

# Mutual Solubilities of Liquids in a Binary Two-Phase System

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To construct the mutual solubility curve of a binary two-phase liquid system (for example, 1-butanol/water or methanol/cyclohexane).<sup>1</sup>

<sup>1</sup> Transcribed from Nibler et al. [1].

## Theory

It is sometimes necessary to know the mutual solubilities of liquids in a two-phase system: for example, how much water is dissolved in an organic liquid with which it is in contact, and also the amount of the organic compound that is in the aqueous phase. Although a number of analytical techniques can be used to obtain this information, a procedure that is both conceptually and operationally simple and does not require the removal of liquid samples for analysis (which might change the equilibrium compositions) was described by Hill [2]. This elegant approach (which Hill called a “thermostatic method”) is based on a volumetric technique and requires knowledge only of the bulk composition of the system, that is, the total mass of each component in the mixture. We assume that the two liquids are in equilibrium in a two-phase system. Thus the phase rule applies.

If you were to combine two pure liquids  $A$  and  $B$ , you might find that a two-phase system is formed at a given temperature and pressure. Consider two samples of this binary system that have different bulk quantities of  $A$  and  $B$ . Assume that each of the two samples, at the same temperature and pressure, is at equilibrium. See fig. 1.

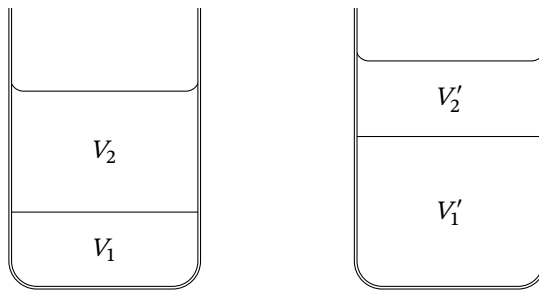


Figure 1: Two samples of a two-phase, two-component system containing arbitrary amounts of each component. Both solutions are at the same temperature and pressure.

If  $m_A$  and  $m_B$  are, respectively, the *bulk masses* of components  $A$  and  $B$  in one sample, and  $m'_A$  and  $m'_B$  are the bulk masses in the other sample, then it follows that

$$m_A = d_{A1}V_1 + d_{A2}V_2 \quad \text{and} \quad m'_A = d_{A1}V'_1 + d_{A2}V'_2 \quad (1)$$

$$m_B = d_{B1}V_1 + d_{B2}V_2 \quad \text{and} \quad m'_B = d_{B1}V'_1 + d_{B2}V'_2 \quad (2)$$

where  $V_1$  and  $V_2$  are the volumes of the lower phase (higher density) and upper phase (lower density) of one sample, and  $V'_1$  and  $V'_2$  refer to the volumes of the respective phases in the other sample. We represent  $d_{A1}$  and  $d_{A2}$  as the equilibrium densities (or mass concentrations) of component  $A$  in phases 1 and 2, respectively. Likewise,  $d_{B1}$  and  $d_{B2}$  are the densities of  $B$  in phases 1 and 2. Since the samples are at the same temperature and pressure, the phase rule requires that the equilibrium compositions be the same for both samples (i.e.,  $d_{A1} = d'_{A1}$ ,  $d_{A2} = d'_{A2}$ , etc.). These equalities are valid assuming that, in the mixed sample,  $A$  and  $B$  can each be treated as a single, chemically independent, component.

This system can also be described by the phase diagram in fig. 2 in which we plot the density against temperature. The locus of points on the curve represents phase equilibrium conditions. Points inside the curve characterize two phases in coexistence while those outside the curve indicate the presence of one phase. The diagram shows that as  $T$  increases, the density of the lower phase increases while that of the upper phase decreases. At some particular temperature, called the critical temperature ( $T_c$ ), these densities become equal and the two phases coalesce into one.

