The Binary Temperature–Composition Phase Diagram

Phillip C. Sanders, James H. Reeves, and Michael Messina*

Department of Chemistry, University of North Carolina at Wilmington, Wilmington, NC 28403; *messinam@uncwil.edu*

It is the custom in an undergraduate physical chemistry course in thermodynamics to present (and derive) the vapor pressure versus composition phase diagram for an ideal binary liquid mixture. This derivation is relatively straightforward and is based on Raoult's law *(1–6)*. The derivation leads to an explicit expression for the liquid and gas lines in the phase diagram, as well as an expression showing the relation between the mole fractions in the gas and liquid phases at a particular pressure. The next topic in the course is usually the temperature–composition phase diagram that is typically drawn on the board (or presented as a figure in a text) without explanation as to where it originated. Some textbooks state that, unlike the vapor pressure phase diagram, the equations for the temperature–composition phase diagram are too complicated to derive and present *(4, 5)*.

Unfortunately, the temperature–composition phase diagram is of far more practical importance than the vapor pressure phase diagram, because it is far easier to vary temperature in the laboratory than pressure and most chemists distill liquid mixtures by varying the temperature of the mixture rather than pressure. In fact, in the physical chemistry laboratory course, students typically perform an experiment on a binary liquid mixture to determine the temperature–composition phase diagram.

So summing up what we have so far: although vapor pressure phase diagrams are not so important, students are led through the derivation of the diagram, while temperature–composition phase diagrams that are very important are seemingly produced out of thin air with no derivation or detailed explanation of where they come from. This is unacceptable because there are many questions a student could ask about the properties of the temperature composition phase diagram that can not be answered unless the professor understands the origin of the diagram. Some obvious questions are (i) Are the liquid and gas lines mirror images of one another, one having positive curvature and the other having negative curvature of the same magnitude? (ii) How do the heats of vaporization of the liquids affect the diagram? (iii) How does the difference in the boiling points of the two components affect the diagram? (iv) Why is the liquid line bowed in the temperature–composition phase diagram, while it is straight in the vapor pressure phase diagram?

We will show that the equations for the liquid and gas lines in the temperature–composition phase diagram are *not* too difficult to derive, within a reasonable approximation, in class. The approximation we make to simplify the diagram is that values of ΔH_{vap} for the two liquids are equal. This approximation is very reasonable. Ideal liquid mixtures are comprised of two similar liquids and a quick perusal of a *CRC (7)* demonstrates that values of ΔH_{vap} for similar liquids are similar. For example: ΔH_{vap} of cyclohexane and hexane are 32.76 kJ mol^{-1} and 31.91 kJ mol^{-1}, respectively, and ΔH_{vap} of benzene and toluene are 34.08 kJ mol^{-1} and 35.90 kJ mol^{-1}, respectively. We analyze the resulting equations and show how the phase diagram is affected by both the ΔH_{vap} of the liquids and the difference in boiling points between the two liquids. We also demonstrate the origin of the curvature of the liquid line in the temperature–composition phase diagram. Finally, we derive a simple equation that can be used to predict the number of theoretical plates needed to distill an initial mixture to a desired purity and present numerical comparisons based on two ideal binary liquid systems: cyclohexane–hexane and benzene–toluene.

Derivation of the Temperature–Composition Phase Diagram

The Liquid and Gas Lines

The starting point for the derivation of the liquid and gas lines in the temperature–composition phase diagram is Raoult's law for a binary liquid mixture. We consider a generic liquid mixture of two liquids, A(l) and B(l). We assume without loss of generality that A(l) is the more volatile liquid so that the boiling point of A is less than that of B. We also define $p_A^*(T)$ and $p_B^*(T)$ as the vapor pressures of pure liquids A and B at temperature T. The total vapor pressure at temperature T, $P_{tot}(T)$, of the mixture is a function of the mole fraction of species A in the gas, y_A, and in the liquid, x_A. These relations are derived in most physical chemistry texts and can be expressed as *(1)*:

$$P_{tot} = p_B^* + \left(p_A^* - p_B^* \right) x_A \qquad (1a)$$

$$P_{tot} = \frac{p_A^* \, p_B^*}{p_A^* + \left(p_B^* - p_A^* \right) y_A} \qquad (1b)$$

The vapor pressures of the pure liquids are given by the integrated form of the Clausius–Clapeyron equation

$$p_A^* = p_A^\circ e^{-\chi_A(T)} \quad \text{and} \quad p_B^* = p_B^\circ e^{-\chi_B(T)} \qquad (2a)$$

with

$$\chi_i(T) = \frac{\Delta_{vap} H_i}{R} \left\{ \frac{1}{T} - \frac{1}{T_i^\circ} \right\} \qquad (2b)$$

where i = component A or B.

