It's Just a Phase You're Going Through

J. Bevan Ott

I wish to start by telling you about Iduna. Iduna is a calorimeter, and part of a family of instruments that very probably makes Brigham Young University the calorimeter center of the world. Iduna's immediate calorimeter family includes Neptune, Mrs. Olsen, Sally, Rita, Marelda, and Big Ben.[1] Iduna also has a number of calorimeter cousins, aunts, uncles, and other more distant relations here at Brigham Young University. But Iduna is a special member of the family to me. Dr. James J. Christensen had his hand in the design and construction of this family of calorimeters, and he and I built Iduna together. Jim and I were close friends for a number of years, but we had never collaborated on a research project until the fall of 1983. At that time, we decided we would work together to build a special, highly accurate calorimeter and use it to establish a reference system to test the reliability of other calorimeters.

During the fall of that year, we gathered together the components to make a calorimeter, finding a computer here and a controller there, along with temperature and pressure measuring devices, a power supply, multiplexer, frequency meter, valves, and tubing. Over the Christmas holidays, Iduna was born. We rolled up our sleeves and worked long and hard putting her together. Ordinarily, a calorimeter like Iduna would cost from fifty to seventy-five thousand dollars. We were pleased that after all the scrounging, out-of-pocket expenses to build Iduna were about 10 percent of that amount.

I wish to pay tribute at this time to Jim Christensen. I am sure most of you know he passed away suddenly last fall. Brigham Young University will sorely miss his genius, and I especially miss his friendship.

J. Bevan Ott is the Joseph K. Nicholes Professor of chemistry and chairman of the department of chemistry at Brigham Young University. This essay was originally presented as the Distinguished Faculty Lecture for 1988. Professor Ott writes: "Special thanks go to my wife RaNae for thirty-five years of understanding and support, to Linda Whittaker for typing thirty-seven drafts of this talk (a conservative estimate), to Brian Woodfield and Jay Purdy for helping with the demonstrations, and to Rex Goates and Jim Christensen for years of exciting and fun collaboration on research."

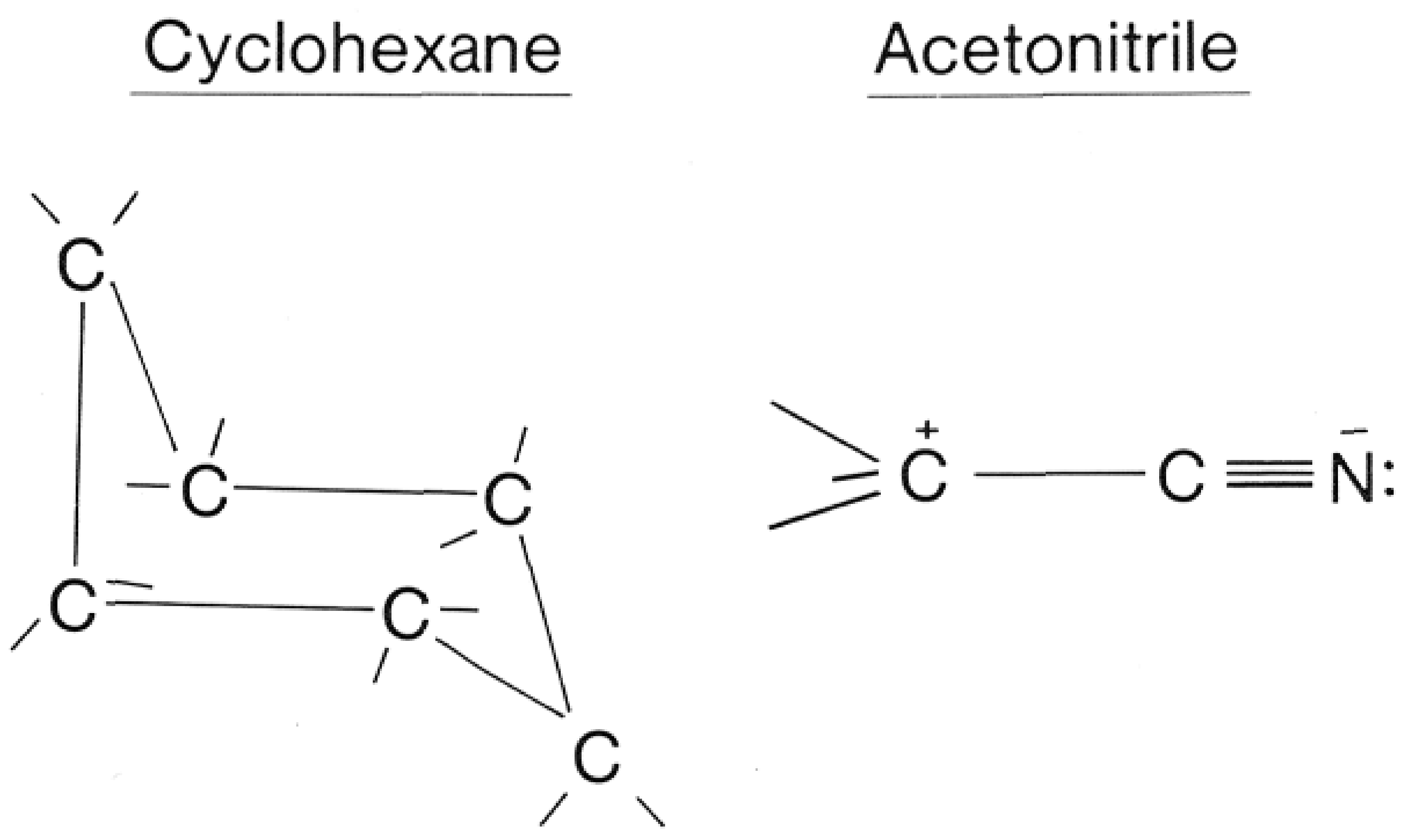
Calorimeters are devices for measuring heat effects. Iduna is specifically a high-temperature, high-pressure, isothermal flow calorimeter. She is capable of measuring the heat absorbed or liberated when liquids are mixed together, and she can do it very accurately at temperatures ranging from twenty to two hundred degrees centigrade and at pressures ranging from atmospheric to 250 times that value. We named Iduna for an ancient but beautiful German goddess who kept the apples of youth that she withdrew from a never-ending supply in her basket and gave to the other gods to keep them from growing old. Iduna is an appropriate name for this instrument. The research or creative work we accomplish with help from an Iduna are the apples that keep our research program alive and help us stay active and on the cutting edge of our professional field.