Equations (1) and (2) represent *material balances* that express the equilibrium compositions of the  $A$ - $B$  system as two equations in two unknowns. [3] Because the bulk masses ( $m_A$ ,  $m'_A$ , etc.) and the equilibrium volumes ( $V_1$ ,  $V'_1$ , etc.) are *measurable* quantities, the simultaneous solution of eqs. (1) and (2) allows the four equilibrium concentrations  $d_{A1}$ ,  $d_{A2}$ ,  $d_{B1}$ , and  $d_{B2}$  to be determined. From the two expressions in eq. (1) for  $m_A$  and  $m'_A$ , we can represent  $d_{A1}$  explicitly using determinants:

$$d_{A1} = \frac{\begin{vmatrix} m_A & V_2 \\ m'_A & V'_2 \end{vmatrix}}{\begin{vmatrix} V_1 & V_2 \\ V'_1 & V'_2 \end{vmatrix}} = \frac{m_A V'_2 - m'_A V_2}{V_1 V'_2 - V'_1 V_2}. \quad (3)$$

We can substitute this value of  $d_{A1}$  into either of the expressions in eq. (1) to find the equilibrium density of component  $A$  in phase 2; using the left-hand one, we get

$$d_{A2} = \frac{m_A - d_{A1} V_1}{V_2} \quad (4)$$

The identical treatment of the two expressions in eq. (2) yields the analogous results for  $d_{B1}$  and  $d_{B2}$ . More intuitively, we can just replace the  $A$  in eqs. (3) and (4) by  $B$ .

If we were to study more than two equilibrium samples of  $A$  and  $B$ , each exhibiting two phases at the same temperature and pressure, we could determine the densities  $d_{A1}$ ,  $d_{A2}$ ,  $d_{B1}$ , and  $d_{B2}$  more precisely using a statistical treatment. This approach is described in the Appendix.

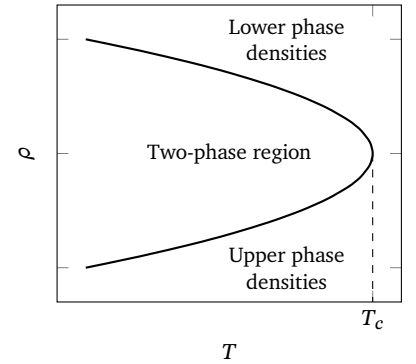


Figure 2: Schematic phase diagram of two immiscible liquids. Density is plotted against temperature. The upper and lower portions of the curve represent the densities of the lower and upper phases, respectively.

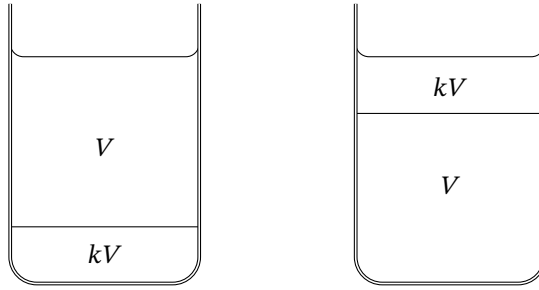


Figure 3: A set of complementary solutions of a two-phase, two-component system at the same temperature and pressure. The volumes of the two phases in the samples are exactly reversed.

The simplicity of the method is very appealing. However, it should be clear (and it is mathematical demonstrable) that the approach begins to break down as the mass ratio  $m_A/m_B$  in one sample is similar to or approaches the mass ratio in the other sample,  $m'_A/m'_B$ . In the extreme case where two *identical* samples are considered, no unique information about the system composition can be obtained. Moreover, as the ratio of  $m'_A/m_A$  becomes very small (or large), the quality of the information deteriorates because the determined concentrations are sensitive to the error associated with reading the positions of the menisci. Thus there exists an *optimal* mass ratio that provides maximum precision in the determination of the equilibrium compositions using this methodology (for a given volumetric error). Hill was aware of this situation, and in a paper with Hill and Malisoff [3] presented the analysis of this system optimization. We will show just the result here, but if you are curious to see how to obtain the result, see the Appendix.

