

# Liquid–Liquid Equilibria: Verification of the Lever Rule

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The mutual solubility curve for a binary system of partly miscible liquids is most often constructed by determining the temperature at which a known composition of the mixture becomes homogeneous (1–3). The resulting phase diagram is then used to determine the composition of the two phases in equilibrium at a given temperature and, using the lever rule (4), their relative masses in a given overall composition of the mixture.

The experiment has always been weak in that it is not convincing enough that two seemingly immiscible liquids dissolve in each other to varying extents. Moreover, even though the derivation of the lever rule is provided, it is taken at its face value and simply used to obtain the required quantities.

The scope of the experiment has been expanded by adding an alternate determination of the composition and mass of one of the layers in a known overall composition of a mixture and then comparing these values to those obtained at the same temperature and overall composition from the phase diagram. The experiment takes very little additional time to perform and the extra apparatus required is minimal.

For the methanol–cyclohexane system studied, students pipet 5 mL of each liquid into a 10-mL stoppered graduated cylinder, shake it vigorously for 5 min, and allow the mixture to equilibrate and the layers to separate. It is immediately visible that the two layers are not of equal volume (bottom layer ~7.5 mL at 24.9 °C). Clearly, two solutions of quite different compositions from the original pure liquids are formed.

About an hour later, the volume of the bottom layer is recorded ( $\pm 0.1$  mL), a syringe is used to remove ~1 mL of that layer, its refractive index is measured, and the temperature of the mixture in the graduated cylinder is recorded ( $\pm 0.1$  °C).

The following calculations are required:

1. The mass of each liquid in the initial mixture from its volume and density (5), the total mass of the mixture, and the weight percent of methanol in the initial mixture.
2. The weight percent of methanol in the bottom layer, determined from its measured refractive index.<sup>1</sup>
3. The mass of the bottom layer, determined from its volume and density at the measured temperature.<sup>2</sup>
4. The ratio of the mass of the bottom layer to the total mass of the mixture.

In addition, the following calculations are carried out using values obtained from the phase diagram at the temperature of the mixture in the graduated cylinder:

5. The weight percent of methanol in the bottom layer.
6. The ratio of the mass of the bottom layer to the total mass of the mixture, using the lever rule and an overall weight percent of methanol corresponding to that of the initial mixture in the graduated cylinder.

The results of ~250 students over a period of 2 years indicated very good agreement between the two methods in those cases where correct calculations had been performed. Typical data for the weight percent composition of methanol in the bottom layer and the ratio of its mass to the total mass of the mixture are exemplified by a student's results at 24.9 °C: 66% and 0.76 from the experiment in the graduated cylinder and 64% and 0.77 from the phase diagram. The agreement between the two methods gives credence to the lever rule. Moreover, the results are in good agreement with the values of 64% and 0.77 estimated at 24.9 °C from the literature (1).

In principle, both layers in the graduated cylinder could have been analyzed, but at typical ambient temperatures the weight percent of methanol in the top layer is very small, about 4% (1), and therefore subject to large errors. The largest source of error is the 10-mL graduated cylinder; a poor value for the volume of the bottom layer leads to errors in the mass of methanol in that layer and in its ratio to the total mass of the mixture. Lack of temperature control and its measurement with an uncalibrated thermometer are also sources of error for both the experiment in the graduated cylinder and the determination of the phase diagram. Despite these shortcomings, acceptable results are obtained and we feel that the experiment is much improved. The revised experiment has led to a better understanding of phase diagrams and the lever rule and a verification of the latter by a simple analytical method.

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## Supplemental Material

Supplemental material for this article is available in this issue of *JCE Online*.

## Notes

1. The refractive index at 25 °C was determined for mixtures in the range of 70.57% to 100% methanol by weight and the data were fitted by least-squares:  $n_D = 1.4030 - 7.8167 \times 10^{-4}$  wt %.

2. The density was determined at 12.7, 23.2, and 32.1 °C for the mixtures in ref 4 and the data were fitted by least-squares:  $D_{\text{meth-cycl}} = 0.7777 - 1.9094 \times 10^{-5} t + 2.220 \times 10^{-6} (\text{wt } \%)^2$ , where  $D_{\text{meth-cycl}}$  is in g mL<sup>-1</sup> and  $t$  in °C.

## Literature Cited

1. Jordan, A. D. *Educ. Chem.* 1994, 31, 10 and references therein.
2. Heald, C.; Smith, A. C. K. *Applied Physical Chemistry*; Macmillan: London, 1974; pp 67–68.
3. Halpern, A. M. *Experimental Physical Chemistry*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1997; pp 191–199.
4. Spicer, W. M.; Metcalf, J. S. *J. Chem. Educ.* 1943, 20, 199.
5. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; McGraw Hill: New York, 1928; Vol III, pp 27–29.