Iduna has lived up to every expectation. Recently, we made heat of mixing measurements with Iduna on mixtures of the two liquids cyclohexane and acetonitrile whose molecular structures are shown in figure 1.[2] The cyclohexane molecule contains a ring of six carbon atoms. The molecule is nonpolar, and the ring is bent to give a nearly spherical shape. Acetonitrile is an egg-shaped polar molecule. That is, there is a difference in electrical charge between the two ends. The (acetonitrile + cyclohexane) system was chosen to study the heat effect, and hence the interaction, when polar and nonpolar molecules are mixed.

The results of the heat of mixing measurements are shown in figure 2, in which we plot heat of mixing against composition of the mixture.[3] The upper curve gives the results obtained at 100°C, while the middle and lower curves summarize the measurements made at 75°C and 50°C, respectively. The heat of mixing is expressed in joules/mole. A joule is the unit of energy in the International System of Units and is the preferred way to express amount of energy in scientific discussion. It takes a little over four joules to give a calorie, which is a unit of energy you may be more familiar with. A mole is a number of atoms or molecules similar to a dozen or a gross, only much, much larger. A mole contains Avogadro's number of particles, nearly 6×10^{23} (that is, a number starting with six followed by 23 zeros). Thus, a heat of mixing in joules/mole is the heat absorbed or evolved in joules when enough acetonitrile and cyclohexane are mixed to give 6×10^{23} molecules of mixture. Although the number of molecules is large, the mass of a mole is usually of the order of grams and is a convenient amount to work with in the laboratory.

The American Chemical Society has a bumper sticker with the caption, "Chemists Have Solutions." The solutions we will be

STRUCTURES OF CYCLOHEXANE AND ACETONITRILE



Cyclohexane

Acetonitrile

Fig. 1. Structures of cyclohexane and acetonitrile. Organic chemists represent molecules with only the carbon and nitrogen skeletons shown. Hydrogen atoms are at the end of each projecting bond. The dots on the nitrogen in acetonitrile represent a pair of electrons not used in bonding.