Consider again two samples of a two-phase liquid system consisting of components  $A$  and  $B$  at the same temperature and pressure. These samples are designed so that the volumes are *exactly reversed* for each of the two phases (see fig. 3). The ratio of the two phases is denoted by  $k(k > 1)$ . It turns out that the system can be designed to yield the most precise determination of the equilibrium densities of component  $A$  in the two phases ( $d_{A1}$  and  $d_{A2}$ ) if  $k$  has the value

$$k_{\text{opt},A} = \frac{d_{A2}}{d_{A1}}. \quad (5)$$

This ratio of densities (or solubilities, since the two liquids are in equilibrium) is called the *distribution ratio* (or distribution coefficient) of component  $A$  in the two phases and is a thermodynamic quantity because its value depends on equilibrium solubilities. Note that  $k$  is presumed to be greater than 1. If in reality, however,  $d_{A1} < d_{A2}$ , then the denotation of the phases must simply be reversed—the upper phase in fig. 2 is 1 and the lower one is 2. An analogous result is found for the optimal volume ratio in the complementary solutions for determining

the solubility of component *B*:

$$k_{\text{opt},B} = \frac{d_{B1}}{d_{B2}}. \quad (6)$$

In general, these optimal conditions are not the same for the two components because the mutual solubilities of *A* and *B* are different. Nevertheless,  $k_{\text{opt},A}$  and  $k_{\text{opt},B}$  are often close enough that a satisfactory (although not absolute) optimization of the experiment can simultaneously accommodate both components. Since the distribution ratio is not known before the experiment is performed,<sup>2</sup> a preliminary experiment can be performed to obtain approximate values of the equilibrium compositions. From a practical point of view, it is desirable to choose a complementary system in which *k* is not too large because in this case relative volumetric errors would become important.

<sup>2</sup> finding  $d_{A1}$  and  $d_{A2}$  is, after all, the objective of the experiment

In this experiment, you will not attempt to seek optimal conditions. Rather, you will prepare samples that will provide reasonable accurate results. These samples will have complementary volumes (after mixing) that are in a ratio of approximately 3:1. This means that if the volume ratio of the upper phase to the lower phase in one sample is 3:1, that ratio for the other sample should be 1:3.

### *Safety Precautions*

- Safety glasses or goggles must be worn in the laboratory.
- Be particularly careful in removing and manipulating the hot sample cylinders.
- Small amounts of organic vapors will be released. Work in an open, well-ventilated laboratory or (preferably) inside a fume hood.
- Do not allow the cylinders to build up pressure as they are heated; vent periodically by briefly removing the stoppers.

### *Procedure*

#### *Required Equipment*

- (2) graduated cylinders (10 mL) with stoppers
- Pasteur pipets
- water bath
- (1) 0 °C to 100 °C thermometer
- cyclohexane (reagent-grade)

- methanol (reagent-grade)
- 1-butanol (reagent-grade)
- distilled water

Several different binary liquid systems can be studied using the Hill-Malisoff method. The choice depends on such factors as convenience, expense, and ventilation considerations. If mutual solubilities are determined at different temperatures, the miscibility diagram of the system can be constructed. In this case, it is desirable to study a system that has an upper consolute temperature that is in an experimentally convenient range (that is, less than 100 °C). The *upper consolute temperature* is the point above which two liquids are miscible in all proportions (see fig. 2).

Unfortunately, many of the systems that manifest easily accessible upper consolute temperatures contain a noxious component and must therefore be handled in a fume hood. For example, the cyclohexane/aniline system has an upper consolute temperature of ~60 °C; that of phenol/water is ~66 °C. Other possible systems are methanol/cyclohexane and 1-butanol/water (or other butanol isomers and water).

In this experiment, you will study the 1-butanol/water system or the methanol/cyclohexane system between 0 °C to ~70 °C. Because the upper consolute temperature of the former is ~125 °C, only a portion of its miscibility curve can be constructed. The upper consolute temperature of the latter system, however, is more accessible.

