

Liquid-Vapor Equilibria in Binary Systems¹

Purpose The purpose of this experiment is to study a binary liquid-vapor equilibrium of chloroform and acetone. Measurements of liquid and vapor compositions will be made by refractometry. The data will be treated according to equilibrium thermodynamic considerations, which are developed in the theory section.

Theory

Consider a liquid-gas equilibrium involving more than one species. By definition, an ideal solution is one in which the vapor pressure of a particular component is proportional to the mole fraction of that component in the liquid phase over the entire range of mole fractions. Note that no distinction is made between solute and solvent. The proportionality constant is the vapor pressure of the pure material.

Empirically it has been found that in very dilute solutions the vapor pressure of solvent (major component) is proportional to the mole fraction X of the solvent. The proportionality constant is the vapor pressure, p^0 , of the pure solvent. This rule is called Raoult's law:

$$p_{\text{solvent}} = p^0_{\text{solvent}} X_{\text{solvent}} \quad \text{for } X_{\text{solvent}} = 1 \quad (1)$$

For a truly ideal solution, this law should apply over the entire range of compositions. However, as X_{solvent} decreases, a point will generally be reached where the vapor pressure no longer follows the ideal relationship.

Similarly, if we consider the solute in an ideal solution, then Eq.(1) should be valid. Experimentally, it is generally found that for dilute real solutions the following relationship is obeyed:

$$p_{\text{solute}} = K X_{\text{solute}} \quad \text{for } X_{\text{solute}} \ll 1 \quad (2)$$

where K is a constant but not equal to the vapor pressure of pure solute. Equation (2) is called Henry's law.

The implication of the foregoing discussion is that ideal solutions are not likely to be found. Only very dilute solutions could be considered ideal. Furthermore, there is no theory available which places limits on just how concentrated a solution must be if deviations from ideality are to be observed. Such limits are set by experimentation and vary, of course, from system to system.

A useful way of treating data relating the vapor pressure of any component to its mole fraction in solution is to plot p_i/X_i versus X_i . Variations of the ratio with X_i indicate deviations from ideality. From the discussion of the previous paragraphs a plot such as that shown in Fig. 1 might be expected for a binary solution. At high concentrations of component i , Raoult's law should be valid and the ordinate should be constant and equal to the vapor pressure of pure component i . At some lower mole fraction of i (more concentrated in solute) deviations from ideality may be observed and p_i/X_i may increase or decrease. At very low concentrations, the solute becomes the solvent and Henry's law becomes valid. Thus, p_i/X_i becomes constant again and takes on the value of Henry's law constant.

Ideality and deviations from it may be qualitatively understood by considering molecular interactions. For the purposes of this discussion, we view the gas-liquid interface at the

molecular level. A crude representation of a dilute binary system is shown in Fig. 2. Component *i* is the more concentrated (solvent).