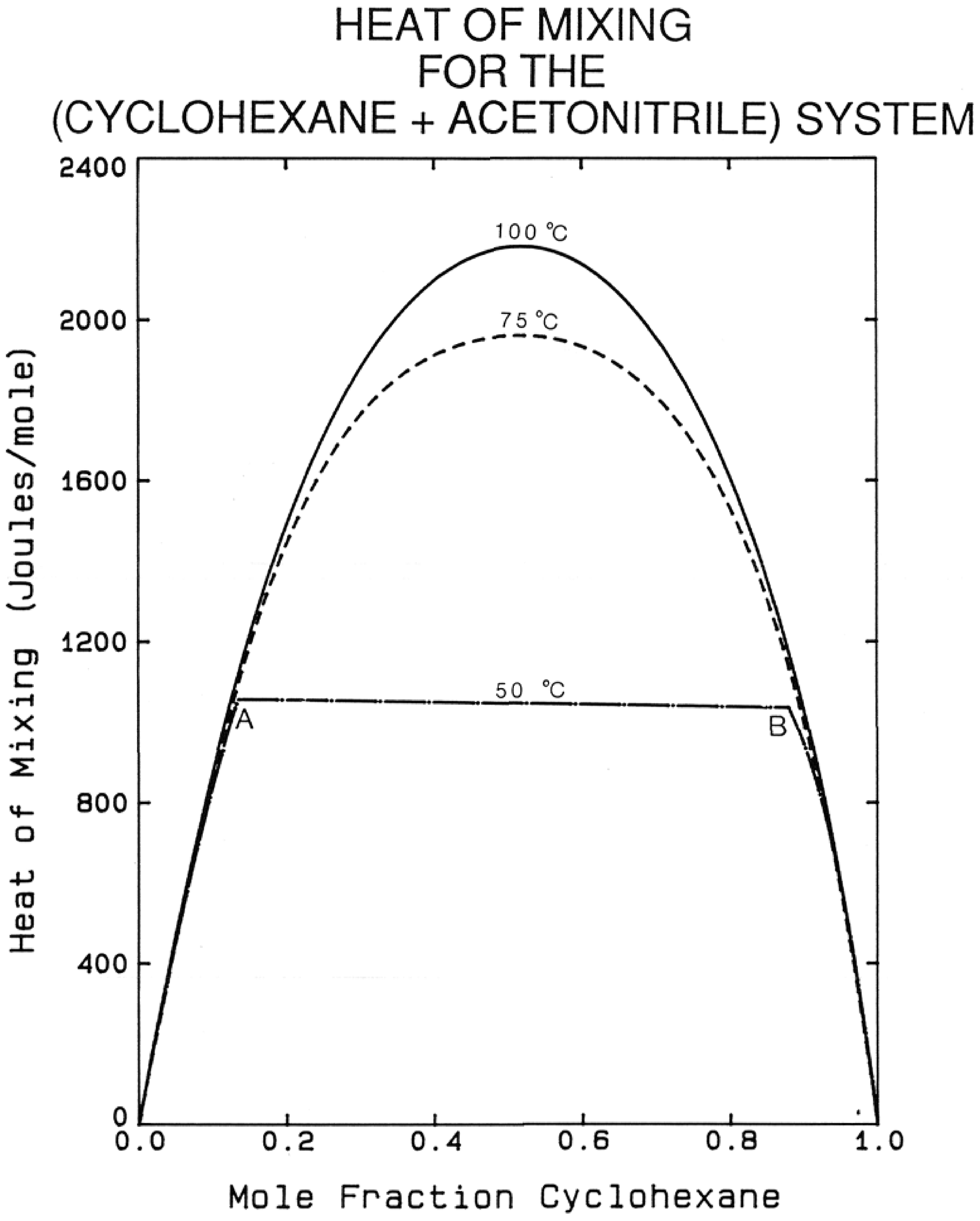


Fig. 2. Heat of mixing versus mole fraction of cyclohexane for mixtures of cyclohexane and acetonitrile. The upper curve (solid line) gives the results at 100°C, the middle curve (dashed line) is for 75°C and the lower curve (dashed-dotted line) is for 50°C. Phase separation occurs at 50°C with the compositions of the saturated solutions given by points A and B.