Prepare two 1-butanol/water (or methanol/cyclohexane) samples that manifest two phases at room temperature. The volumes of the two phases need not be complementary, but should be distinctly unequal, in a roughly 3:1 ratio. You will determine the densities of the phases for this unoptimized system from eqs. (3) and (4) (see fig. 1).

1. Weigh directly into a tared 10 mL graduated cylinder (graduations of 0.1 mL) appropriate amounts ( $\pm 10$  mg) of 1-butanol and distilled water (or methanol and cyclohexane) to make a two-phase system with a roughly 3:1 volume ratio for a total volume of about 6 mL to 7 mL.<sup>3</sup> Use a Pasteur pipet to transfer the liquids. Likewise, add the amounts of these components to the other graduated cylinder to make up an approximately complementary two-phase mixture. Label or otherwise identify each cylinder and its stopper. Stopper the cylinders and *gently* invert each several times, venting the cylinder periodically.
2. Remove the stoppers and place each of the cylinders in the bath at the lowest temperature (this temperature will be different for the

<sup>3</sup> Remember, meeting a target value is unimportant, but recording the *actual* value is very important.

two systems). After a minute, firmly replace each stopper on its respective cylinder. After another minute or so, remove the cylinders one at a time using a test tube holder (or other appropriate device) and carefully invert several times. Replace the cylinder in the bath as quickly as possible. If possible, invert the cylinders directly in the bath. If at this point or in subsequent stages the two phases do not separate cleanly, remove the cylinder and *very gently* tap it on a firm surface. *It is important that the two phases are mixed thoroughly to ensure that phase equilibrium is reached.*

3. Repeat the inversions after 1 min to 2 min. Wait for a few minutes until the meniscus positions of each samples have become established. Record these positions to the nearest 0.03 mL.
4. Remove the cylinders and place them in the next higher temperature bath (or use an immersion heater to raise the temperature by 5 °C to 10 °C). Following the procedures in items 2 and 3, invert the cylinders and read the meniscus positions after equilibrium is reached. Be sure to vent the cylinder cap briefly to relieve the pressure buildup. *Be careful of escaping vapor.*
5. Continue this procedure until you reach about 60 °C.
6. For the methanol/cyclohexane system, the upper consolute temperature (or critical solution temperature),  $T_c$ , can be determined approximately. Fill a clean cylinder with a mixture (total mass ~6 g to 8 g) that is about 77 % cyclohexane by mass. Mix thoroughly and place a 2 L beaker that contains sufficient hot water (~55 °C to 60 °C) to completely cover the liquid in the cylinder. Invert the cylinder several times; vent periodically to release vapor. The liquid should appear as a homogeneous, one-phase system. Add sufficient quantities of crushed ice to the bath water so that the temperature drops 1 °C to 2 °C per minute. Record the temperature at the first sign of a pale blue, hazy appearance to the cooling methanol/cyclohexane mixture. This phenomenon, called *critical opalescence*, appears just above  $T_c$ . It is caused by the strong light scattering that accompanies large fluctuations in the density within the sample as the two phases begin to separate. If you overshoot  $T_c$ , the system will appear distinctly milky or cloudy. Slowly reheat the system by a few degrees until it homogenizes and then repeat the cooling process.

The detection of the onset of critical opalescence is best done by having a light source—a bright window, lightbulb, or, better yet, a low-power helium-neon laser—illuminate the sample at *right angles* to the viewing axis (*avoid looking into the laser beam!*).

## Data Analysis

1. Tabulate the equilibrium volumes of the two phases in each cylinder at the different temperatures studied.
2. Using these data, along with the bulk masses of the two components, determine the equilibrium densities  $d_{A1}$ ,  $d_{A2}$ ,  $d_{B1}$ , and  $d_{B2}$ . From this information, obtain the mole fractions of the two components in the two phases at each temperature studied.
3. Construct the  $T$ - $x_A$  phase diagram for the system. It should resemble fig. 4. For specific guidance, consult your physical chemistry text or your instructor.
4. Determine the mutual solubilities of the two components, as well as the distribution (or partition) coefficients at the various temperatures and compare your results with literature values where possible.

