbed species on metal surfaces has been observed to affect subsequent interactions of the metal with reactive gases¹⁻³. To determine the effect adsorbed olefines have on the oxidation of aluminium, clean aluminium films were exposed to olefine vapour and the subsequent rate of oxygen adsorption was measured. The olefines used included ethylene, butene-1, hexene-1, octene-1, and cetene-1.