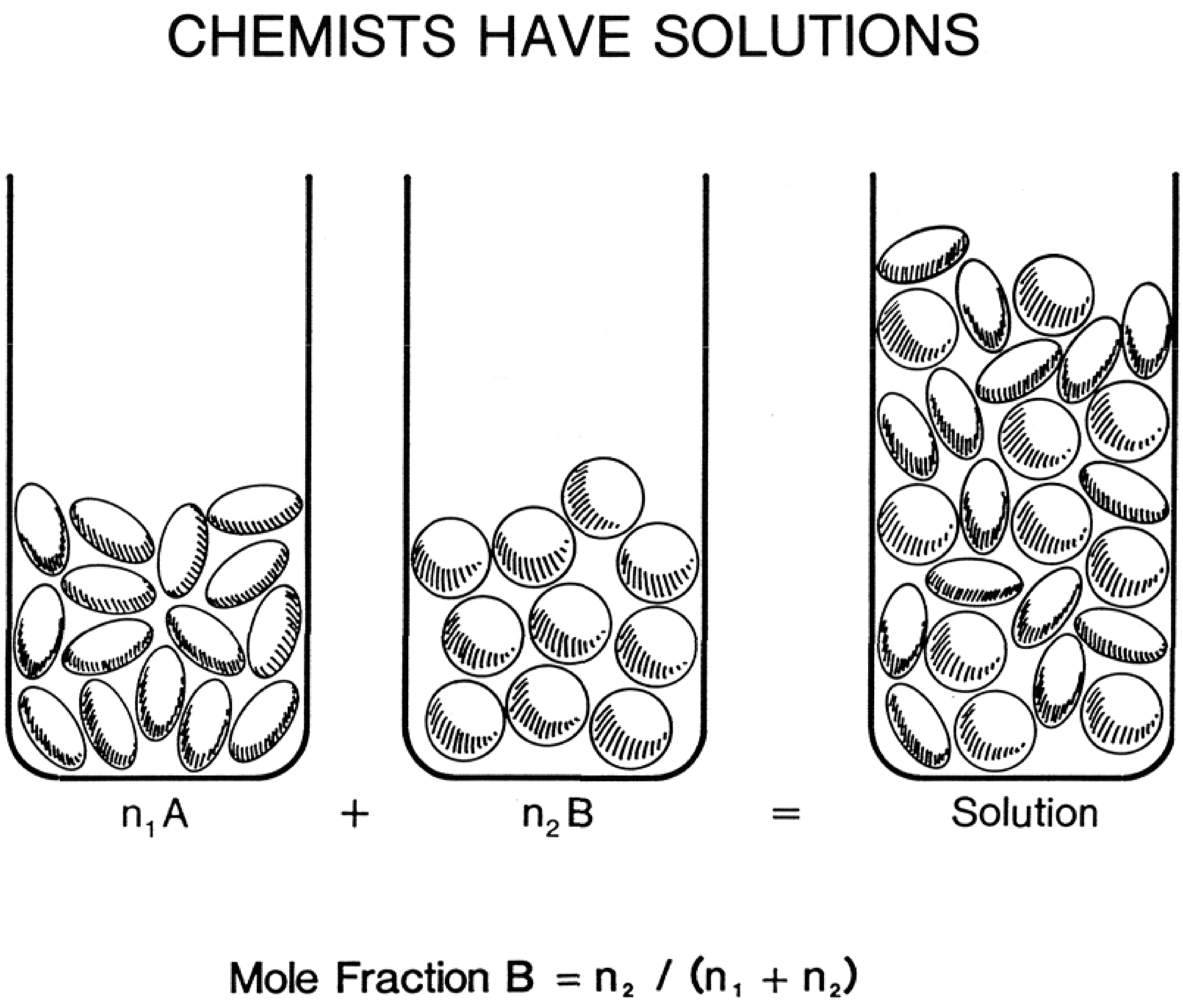


Fig. 3. The mixing of two liquids to form a solution. The mole fraction of B in the mixture is equal to n_2, the number of B molecules divided by $(n_1 + n_2)$, the total number of molecules.

talking about are homogeneous mixtures of two or more substances. In figure 2 the heat of mixing is plotted against the mole fraction, which is the measure we use for the composition of the solution. It may also be thought of as the molecular fraction. Thus, when the mole fraction is 0.5 the mixture has an equal number of cyclohexane and acetonitrile molecules. Figure 3 illustrates the mixing of egg-shaped A molecules with spherical B molecules to form a solution. The mole fraction of B is equal to n_2, the number of B molecules in the mixture divided by $(n_1 + n_2)$, the total number of molecules.

Look again at the heat of mixing graph shown in figure 2. The rounded heat of mixing curves obtained at 75 and 100°C are as expected for a system of this type, but the flat region of the curve at 50°C requires some explanation and interpretation.

We can understand what happens if we attempt to mix cyclohexane and acetonitrile. At room temperature they do not dissolve in one another completely and separate into two liquid phases. We have measured the compositions of the two liquids as a function of temperature and determined that the one on the bottom is mostly acetonitrile and the one on top is mostly cyclohexane. But neither layer is a pure substance; the top layer contains some acetonitrile and the bottom layer some cyclohexane. Furthermore, the compositions of the layers vary with temperature. The quantitative description of the system is given in the diagram shown in figure 4 in which solubility is plotted against temperature.[4]

The temperature is expressed in °C on the right side of the diagram. Also plotted on the left side is the Kelvin (K) or absolute temperature, which is the one most commonly used by scientists. The Kelvin and centigrade scales have the same size of temperature increment, but the Kelvin scale is displaced by 273.15 units so that the temperature becomes zero at absolute zero. Thus, ice melts at 0°C or 273.15 K, liquid water boils at 100°C or 373.15 K, and room temperature is usually around 25°C or 298.15 K.

In figure 4, the solid curved line gives the solubility. Any mixture with an overall composition and temperature that lies inside the curve separates into the two liquid phases with compositions given by the lines on each side. The dashed lines show that at 50°C the two phases have compositions of 0.135 and 0.880 mole fraction cyclohexane. Notice that the solubilities increase and the compositions of the two solutions approach each other with increasing temperature. At 74.5°C, the two phases become one. This highest point on the solubility curve is known as the critical point. Above this temperature only one phase is present, and the liquids are miscible. Once this phase behavior is understood, the