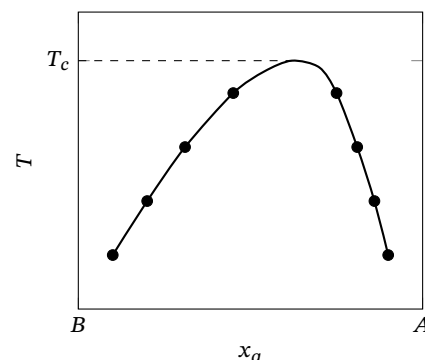


Figure 4: Schematic  $T$ - $x_A$  diagram.  $T_c$  is the upper consolute temperature. Each of the four pairs of horizontal circles represents the equilibrium mole fractions of A in the two phases at the particular temperatures.

## Lab Report Guidelines

Your lab report should consist of the following parts:

*Title, Author and Date*

*Introduction* Describe the experiment and expected results in a few sections.

*Experimental Theory* Reference this document.

*Experimental Procedure* This should be a very brief general outline of the procedure, written out as a paragraph or two. Give the make and model for any major instruments you used, as well as any important settings. The description should be thorough enough that another student can repeat your experiments. This means you must provide explicit volumes, weights, and temperatures. Use the past tense in all of your descriptions. Don't just copy the procedure from the manual, state what work *you* performed.

*Results and Discussion* This should include an overview of the analyzed data and responses to the questions worked into a natural narrative. Include your data in a *tabular* format, including all the information necessary to repeat your calculations. Include all graphs as figures (with captions). Your graphs should include axes labels (with units). Address the following points in your discussion

- Suppose the distribution coefficient of component A in a binary system is 20. According to the Hill-Malisoff method, the mass ratio  $m_A/m_B$  for optimal solubility precision is 20:1. If a 10 mL

graduated cylinder is used in the experiment, the smaller volume contained in each tube is less than 0.5 mL. Does this correspond to maximal volumetric precision? How do you decide how to achieve the maximal *overall* experimental accuracy in an experiment such as this?

- What other types of analytical methods can be used to determine the compositions of a two-phase liquid system? Discuss approaches that can be used a) without removing samples, and b) by withdrawing small aliquots.
- What is the advantage of applying the Hill-Malisoff method to a binary system contained in a series of  $N$  samples ( $N > 2$ )?
- Can the methodology be extended to a ternary two-phase system? Set up the initial equations analogous to eqs. (1) and (2). Ternary liquid equilibrium is conveniently studied by “titrating” a homogeneous binary phase consisting of components  $A$  and  $B$  with the other component—for example, pure liquid  $A$ —until the mixed ternary system manifests a two-phase appearance. This condition is easily detected as an emulsion.

*References* Include any external material you incorporated into this report (including literature values for physical data).

*Appendix* At the very end of your report, include examples of any calculations that you did by hand. Include any additional files and code that you used to generate your graphs.

## References

- [1] JW Nibler et al. *Experiments in Physical Chemistry*. 9th ed. McGraw-Hill, New York, 2014.
- [2] Arthur E Hill. “The mutual solubility of liquids. I. The mutual solubility of ethyl ether and water. II. The solubility of water in benzene”. In: *Journal of the American Chemical Society* 45.5 (1923), pp. 1143–1155. DOI: [10.1021/ja01658a007](https://doi.org/10.1021/ja01658a007).
- [3] Arthur E Hill and William M Malisoff. “The mutual solubility of liquids. III. The mutual solubility of phenol and water. IV. The mutual solubility of normal butyl alcohol and water”. In: *Journal of the American Chemical Society* 48.4 (1926), pp. 918–927. DOI: [10.1021/ja01415a011](https://doi.org/10.1021/ja01415a011).