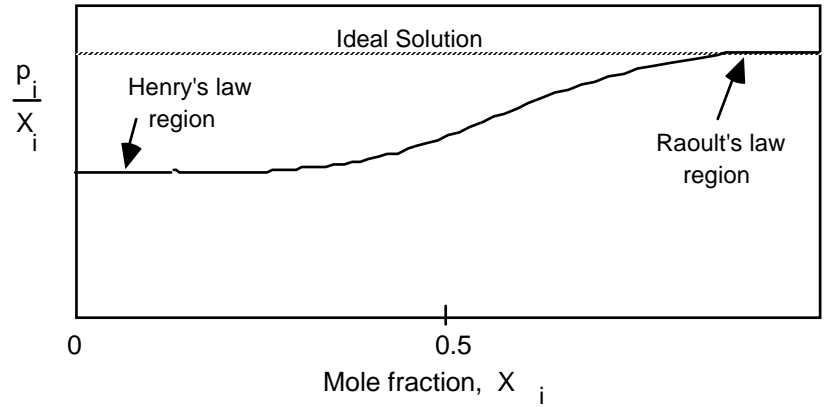


Figure 1. Variation of p_i/X_i

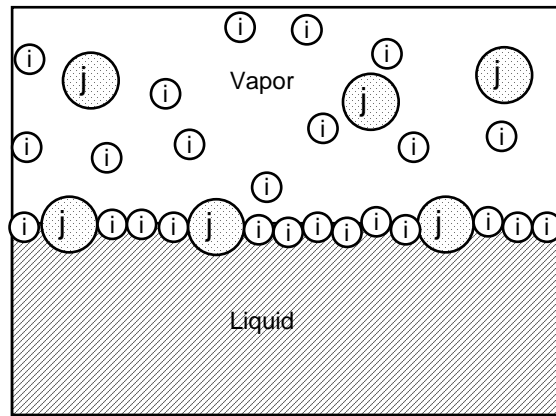


Figure 2. Molecular representation of a binary gas-liquid system.

If the system were pure *i*, then all the molecules in the surface layer would be *i* molecules and the observed vapor pressure would be that of the pure liquid. Addition of *j* molecules to the liquid so that the mole fraction of *i* is less than unity reduces the concentration of *i* molecules in the surface layer just as it does in the body of the liquid. Energy is required to transfer a molecule from the liquid to the gas phase, implying that intermolecular potentials are important in determining partial vapor pressures. If molecule *i* "looks about" and "sees" the same potential field as molecule *j* regardless of what its neighbors are, then molecule *i* will require the same energy as molecule *j* to transfer from the liquid phase to the gas phase. The partial vapor pressures will then be directly proportional to the concentration of each component in the solution and will extrapolate to the vapor pressure of each component when pure *i* or pure *j* is used. Thus, a sufficient condition for an ideal solution is to require the interaction potential between (*i*, *j*) pairs to be identical to that between (*i*, *i*) pairs and (*j*, *j*) pairs.

Experimentally observed deviations from ideality are then attributed to differences in interaction potentials between different pairs of molecules. From this point of view deviations

from ideality become very intuitive since there is no a priori reason to expect molecules of widely differing properties to have the same interactions. At very high or very low concentrations of one component the constancy of p_i/X_i is easily understood since the partners in these extremes are mostly of a single kind.

From an experimental point of view, a binary, two-phase equilibrium system at constant pressure can be characterized by plotting the equilibrium boiling point as a function of the liquid- and vapor-phase compositions (usually mole fractions). These two compositions are different because of variations in the escaping tendency of the molecules involved. Figure 3 shows temperature versus composition diagrams for hypothetical ideal and nonideal mixtures. At the left is a typical ideal (or nearly ideal) system. The center figure shows the case of a strong negative deviation from ideality in which the boiling point of some mixtures rises above that of the highest boiling pure component. At the molecular level there are stronger forces between solvent and solute than between solvent and solvent.