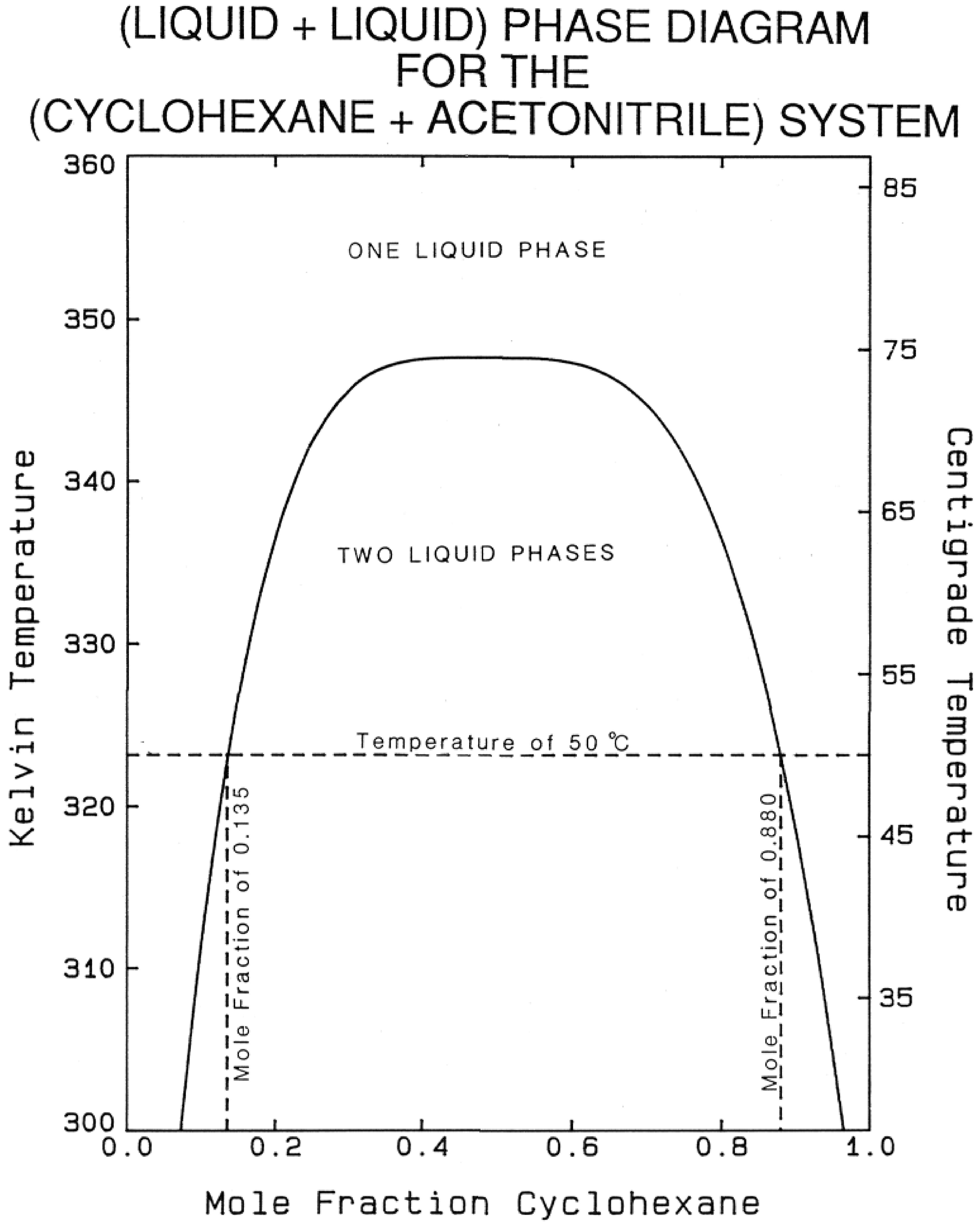


Fig. 4. Compositions as a function of temperature of the two liquid layers which form when cyclohexane and acetonitrile are mixed. The dashed line at 50°C shows that, at this temperature, the two liquid phases have the compositions 0.135 and 0.880 mole fraction cyclohexane respectively.

heat of mixing curve is easy to explain. At 75 and 100°C, we are above the critical temperature, complete mixing occurs over the entire composition range, and a normal heat of mixing curve is obtained. The nearly horizontal linear portion of the heat of mixing curve at 50°C results when complete mixing does not occur. The breaks in the curve (points A and B) occur at the solubility limits. The mole fractions corresponding to these breaks are 0.135 and 0.880, which are the same as the solubilities predicted from the solubility curve.

The effect we have just described is an example of (liquid + liquid) phase equilibrium. That is, two liquid phases are in equilibrium. The graph of temperature versus solubility shown in figure 4 is an example of a binary (liquid + liquid) phase diagram. (Liquid + liquid) equilibrium is only one of several kinds of phase equilibria that can occur. The different types are summarized in figure 5. Two liquids are together in (liquid + liquid) phase equilibrium as shown in the first example. (Solid + solid) phase equilibrium occurs at a transition temperature where the two forms of the solid, represented in figure 5 by prisms and cubes, can exist together. Solid and liquid forms of a substance are together at the melting point where (solid + liquid) phase equilibrium is established. Vapor and liquid exist together when (vapor + liquid) phase equilibrium is obtained. The equilibrium gas pressure is known as the vapor pressure. The boiling point is the temperature at which the vapor pressure equals atmospheric pressure. Finally, (vapor + solid) phase equilibrium occurs when solid and gas exist together. The equilibrium gas pressure is known as the sublimation pressure, and the sublimation point is the temperature at which the sublimation pressure equals atmospheric pressure. Melting points, boiling points, sublimation points, and transition temperatures are invariant for a pure substance. That is, the temperature stays the same as long as both phases are present and in equilibrium.