We choose the reference temperatures, T_A° and T_B°, to be the normal boiling points of liquids A and B. This means that the reference pressures, p_A° and p_B°, in eq 2a are 1 bar each. The equations for the liquid and gas lines are found by substituting eqs 2a into eq 1a and eq 1b, respectively,

$$P_{tot}(T) = \left\{ e^{-\chi_B(T)} + \left[e^{-\chi_A(T)} - e^{-\chi_B(T)} \right] x_A \right\} P^\circ \qquad (3a)$$

$$P_{\text{tot}}(T) \;=\; \frac{P^{\circ}e^{-[\chi_A(T)+\chi_B(T)]}}{e^{-\chi_A(T)} \;+\; \left[e^{-\chi_B(T)} \;-\; e^{-\chi_A(T)}\right]y_A} \quad (3b)$$

where P° is the standard pressure of 1 bar. The liquid mixture boils when its vapor pressure is equal to the external laboratory pressure. If the laboratory pressure is assumed to be 1 bar and the enthalpies of vaporization of A(l) and B(l) are equal, setting the left-hand side of eqs 3a and 3b equal to unity and solving for T leads to the following equations for the liquid and gas lines in the temperature–composition phase diagram at $P = 1$ bar:

$$T_{\text{liq}} \;=\; \frac{T_B^{\circ}}{1 \;+\; C\ln\left[1 \;+\; (\gamma \;-\; 1)x_A\right]} \quad (4a)$$

$$T_{\text{gas}} \;=\; \frac{T_B^{\circ}}{1 \;-\; C\ln\left[1 \;+\; \left(\gamma^{-1} \;-\; 1\right)y_A\right]} \quad (4b)$$

The physical parameters C and γ are given by

$$C \;=\; \frac{R\,T_B^{\circ}}{\Delta H} \quad (5a)$$

$$\gamma \;=\; \exp\left[\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T_A^{\circ}} \;-\; \frac{1}{T_B^{\circ}}\right)\right] \quad (5b)$$

where ΔH is the common enthalpy of vaporization of the two liquids and $R = 8.314$ J K^{-1} mol^{-1}. It is easy to see that eqs 4a and 4b have the correct limiting behavior. When the liquid is pure B, $x_A = 0$, and eqs 4a and 4b reduce to T_B° the boiling point of pure B(l). When the liquid is pure A, $x_A = 1$, and eqs 4a and 4b reduce to $T_B^{\circ}(1 + C\ln\gamma)^{-1}$ for the liquid line and $T_B^{\circ}(1 - C\ln\gamma^{-1})^{-1}$ for the gas line, which, in each case, is equal to the boiling point of pure A(l).

Distilling the Mixture: Theoretical Plates

Here we derive an equation that will allow for the calculation of the number of theoretical plates needed to distill an initial mixture to a desired purity. This derivation starts from the relation between the mole fractions of A in the gas and liquid. The liquid and gas compositions at a particular temperature are found by drawing tie lines between the liquid and gas lines at that temperature. Thus, setting eqs 4a and 4b equal gives the following relation for the mole fraction of the more volatile component, A, in the gas phase as a function of mole fraction of A in the liquid phase

$$y_A \;=\; \frac{\gamma\,x_A}{1 \;+\; (\gamma \;-\; 1)x_A} \quad (6)$$

The mole fraction of A in the gas phase after the Nth theoretical plate, $y_{A,N}$, is obtained by

$$y_{A,N} \;=\; \frac{\gamma\,y_{A,N-1}}{1 \;+\; (\gamma \;-\; 1)y_{A,N-1}} \quad (7)$$

This means, algebraically, one solves eq 6 for y_A for a given x_A, then sets $y_{A,N} = x_{A,N-1}$ and uses eq 6 again to find the next gas mole fraction. It is not hard to show that, in general, after N theoretical plates this process leads to the following result for the mole fraction of A in the gas phase

$$y_{A,N} \;=\; \frac{\gamma^N x_A^{\circ}}{1 \;+\; \left(\gamma^N \;-\; 1\right)x_A^{\circ}} \quad (8)$$