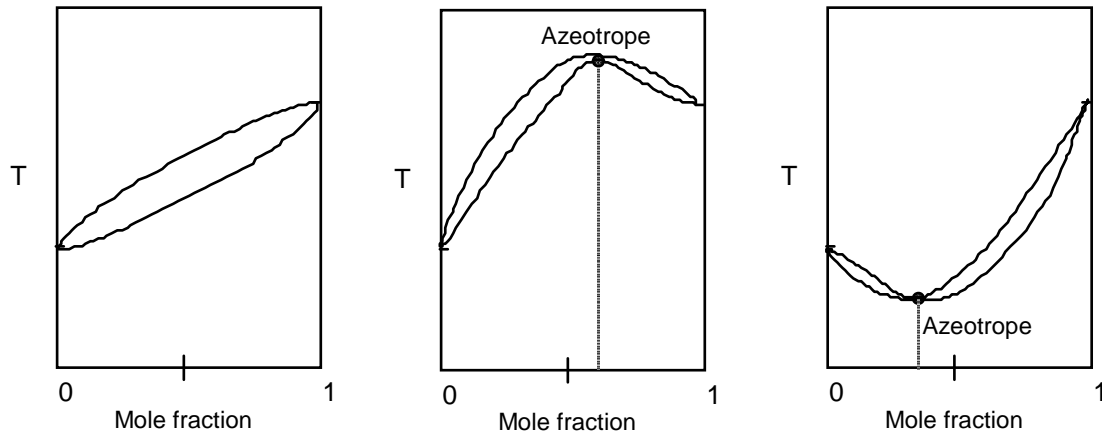


Figure 3. Temperature versus composition for a binary two component system.

At some intermediate composition the liquid- and vapor-phase compositions come together at the so-called azeotropic composition. Separation of one component from another by fractional distillation is impossible at this composition because the vapor and liquid phase have the same composition. The figure at the right in Fig. 3 is also a nonideal mixture in which a positive deviation from ideality is found.

As usual, the equilibrium properties of these solutions are developed by considering the Gibbs free energy or the chemical potential. For the present case of a binary two-phase system at equilibrium, we require the chemical potential, μ_i , of each component to have the same value in every phase:

$$\mu_i^{(l)} = \mu_i^{(g)} \quad (3)$$

The chemical potential is related to molar volume \bar{V}_i and pressure p_i by the relation

$$d\mu_i^{(g)} = \bar{V}_i dp_i \quad (4)$$

If the gas is ideal, substituting for \bar{V}_i of the gas in terms of the ideal gas law furnishes

$$d\mu_i^{(g)} = RT \frac{d p_i}{p_i} \quad (5)$$

which upon integration, from a standard state pressure of $p^0=1$ bar to a pressure for component i of p_i , leads to

$$\mu_i^{(g)} = \mu_i^{o(g)} + RT \ln \frac{p_i}{p^0} \quad (6)$$

where $\mu_i^{o(g)}$ is the standard-state chemical potential. Substituting Raoult's law for ideal solutions into Eq. (6) and noting that at equilibrium $\mu_i^{(l)} = \mu_i^{(g)}$ leads to

$$\mu_i^{(l)} = \mu_i^{\bullet(l)} + RT \ln X_i \quad (7)$$

where $\mu_i^{\bullet(l)} \neq \mu_i^{o(g)}$, which serves to emphasize an important point. If you are making calculations involving standard states, make certain the standard state used is consistent with the concentration units being used (i.e., just as $p_i \neq X_i$, so $\mu_i^{\bullet(l)} \neq \mu_i^{o(g)}$).

Equation (7) depends for its development on both the ideal gas law and the ideal solution law. Use of these laws permitted the connection between \bar{V}_i and p_i and then X_i . Deviations from both these laws do occur. To examine how deviation from ideal solution behavior is formally treated, we return to Eq. (6) which is valid as long as the vapor phase is ideal for any solution.

To make progress toward nonideal solution conditions, the vapor pressure of a component above the real solution must be known. Generally speaking, valid equations are not readily available in analytical form. Rather, the experimental data have simply been tabulated for those systems that have been studied. With these data, Eq. (6) can then, in principle, be used to furnish the chemical potential of the solution.

An alternative, introduced by G. N. Lewis, preserves the form of Eq. (6) or (7) but does not require ideality. In this formulation the mole fraction is replaced by a quantity a_i , called the activity of component i , and Eq. (7) becomes

$$\mu_i^{(l)} = \mu_i^{\bullet(l)} + RT \ln a_i \quad (8)$$

In this formulation all deviations from ideality are contained in the activities. Generally they are not amenable to quantitative theoretical interpretation and, as such, are simply empirical experimental quantities. The form of Eq. (8) however, is quite convenient because it preserves the form of all equilibrium constant expressions.