## Further Reading

- PW Atkins and J. de Paula. *Physical Chemistry*. 8th ed. New York, NY: W.H. Freeman, 2006, p. 795.



- IN Levine. *Physical Chemistry*. 4th ed. McGraw-Hill, New York, 1995, p. 469.

## Appendix

### Multiple Samples

Suppose we have three samples, denoted as 1, 2, and 3. As before, we represent the components as *A* and *B*, but now we denote the two phases as upper, *u*, and lower, *l*. The total mass of *A* in each of the three samples is

$$m_{A1} = d_{Au}V_{u1} + d_{Al}V_{l1}$$

$$m_{A2} = d_{Au}V_{u2} + d_{Al}V_{l2}$$

$$m_{A3} = d_{Au}V_{u3} + d_{Al}V_{l3}$$

In general, for the *i*th sample,

$$m_{Ai} = d_{Au}V_{ui} + d_{Al}V_{li} = d_{Au}(V_{\text{tot}} - V_{li}) + d_{Al}V_{li}, \quad (7)$$

or

$$\frac{m_{Ai}}{V_{\text{tot}}} = d_{Au} \left( 1 - \frac{V_{li}}{V_{\text{tot}}} \right) + d_{Al} \frac{V_{li}}{V_{\text{tot}}}. \quad (8)$$

This equation can be rearranged to give

$$\frac{m_{Ai}}{V_{\text{tot}}} = (d_{Al} - d_{Au}) \left( \frac{V_{li}}{V_{\text{tot}}} \right) + d_{Au}. \quad (9)$$

A plot of  $m_{Ai}/V_{\text{tot}}$  versus  $V_{li}/V_{\text{tot}}$ , where, in this instance,  $i = 1, 2$ , and  $3$ , should be linear, and you can obtain the equilibrium mass densities of *A* in the two phases from the slope and intercept. A similar approach is used with respect to component *B*.

### Optimizing the System

Refer to fig. 3, which shows a set of complementary solutions of *A* and *B* at the same temperature and pressure.

Thus, if  $V'_1 = V$  and  $V'_2 = kV$ , then  $V_1 = kV$  and  $V_2 = V$ .  $k$  is the equilibrium volume ration in the complementary samples and is greater than 1 in the example illustrated in fig. 3. Moreover, the subscripts 1 and 2 denote, respectively, the lower and upper phases. The material balance for component *A* in *each* sample is

$$\begin{aligned} m_A &= d_{A1}kV + d_{A2}V, \\ m'_A &= d_{A1}V + d_{A2}kV. \end{aligned} \quad (10)$$

A similar set of equations can be written for component *B*. The composition of *A* in phase 1 can be conveniently expressed using determinants:

$$d_{A1} = \frac{\begin{vmatrix} m_A & V \\ m'_A & kV \end{vmatrix}}{\begin{vmatrix} kV & V \\ V & kV \end{vmatrix}} = \frac{km_A - m'_A}{(k^2 - 1)V}. \quad (11)$$

Equation (11) gives the equilibrium mass-based concentration of  $d_{A1}$  as a function of the experimental measurables  $m_A$ ,  $m'_A$ , and  $V$  and the methodological variable  $k$ . Using the propagation of errors expression, the uncertainty in  $d_{A1}$  can be written

$$u(d_{A1}) = \left[ \left( \frac{\partial d_{A1}}{\partial k} \right)_{m_A, m'_A, V}^2 u^2(k) + \left( \frac{\partial d_{A1}}{\partial m_A} \right)_{m'_A, V, k}^2 + \dots \right]^{1/2} \quad (12)$$

where the remaining terms deal with the standard uncertainties associated with  $m'_A$  and  $V$ . In eq. (12), all terms but the first arise from intrinsic *experimental* uncertainties beyond our control. Since the first term involves  $k$ , the arbitrarily chose volume ratio, its impact on  $u(d_{A1})$  can be modified (minimized) by careful experimental design.