Equation 8 shows that, if given an initial liquid composition with x_A°, one can compute the mole fraction in the gas phase directly after the application of N theoretical plates. For example, if one starts with an initial composition of x_A° and wants to find the number of theoretical plates needed to distill to a purity of greater than 90% in A(l), setting the left-hand side of eq 8 equal to 0.9 and solving for N yields

$$N \;\approx\; \frac{\ln\left(\dfrac{9}{x_A^{\circ}}\right)}{\ln(\gamma)} \quad (9)$$

The approximate equality means that one should take the nearest integer result of eq 9 as the number of theoretical plates.[1] Equation 8 also shows that only as the number of theoretical plates $N \to \infty$ does the purity of the condensate, $y_{A,N}$ approach unity. Thus one can not completely purify an ideal liquid mixture through distillation in a finite number of boiling–condensation steps.

Analysis of the Diagram

Curvature of the Phase Lines

It is well known that both the liquid and gas phase lines in the temperature–composition phase diagram are curved. Here we show how the curvature of the phase lines depends on the physical properties of the liquid mixture, that is, ΔH_{vap} of the liquids and the difference in boiling points of the liquids.

The constant, C, in eqs 4a and 4b for the phase lines is typically small. Since the $\Delta H_{\text{vap}} \sim$ 20–40 kJ mol^{-1} and boiling points are on the order of 350–400 K the ratio given in eq 5a is on the order of $\sim 1/10$. This means one can expand eqs 4 for the phase lines using $(1 + x)^{-1} \sim (1 - x)$ for $|x| < 1$. This results in the following equations for the phase lines

$$T_{\text{liq}} \;\approx\; T_B^{\circ} \;-\; \frac{R\left(T_B^{\circ}\right)^2}{\Delta H}\ln\left[1 \;+\; (\gamma \;-\; 1)x_A\right] \quad (10a)$$

$$T_{\text{gas}} \;\approx\; T_B^{\circ} \;+\; \frac{R\left(T_B^{\circ}\right)^2}{\Delta H}\ln\left[1 \;+\; \left(\gamma^{-1} \;-\; 1\right)y_A\right] \quad (10b)$$

If the quantities $\gamma - 1$ and $\gamma^{-1} - 1$ are small then the logarithm in eqs 10a and 10b can be expanded using the relation $\ln(1 + x) \sim [x - (x^2/2)]$, which results in the following

equations for the phase lines

$$T_{\text{liq}} \approx T_{\text{B}}^{\circ} - \frac{R\left(T_{\text{B}}^{\circ}\right)^2}{\Delta H}(\gamma - 1)x_{\text{A}}$$

$$+ \frac{R\left(T_{\text{B}}^{\circ}\right)^2}{2\Delta H}(\gamma - 1)^2 x_{\text{A}}^2 \qquad (11a)$$

$$T_{\text{gas}} \approx T_{\text{B}}^{\circ} + \frac{R\left(T_{\text{B}}^{\circ}\right)^2}{\Delta H}\left(\gamma^{-1} - 1\right)y_{\text{A}}$$

$$- \frac{R\left(T_{\text{B}}^{\circ}\right)^2}{2\Delta H}\left(\gamma^{-1} - 1\right)y_{\text{A}}^2 \qquad (11b)$$

If $\gamma - 1$ and $\gamma^{-1} - 1$ are small, the phase lines would be linear in the mole fraction resulting in noncurved phase lines. That the phase lines *are* curved arises from the fact that $\gamma - 1$ and $\gamma^{-1} - 1$ are *not* small enough to keep only the linear term in the $\ln(1 + x)$ expansion and, as eqs 11a and 11b show, the next term goes as the square of the mole fractions, resulting in curved phase lines.

Thus the curvatures of the lines increase as the quantities γ and γ^{-1} become increasingly larger or smaller than unity. These parameters become different from unity as the exponent in eq 5b increases. This exponent is given by $(\Delta H \Delta T / R T_{\text{A}}^{\circ} T_{\text{B}}^{\circ})$, where $\Delta T = T_{\text{B}}^{\circ} - T_{\text{A}}^{\circ}$. Thus the phase lines should become more bent as ΔH increases or the difference of boiling points between the two liquids, ΔT, increases.