The activity of component i is given by

$$a_i = \frac{p_i}{p_i^\bullet} \quad (9)$$

where p_i is the partial vapor pressure of component i and p_i^\bullet is the vapor pressure of pure i at the same temperature.

Conclusion: We have exchanged one difficulty for another. The form of thermodynamic relations has been preserved through the introduction of the activity. However, the problem of understanding nonideality has not been advanced at all. From one point of view, the activity is simply a *fudge factor* which brings experimental data into the form of an ideal equation. From a different point of view, the use of Eq. (8) requires a method of obtaining activities from experimental measurements of concentrations.

The activity a_i appearing in Eq.(8) is related to a concentration variable through the use of an activity coefficient γ_i . This coefficient depends on both the species i and the concentration scale. For the present experiment the activity coefficient of interest is that of a species present in a solution at mole fraction X_i and $a_i = \gamma_i X_i$. Substituting into Eq.(9) and rearranging gives

$$\gamma_i = \frac{p_i}{X_i p_i^\bullet} \quad (10)$$

The vapor pressure of the pure liquid, p_i^\bullet , is a function of temperature and can be predicted using the relationship

$$\log p_i^\bullet = A - \frac{B}{t + C} \quad (11)$$

with t the temperature in degrees Centigrade and tabular values for A , B , and C (see Lange's Handbook).

Experimental

A refractometer is used in this experiment to measure mole fractions. To obtain mole fraction information from refractive index measurements, the refractometer must be calibrated (i.e., construct a graph of refractive index versus composition) using solutions of known composition. This calibration curve can then be used "in reverse" to find the composition of unknown mixtures from an experimental measurement of the refractive index. The calibration chart for chloroform-acetone mixtures is given in Table 1.

The boiling apparatus is shown in Fig. 4. An integral part is a reservoir heated by a resistive filament,. With a solution in the reservoir and boiling, the vapor phase is condensed and trapped in the tube below the condenser. Under equilibrium conditions in the boiling solution-vapor-phase system, the trapped condensate represents the vapor phase, while the liquid remaining in the reservoir represents the solution phase.

In what follows chloroform-acetone mixtures are assumed. The same procedure of sample treatment and analysis works very well for toluene-ethanol mixtures.

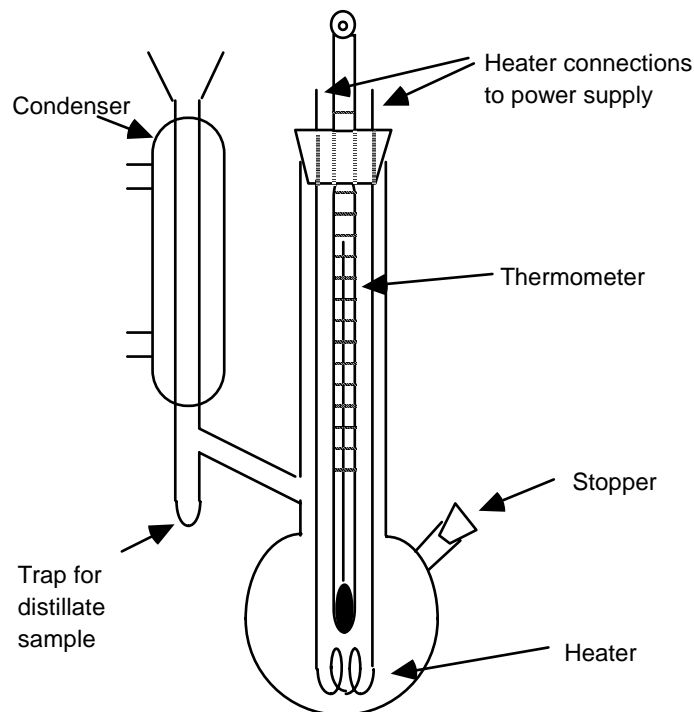


Figure 4. Apparatus for determining liquid and vapor compositions as a function of temperature.