The value of  $k$  will be optimal when it yields the *minimum* error in  $d_{A1}$ . Thus its optimal value may be determined by setting the coefficient  $(\partial d_{A1} / \partial k)$  equal to zero and solving the resulting equation. In this way, the value of  $k$  for which the measured  $d_{A1}$  is *least* sensitive ( $k_{\text{opt}}$ ) is obtained; it corresponds to a minimization of the reading error in the meniscuses. Differentiating eq. (12) with respect to  $k$  and equation to zero gives, after simplification,

$$k^2 - 2k \frac{m'_A}{m_A} + 1 = 0. \quad (13)$$

The solution of eq. (13) is

$$k_{\text{opt}} = \frac{m'_A}{m_A} \pm \left[ \left( \frac{m'_A}{m_A} \right)^2 - 1 \right]^{1/2} \quad (14)$$

or, rearranging eq. (14)

$$\left( \frac{m'_A}{m_A} \right)_{\text{opt}} = \frac{k^2 + 1}{2k}. \quad (15)$$

Equation (15) provides a value of the optimal *volume* ratio  $k$  in terms of the mass ratio of one component, *A*, in the two complementary samples.<sup>4</sup>

The result in eq. (15) would clearly be more useful if we could express  $(m'_A / m_A)_{\text{opt}}$  in more specific terms. To obtain such information,

<sup>4</sup> Note that according to the initial premise,  $k > 1$  and thus eq. (15) requires that  $m'_A > m_A$ ; moreover, the positive root in that equation must be used. If in reality, however,  $m'_A < m_A$ , eqs. (14) and (15) are physically meaningless. In this case, the optimization relates instead to  $d_{A2}$ .

we divide the second equation in eq. (10) by the first; after dividing by  $V$ , we get

$$\frac{m'_A}{m_A} = \frac{d_{A1} + kd_{A2}}{kd_{A1} + d_{A2}}. \quad (16)$$

Now, equating the expressions for  $m'_A/m_A$  in eqs. (15) and (16), after clearing terms we have in the cubic equation

$$d_{A1}k^3 - d_{A2}k^2 + d_{A1}k + d_{A2} = 0. \quad (17)$$

This can be simplified by dividing by  $d_{A2}$  and defining  $r$  as  $d_{A1}/d_{A2}$ :

$$rk^3 - k^2 - rk + 1 = 0. \quad (18)$$

The solution of eq. (18) yields one real and two conjugate complex roots. The physically meaningful result from eq. (18) is

$$k_{\text{opt}} = \frac{1}{r} = \frac{d_{A2}}{d_{A1}}, \quad (19)$$

where  $r$  (or  $1/r$ ) is called the *distribution ratio* (or distribution coefficient) of component  $A$  in the two phases and is a thermodynamic quantity because its value depends on equilibrium solubilities. From eq. (15), the optimal mass ratio in the two samples is

$$\left( \frac{m'_A}{m_A} \right)_{\text{opt}} = \frac{r^2 + 1}{2r}. \quad (20)$$

Consider this result. It is reasonable to expect the optimal volume ratio  $k$  (or mass ratio) to be equal to some *characteristic* property of the system, and this turns out to be its distribution ratio,  $r$ .<sup>5</sup>

An analogous result can be obtained for the optimal volume and mass ratios for component  $B$ . In general, these optimal conditions are not the same for the two components because the mutual solubilities of  $A$  and  $B$  are different; thus, if the optimization condition derived is  $k_A = d_{A2}/d_{A1}$ , the constraint pertinent to component  $B$ ,  $k_B$ , is

$$k_B = \frac{d_{B1}}{d_{B2}}. \quad (21)$$

<sup>5</sup> Note that it is assumed  $k > 1$ . If in reality, however,  $d_{A2} < d_{A1}$ , then the denotation of phases must be reversed; that is, the upper phase in fig. 3 is 1 and the lower one is 2.