Curvature of the Liquid Line

As pointed out previously, students are often curious as to why the liquid line is straight in the vapor pressure phase diagram yet curved in the temperature–composition phase diagram. The discussion above is a relatively rigorous demonstration of why the liquid line is curved in the temperature–composition phase diagram. There is a simpler explanation for its curvature.

The liquid line in the vapor pressure phase diagram is given by eq 1a. This equation shows that the total vapor pressure (the y variable) is directly proportional to the mole fraction (the x variable) leading to a straight line. If one was to make the simple assumption that the vapor pressure of a pure liquid varies linearly with the temperature then $p_{\text{A}}^*(T) = aT$ and $p_{\text{B}}^*(T) = bT$ where a and b are constants. Substituting these equations into eq 1a results in

$$P_{\text{tot}} = \left[b + (a - b)x_{\text{A}}\right]T \qquad (12)$$

At the boiling point the total vapor pressure is 1 bar and eq 12 will give the following for the liquid line,

$$T_{\text{liq}} = \frac{1}{b + (a - b)x_{\text{A}}} \qquad (13)$$

which is *not* a straight line but rather a curve. Thus the liquid line must be curved because both the dependent variable, T, and the independent variable, x, appears as a product in the expression for the total vapor pressure (eq 12). Further, this demonstrates that the curvature of the liquid line in the temperature–composition phase is *not* due to the nonlinear behavior of a liquid's vapor pressure with temperature.
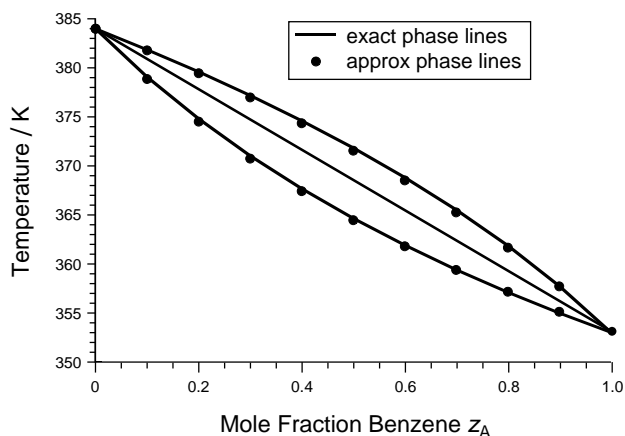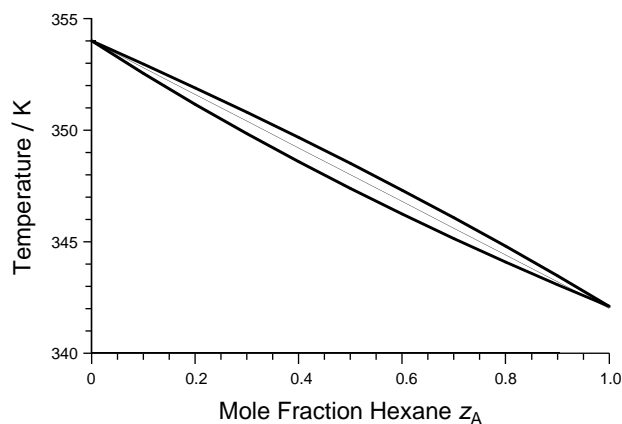

Figure 1. Temperature–composition phase diagram for benzene–toluene mixture. The lines show exact calculation of phase line and solid circles show approximate result when ΔH_{vap} [benzene] is set equal to ΔH_{vap} [toluene]. The straight line joins the pure boiling points of the two liquids. The overall composition of the more volatile liquid in all figures is z_{A}.

Figure 2. Temperature–composition phase diagram for hexane–cyclohexane mixture as computed by approximating ΔH_{vap} [hexane] = ΔH_{vap} [cyclohexane]. Again, the straight line joins the pure boiling points of the two liquids.

Distillation of Mixtures

The number of theoretical plates needed to distill to a purity greater than 90% in the more volatile component, A, is given by eq 9. As shown by this equation the number of theoretical plates decreases as the value of γ increases. As shown previously, the value of γ increases as its exponent, $(\Delta H \Delta T / R T_A^{\circ} T_B^{\circ})$, increases. Thus the number of theoretical plates should increase as the boiling-point difference between the two liquids decreases and ΔH decreases. One could have intuitively guessed that it should become harder to separate a liquid mixture by distillation as the boiling points of the two liquids become the same. What is not so obvious is that it is easier to distill a mixture of two liquids with a large enthalpy of vaporization than a smaller enthalpy of vaporization.