The system studied will be chloroform-acetone. Samples of the following solutions should be run starting set A with 12 ml of acetone and set B with 12 ml of chloroform:

Increments added to existing solutions	A (ml of acetone added to 12 ml of chloroform)	B (ml of chloroform added to 12 ml of acetone)
First	2.0	2.5
Second	2.0	2.5
Third	1.5	2.5
Fourth	1.5	2.5
Fifth	1.5	2.5
Sixth	1.5	2.5

Chloroform is a suspected carcinogen-Use gloves and keep solutions in the hood

Notice that you will begin set A with pure chloroform and add six consecutive portions of acetone to the boiling liquid. If in the course of the run the flask becomes too full, pour out about 10 ml-make certain the heater is off-and continue the addition of acetone. Set B begins with pure acetone. To empty the reservoir, tilt the flask and ring stand together; don't loosen the clamps holding the flask.

The following should be followed:

1. Place 12 ml of pure chloroform in the flask through the side arm. Stopper the flask and start water flowing through the condenser. Record the barometric pressure.
2. Close the switch to the heater to start the liquid boiling. Caution: Never operate the heater unless liquid covers it. If the heater is operated dry, the filament will burn out.
3. After the distillate trap is filled, empty by using the stirrer so that the distillate will flow back into the body of the liquid. The distillate trap should be emptied at least three times before the sample of any solution is withdrawn. Continue to empty the trap until the temperature remains constant.
4. After the distillate trap has been filled a third time, allow 2 min for overflow to establish steady-state conditions and then stop heating. Remove the distillate sample with a pipet and immediately place into one of the sample holders. Several small test tubes will be needed for samples. Place the sample holders into an ice water bath. The distillate sample represents the vapor-phase composition.
5. Take a sample from the flask as representing the liquid phase at the same time the distillate sample is taken.
6. Record the equilibrium temperature corresponding to these two equilibrium compositions.
7. Measure the refractive index of both samples shortly after taking the sample to avoid sample loss via evaporation. Repeat the refractive index measurements to check for evaporative losses and reproducibility.
8. Record the barometric pressure.

Calculations

1. Use the index of refraction of pure chloroform and pure acetone to calibrate the refractometer. If there is an error, use the average error from the two measurements to correct all your readings. From the calibration curve, Table 1, determine the composition of the samples taken from the vapor and liquid phases in each experiment.
2. Construct a phase diagram using temperature versus mole percent composition. In the present case, there will be two compositions plotted at each equilibrium boiling temperature—one for the liquid phase and one for the vapor phase. Construct this one, single phase diagram by combining the results from both set of runs on one diagram. Make sure to include the pure liquids. Draw smooth curves for the liquid and vapor composition lines. You can draw these curves by hand using a “rubber ruler” or French curve if Excel curve fitting proves problematic.
3. In liquid-vapor equilibrium systems, there sometimes exists a particular composition at which the liquid phase and the vapor phase both have the same composition. This is called an azeotropic mixture. What is the azeotropic composition in the chloroform-acetone system and what is its boiling point?
4. Calculate the vapor pressure of acetone from Dalton's law, $P_i = Y_{\text{acetone}} P_{\text{tot}}$ for each measurement. Calculate the vapor pressure of pure acetone at the temperature of each measurement using Eq. 11. Calculate the activity coefficient for acetone for each measurement using Eq. 10. Use significant figure rules to estimate the uncertainty in the activity coefficients.

- Construct a plot of p_i/X_i versus X_i and comment on the ideality or nonideality of chloroform-acetone mixtures. Discuss any observations from a molecular view-point.
- Plot the activity coefficient γ_a for acetone as a function of the mole fraction of acetone. What inferences may be made from this plot?