When a second component is added to form a solution, these previously invariant temperatures change. This is especially true of the melting point and the boiling point, and these are the effects we want to describe in more detail. We will now consider an example of a binary or two component (vapor + liquid) phase diagram to see how the boiling point changes with composition and then describe several (solid + liquid) binary phase diagrams where we see how the melting point changes when we add a second component.

The (vapor + liquid) phase equilibrium we will use as an example involves mixtures of liquid nitrogen and liquid oxygen. We will make some boiling temperature measurements on this system from which we will construct the phase diagram. The

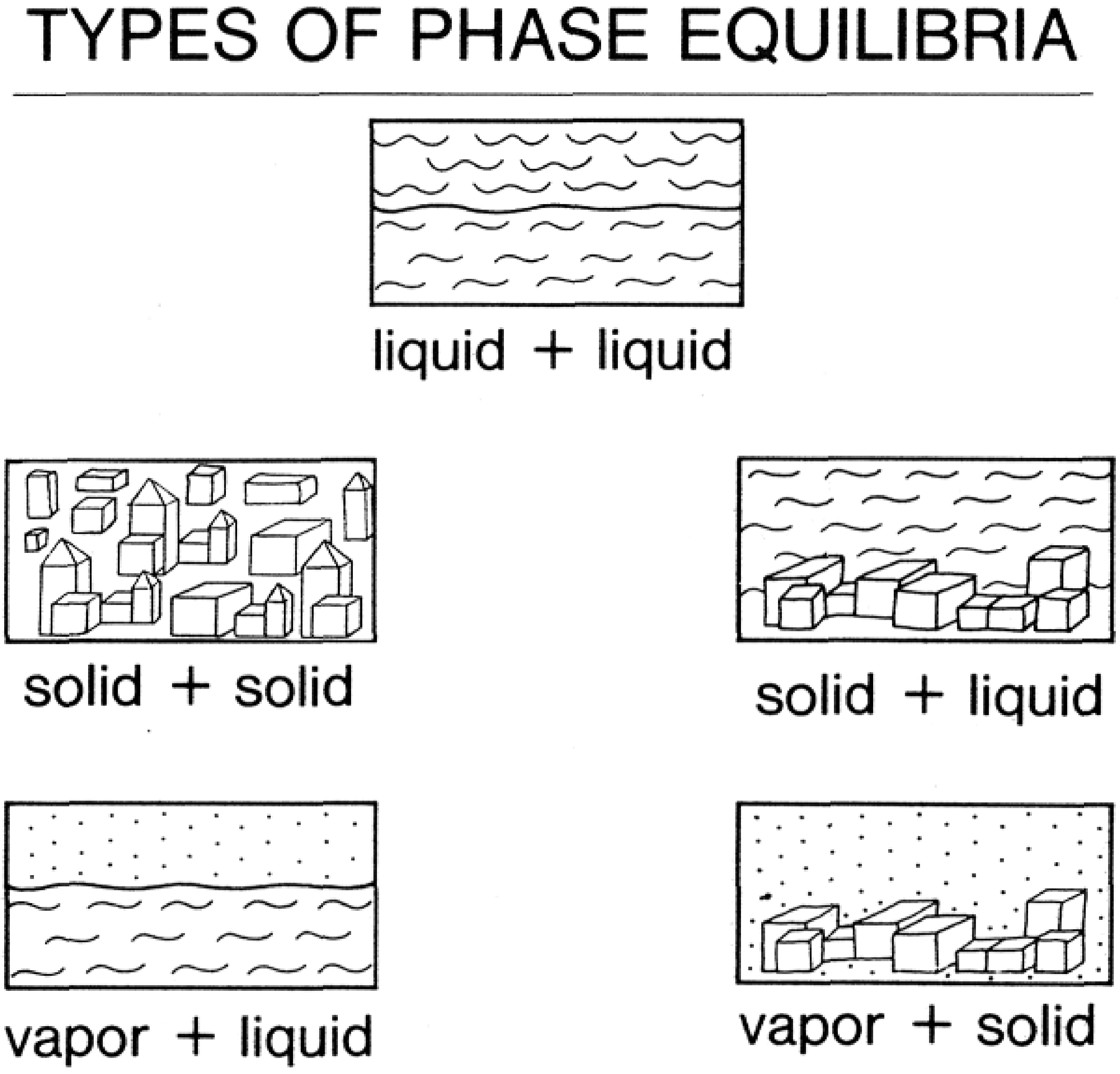


Fig. 5. Types of phase equilibria

temperature measuring device we will use is not one you would find lying around the house, or in the usual research laboratory for that matter.[5] The end of the temperature probe contains a coil of platinum wire wound in such a way as to be free of mechanical strains. The electrical resistance of this strain-free platinum resistance thermometer changes with temperature and is the measure of temperature. This thermometer has been calibrated to be part of the International Practical Temperature Scale.