Some Numerical Results

We present some numerical results on two binary liquid mixtures, a cyclohexane–hexane mixture, and a benzene–toluene mixture. These mixtures should behave ideally, have similar enthalpies of vaporization,[2] and the boiling points of the two mixtures are quite different.[3] The ΔT value for the hexane–cyclohexane mixture is 13 K while for the value for benzene–toluene mixture is larger, 31 K. Thus we can explore the effect of the boiling point difference on the phase diagram.

The temperature–composition phase diagram for the benzene–toluene mixture is shown in Figure 1. The solid lines are the phase lines as computed exactly, that is, without assuming ΔH_{vap} of the liquids are equal. The solid circles are the results from eqs 4a and 4b, using the average ΔH_{vap} = 35.0 kJ mol^{-1}. As shown by Figure 1 the approximate results are nearly identical to the exact phase lines. We also include a straight line in the phase diagram that joins the boiling points of the pure liquids.

The temperature–composition phase diagram for the hexane–cyclohexane mixture is shown in Figure 2. These phase lines result from eqs 4a and 4b, using the average ΔH_{vap}
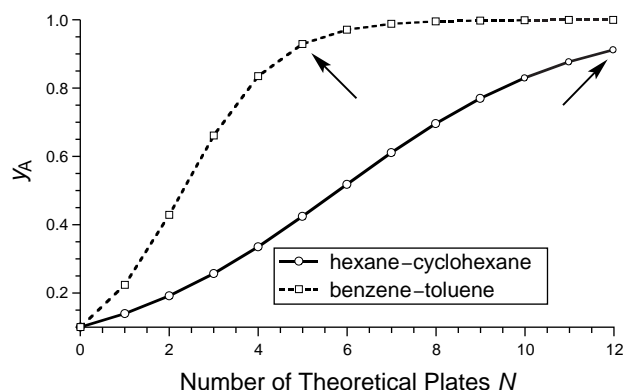
= 32.4 kJ mol^{-1}. We also show a straight line in the phase diagram that joins the boiling points of the pure liquids.

Comparing Figures 1 and 2 shows that the mixture with the larger difference in boiling point (the benzene–toluene mixture) has the larger curvature of the phase lines and larger area between the phase lines. This should result in making the benzene–toluene mixture easier to distill towards purity than the hexane–cyclohexane mixture. In Figure 3 we show the mole fractions of the more volatile components in each mixture (hexane and benzene) in the gas phase versus the number of theoretical plates. These curves are computed using eq 8. The figure clearly shows that the benzene–toluene mixture (the dashed line) becomes 90% pure in benzene at the 5th theoretical plate, while it takes approximately 12 theoretical plates to get 90% purity in hexane. The arrows in Figure 3 indicate where eq 9 predicts the mixture should become greater than 90% pure starting from an initial mole fraction of 0.1 more volatile component. The figure shows that eq 9 is very accurate in predicting the number of theoretical plates.

Finally, in Tables 1–3, we use eq 9 to show how the number of theoretical plates varies under three different conditions. In Table 1, we show how *N*, the number of theoretical plates depends on the boiling temperature difference, ΔT, between the two liquids, holding the ΔH_{vap} of the two liquids constant.[4] As shown in Table 1, as the ΔT increases the num-

Table 1. Change in Number of Plates with Constant Δ*H* and Variable Δ*T*

Δ*H*/kJ	*T*$_A$/K	*T*$_B$/K	Δ*T*	Number of Plates
30	350	360	10	16
30	350	370	20	8
30	350	380	30	6
30	350	390	40	4
30	350	400	50	3

Table 2. Change in Number of Plates with Constant Δ*T* and Variable Δ*H*

Δ*H*/kJ	*T*$_A$/K	*T*$_B$/K	Δ*T*	Number of Plates
15	350	360	10	31
20	350	360	10	24
25	350	360	10	19
30	350	360	10	16
35	350	360	10	13
40	350	360	10	12