Discussion

- Consider an azeotropic mixture of two components. Would fractional distillation be an appropriate way to separate the two components? Why?
- According to the phase diagram, what can be said about the attraction between acetone molecules as compared to the attraction between chloroform and acetone molecules? What might be the origin of this attraction?
- Does this system show positive or negative deviations from ideality?
- Is the vapor pressure at the azeotropic composition more or less than that predicted by Raoult's law? Explain.

Table 1. Refractive-index vs. Composition for Acetone-Chloroform Mixtures

n_D^{25}	M% CHCl ₃	n_D^{25}	M% CHCl ₃	n_D^{25}	M% CHCl ₃	n_D^{25}	M% CHCl ₃
1.3562	0.00	1.3780	23.50	1.4000	47.55	1.4220	72.85
1.3570	0.75	1.3790	24.60	1.4010	48.70	1.4230	74.10
1.3580	1.75	1.3800	25.65	1.4020	49.80	1.4240	75.30
1.3590	2.75	1.3810	26.70	1.4030	50.90	1.4250	76.50
1.3600	3.80	1.3820	27.80	1.4040	52.00	1.4260	77.70
1.3610	4.85	1.3830	28.85	1.4050	53.10	1.4270	78.95
1.3620	5.90	1.3840	29.95	1.4060	54.20	1.4280	80.20
1.3630	7.00	1.3850	31.00	1.4070	55.30	1.4290	81.40
1.3640	8.10	1.3860	32.05	1.4080	56.45	1.4300	82.65
1.3650	9.20	1.3870	33.15	1.4090	57.60	1.4310	83.90
1.3660	10.30	1.3880	34.25	1.4100	58.75	1.4320	85.15
1.3670	11.40	1.3890	35.30	1.4110	59.90	1.4330	86.40
1.3680	12.50	1.3900	36.40	1.4120	61.05	1.4340	87.70
1.3690	13.60	1.3910	37.50	1.4130	62.25	1.4350	89.00
1.3700	14.70	1.3920	38.60	1.4140	63.40	1.4360	90.35
1.3710	15.80	1.3930	39.75	1.4150	64.55	1.4370	91.65
1.3720	16.90	1.3940	40.85	1.4160	65.75	1.4380	93.00
1.3730	18.00	1.3950	42.00	1.4170	66.90	1.4390	94.35
1.3740	19.10	1.3960	43.10	1.4180	68.10	1.4400	95.75
1.3750	20.20	1.3970	44.25	1.4190	69.30	1.4410	97.20
1.3760	21.30	1.3980	45.35	1.4200	70.50	1.4420	98.55
1.3770	22.40	1.3990	46.45	1.4210	71.70	1.4431	100.00

Or if you prefer, you can use the following polynomial fit to the tabular data, with somewhat larger uncertainty:

$$\text{mol \%} = -5.8341 \times 10^4 + 1.2490 \times 10^5 n_D - 8.9849 \times 10^4 n_D^2 + 2.1734 \times 10^4 n_D^3$$

If you use this fit equation, it is best to use the Table for the few compositions closest to 0% or 100%.

References

1. John M. White, Physical Chemistry Laboratory Experiments, Prentice-Hall, Englewood Cliffs, NJ, 1975, Experiment 5.5.

Appendix: Index of Refraction

The index of refraction is the ratio of the speed of light in vacuum to the speed of light in the sample medium, $n=c_v/c_m$. Index of refraction is a fundamental property of matter that is easily measured. Index of refraction is important in determining fundamental molecular properties such as polarizability, as an analytical tool, and as a practical matter in optical waveguide technology. Refractometers are used as analytical tools, for example in the determination of sugar in beverages (wine) and the water content of hydraulic fluids used in automobiles, among many uses. Most refractometers determine the critical angle of a substance as a measure of the index of refraction. The critical angle is also the parameter necessary to understand optical fibers. Optical fibers play a critical role in communications technology, including the Internet and satellite technology, and also in analytical instrumentation.

The Critical Angle: When light passes from a medium with a higher index of refraction to a medium with a lower index of refraction, the angle with respect to the perpendicular to the interface increases, Figure 1.