The electrical resistance of the probe is measured with a special high-precision resistance meter. The resistance reading of the probe is sent to a computer through an IEEE bus. The computer traces this resistance reading on the monitor as a function of time and also converts resistance to temperature and displays it at the top of the monitor screen in K or °C. The temperature trace is shown as a yellow line on the screen. Full scale is one ohm of resistance or 10°C, and the trace repeats each time it goes off scale. This apparatus is very accurate, very reproducible, and very expensive! The thermometer probe itself costs almost three thousand dollars, and it would cost more than twenty-five thousand dollars to assemble the entire apparatus.

We will use this thermometer to make some boiling point measurements from which we can construct the (vapor + liquid) phase diagram for the (oxygen + nitrogen) system. The temperature probe has been placed in a flask of boiling liquid nitrogen. This flask is made of glass and is transparent so that we can see what is happening. It has a double wall with a vacuum between the walls to insulate the sample from the surroundings. The sample is being stirred with a magnetic stirrer to keep it at a uniform temperature. The monitor shows that the boiling temperature of the liquid nitrogen is constant at 76.26 K or -196.89°C, and we store this value in the computer. If atmospheric pressure does not change, the temperature will hold at this value as long as both liquid and gaseous nitrogen are present, or until we add a second component. We also have a sample of liquid oxygen in a similar container. It boils at a constant but different temperature from the liquid nitrogen. The thermometer is transferred to the liquid oxygen. When equilibrium is obtained, the boiling temperature is found to be 89.00 K. This value is also stored in the computer.

In a third container, again made of glass and insulated with a vacuum jacket, we have liquid oxygen in an inner chamber surrounded by boiling liquid nitrogen so that the oxygen is at the boiling temperature of the nitrogen. This inner container is graduated so that we can determine the amount of liquid present. By reading the oxygen level, we see that we have 26 ml of liquid oxygen. We now input this volume into the computer and add liquid nitrogen to the inner container. A magnetic stirring bar in the bottom stirs the mixture. The total volume is 51 ml, and this number is also stored in the computer.

We now take the thermometer out of the liquid oxygen and put it in the mixture. We remove the liquid nitrogen from the jacket surrounding the mixture and blow room temperature nitrogen gas through this jacket. The nitrogen gas warms the mixture, and the temperature increases. Very soon, boiling will start, at which time, the temperature will hold steady.

From our measurement, we see that the mixture boils at 80.30 K. This temperature will slowly change since boiling changes the composition, and we store this temperature in the computer as quickly as possible. The computer is programmed to plot the (vapor + liquid) phase diagram after we have input the three temperatures and the two volumes. We now instruct the computer to perform this operation. The three temperatures we have measured, along with the complete phase diagram, are displayed on the screen, and show how boiling temperature changes with mole fraction. This diagram is reproduced in figure 6. We can use it to find the boiling temperature of other mixtures. For example, air is 0.20 mole fraction oxygen. The dashed line displayed in figure 6 at this composition shows that liquid air would boil at 76.8 K.

Our apparatus is a crude one for measuring a (vapor + liquid) phase diagram at atmospheric pressure. If we were going to measure this phase diagram to obtain results suitable for publication in the scientific literature, we would use a much more sophisticated apparatus that would keep track of pressure, temperature, and concentration more precisely and obtain boiling points over the entire range of composition instead of at one point. Usually, (vapor + liquid) phase diagrams are simple like the one we have constructed. We will now consider some (solid + liquid) phase diagrams that are more complicated, and often more interesting.

The first (solid + liquid) phase diagram we want to consider has water as one of the components. To demonstrate the effect of composition on the melting temperature, our thermometer probe has been placed in an insulated flask containing a mixture of ice and liquid water. When solid and liquid water are present together, we have (solid + liquid) phase equilibrium of a pure substance, and the temperature is fixed. The value we obtain with our thermometer for the melting point of water is 0°C or 273.15 K.