Table 3. Change in Number of Plates with Constant Δ*T* and Variable Δ*H*

| Δ*H*/kJ	*T*$_A$/K	*T*$_B$/K	Δ*T*	Number of Plates
15	350	400	50	7
20	350	400	50	5
25	350	400	50	4
30	350	400	50	3
35	350	400	50	3
40	350	400	50	2

Figure 3. Plot of the mole fraction of the more volatile component in each mixture versus number of theoretical plates. These curves are plotted using eq 8. The arrows on each curve shows the point at which purity is greater than 90%.

ber of theoretical plates diminishes. In short, it is easier to distill an ideal mixture of two liquids having a larger difference in boiling points. In Table 2, we show how the number of theoretical plates depends on the ΔH_{vap} of the liquids, holding the ΔT between the liquids boiling temperatures constant, and small, that is, $\Delta T = 10$ K. The overall trend demonstrated by Table 2 is that the number of theoretical plates decreases as the ΔH_{vap} of the two liquids increases. Further, comparing Table 1 to Table 2 shows that the worst case scenario for distillation of two liquids is when they have similar boiling points and a low ΔH_{vap}. Finally, in Table 3 we show how the number of theoretical plates depends on the ΔH_{vap} of the liquids, holding the ΔT between the liquids boiling temperatures constant, and large, that is, $\Delta T = 50$ K. Again, the overall trend is that as the ΔH_{vap} of the two liquids increases the number of theoretical plates needed to distill the mixture to greater than 90% purity decreases.

Discussion and Conclusion

In this article we derived the equations for the liquid and gas lines in the binary temperature–composition phase diagram. We derived these equations by approximating that ΔH_{vap} of the two liquids are equal. We have shown that, within this approximation, the resulting equations are *not* too difficult to present in an undergraduate physical chemistry lecture.

We acknowledge that there is a large degree of mathematical analysis in this article, some of which probably has no place in an undergraduate lecture. We *do* feel that some of the results do, in fact, belong in an undergraduate discussion on binary liquid systems. The equations for the liquid and gas line in the phase diagrams, that is, eqs 4a and 4b, should be presented to undergraduates. The major properties of these equations can be discussed with a minimal degree of analysis. Also, an instructive homework problem can be designed that makes the student plot the temperature–composition phase diagram on an Excel spreadsheet. The equations that give the number of theoretical plates, that is, eqs 8 and 9, can also be presented in lecture.

Finally, we showed in eqs 12 and 13 why the liquid line must be curved in the temperature–composition diagram. This analysis does not need to be shown in its entirety but is simple enough for the instructor to discuss the essential ideas of the derivations. This equation is extremely important, easy to use, and can be discussed with a minimal degree of mathematical analysis.

Notes

1. To obtain eq 9 we approximate $(\gamma^N - 1) \sim \gamma^N$ in the denominator of eq 8. This is a good approximation as N gets large since $\gamma > 1$.

2. The ΔH_{vap} values of the liquids are benzene–34.1 kJ mol^{-1}, toluene–35.9 kJ mol^{-1}, cyclohexane–32.8 kJ mol^{-1}, and hexane–31.9 kJ mol^{-1}.

3. The boiling points of pure hexane and cyclohexane are 342 K and 354 K, respectively. The boiling points of pure benzene and toluene are 353 K and 384 K, respectively.

4. All calculations in Tables 1–3 are performed using eq 9 and rounding N to the nearest integer. Note, according to eq 9 we asking how many theoretical plates are needed to distill to the mixture to greater than 90% purity.

Literature Cited

1. Adamson, A. W. *Physical Chemistry,* 3rd ed.; Academic Press, Inc.: Orlando, FL, 1986.
2. Alberty, R. A.; Silbey, R. J. *Physical Chemistry,* 3rd ed.; John Wiley & Sons, Inc.: New York, 2000.
3. Atkins, P. W. *Physical Chemistry,* 6th ed.; W. H. Freeman and Company: New York, 1998.
4. Barrow, G. M. *Physical Chemistry,* 5th ed.; McGraw-Hill Book Company: New York, 1988.
5. Castellan G. W. *Physical Chemistry,* 3rd ed.; Addison-Wesley Publishing Company: Reading, MA, 1983.
6. Mortimer, R. G. *Physical Chemistry,* 2nd ed.; Harcourt Academic Press: San Diego, CA, 2000.
7. *CRC Handbook,* 52nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1971.