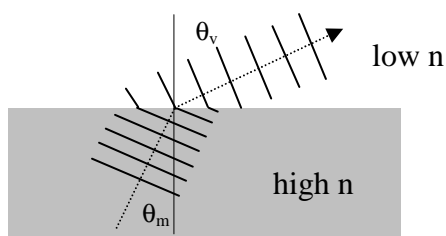


Figure 1. Refraction of light passing from a medium, m, with high index of refraction to one of lower index of refraction, such as in passing from glass into vacuum or air. The wave crests are shown with solid lines. The propagation direction is normal to the wave crests. The speed of light in the medium with lower index of refraction is faster causing the wave to bend and then $\theta_v > \theta_m$.

As the angle of incidence is increased, the refracted beam angle also increases until the refracted beam lies along the surface of the sample, Figure 2. This angle is called the critical angle. If the incidence angle is greater than the critical angle, the light is totally reflected from the interface.

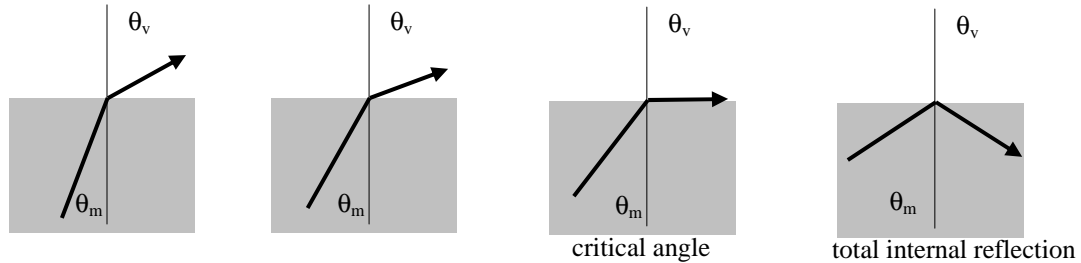


Figure 2. Critical angle. The angle of incidence is increased until the refracted beam makes a 90° angle with the surface normal. Total internal reflection results if the incidence angle is greater than the critical angle.

Total internal reflection explains how optical fibers can transmit light with little loss over large distances through a flexible core. The requirement is that the outside layer of the fiber, which is called the cladding, must have a lower index of refraction than the glass core.

The angles in Figure 2 can be related to the index of refraction:¹

$$n = \frac{c_v}{c_m} = \frac{\sin \theta_v}{\sin \theta_m}$$

Measuring the critical angle is relatively easy. The relationship between the critical angle and the index of refraction is given by setting $\theta_v = 90^\circ$:

$$n = \frac{c_v}{c_m} = \frac{1}{\sin \theta_{\text{crit}}}$$

Normally the measurement is made in air rather than vacuum, and then

$$n(\text{vacuum}) = 1.00027 n(\text{air}).$$

Index of refraction is both wavelength and temperature dependent. The glass prism in a refractometer is usually kept at constant temperature by circulation of water from a constant temperature bath at 25°C. The index of refraction is normally determined using a sodium arc emission lamp as a monochromatic light source. These lamps are also used for high intensity street lighting. The bright yellow color of a sodium arc lamp is due to the sodium “D” line, therefore the index of refraction measured at this wavelength is denoted n_D .

The most common type of refractometer is called an Abbe’ refractometer, Figure 3. The light from an incandescent bulb is passed through a thin film of the sample, which is placed on a refracting prism. The light from the refracting prism is reflected from a rotating mirror to an eye piece. When the rotating mirror is set properly, the user sees a field of view that is half-dark and half-bright. The interface between the dark and light region corresponds to the critical angle.

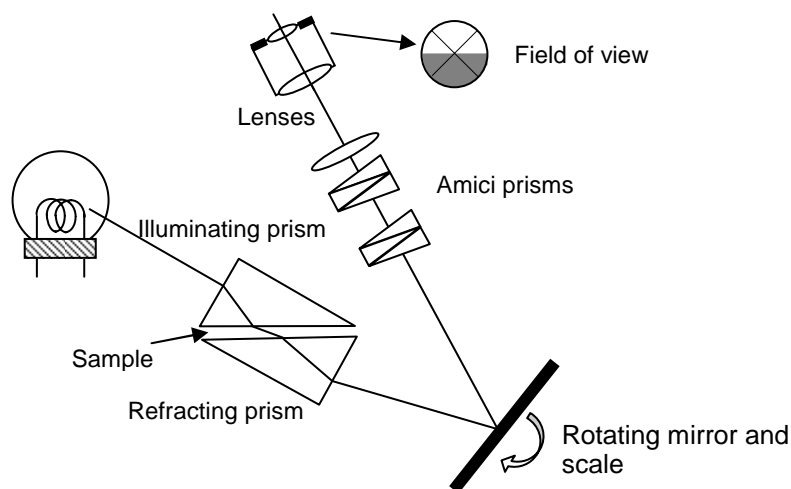


Figure 3. Abbe' refractometer.

The optical measurement is complicated by the refraction of the refracting prism which is in addition to the sample.¹ However, the instrument is calibrated versus a sample of known index of refraction. The measurement is taken by illuminating a printed scale on the rotating mirror that is read directly in index of refraction units.

You might wonder how a property that is wavelength dependent can be measured using a white light source. A clever optical trick is used to cause all wavelengths to refract at the angle that would be obtained using a monochromatic arc lamp. Two Amici prisms are placed in the refracted beam. Each Amici prism is actually three prisms that are cut at the proper angle from glass with the appropriate indexes of refraction. The Amici prisms must be set properly for each measurement to focus all the different wavelengths at the eye piece of the instrument.

Procedure:

The refracting prism of most refractometers is made from relatively soft glass. To avoid scratching, clean the prism with clean cotton swabs. Never touch the prism surface with a glass pipette or other hard object. Turn on the constant temperature bath several hours in advance. Have available a pure liquid with known index of refraction to check the calibration of the instrument. Use spectrophotometric grade solvents for calibration.

Use the following procedure for each measurement.

1. Open the prism cell by lifting the top prism using the stainless steel handle. The illuminating prism will rotate to the left.
2. Using a Pastuer pipette add a few drops of the sample to the prism surface. Take care not to touch the surface with the pipette to avoid scratching the refracting prism.
3. Quickly close the illuminating prism. Lift the light so that it almost touches the illuminating prism. Turn on the light by lifting the switch on the left-hand side of the instrument.

4. Looking through the eye-piece, turn the large metal knob on the right-side of the instrument until the visual field has the dark-light interface aligned at the cross-hairs. You can adjust the focus by pulling or pushing on the barrel of the eye piece.
5. Adjust the Amici prisms by rotating the dial on the front of the instrument. When set properly the dark-light interface under the cross-hairs will be colorless. The interface will be red on one side and blue on the other, but colorless in the center under the cross-hairs. Carefully realign the the dark-light interface to the center of the cross-hairs, Figure 3.
6. Depress the switch on the left-hand side of the instrument to illuminate the scale. Looking in the eye-piece, record the index of refraction to five significant figures.
7. Open the prism cell. For volatile samples, simply let the sample evaporate. No additional cleaning is necessary. For high boiling liquids, wash the prisms using a cotton swab and methanol. If the sample isn't soluble in methanol, try acetone or methylene chloride.
8. When you have finished all your samples, turn off the constant temperature bath and make sure the lamps are turned off. Leave the prism cell clean, dry, and closed to avoid scratches.

Reference: 1. D. P. Shoemaker, C. W. Garland, J. I. Steinfeld, J. W. Nibler, "Experiments in Physical Chemistry," McGraw-Hill, New York, NY, 1989.