Let us take the (ice + liquid water) mixture and add liquid ethylene glycol to it. By following the temperature trace on the monitor, we see that the temperature decreases as the ethylene

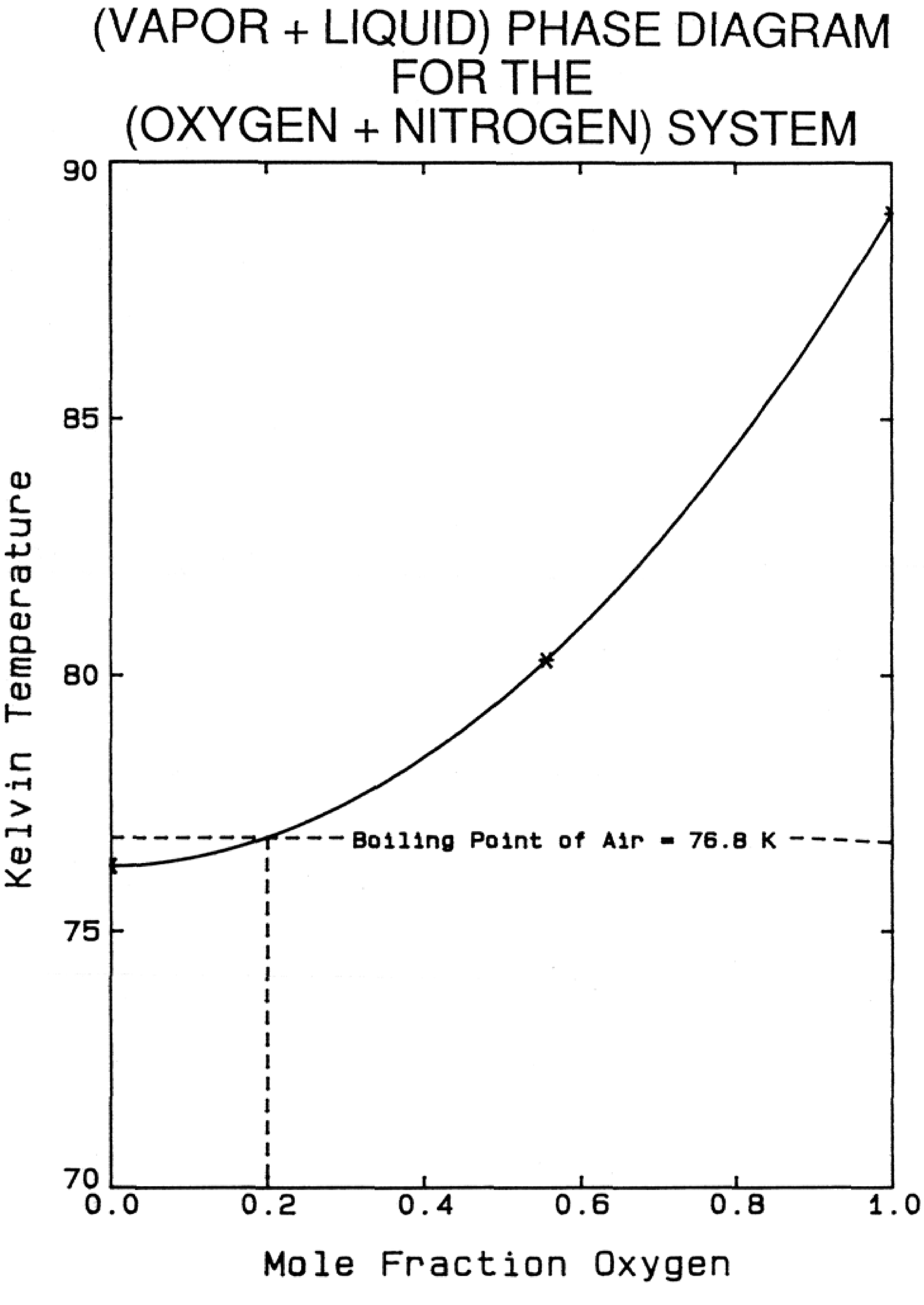


Fig. 6. (Vapor + liquid) phase diagram for the (oxygen + nitrogen) system. *, experimental measurements from the demonstration.

glycol dissolves in the water until the freezing temperature of the mixture is obtained.

The (ethylene glycol + water) system is of considerable practical importance since ethylene glycol is the antifreeze added to the water in the radiator of an automobile to keep the coolant in the engine from freezing in the winter. A number of years ago, we measured the freezing points of mixtures of (ethylene glycol + water) from which we constructed the (solid + liquid) phase diagram.[6] An obvious question to ask is why did we bother to make freezing point measurements on mixtures of ethylene glycol and water? This mixture was used as a radiator coolant long before we arrived on the scene. Any bottle of antifreeze gives a table with directions for preparing a mixture with a particular melting point, and such directions were available long before we made our measurements.

The answer to the question is that until we came along no one made the correct measurements. The phase diagram, from which the directions on an antifreeze bottle were prepared, is shown in figure 7. In this diagram, melting temperature is plotted against mole fraction of ethylene glycol. Point A in the upper left hand corner is the melting temperature of pure ice, and line AE shows how this melting temperature decreases as we add ethylene glycol. Point B in the upper right hand corner is the melting temperature of ethylene glycol and line BE shows how its melting temperature decreases as we add water. Thus, if a liquid mixture of ethylene glycol and water with a composition given by point *u* is cooled along the vertical dashed line *uv,* ice freezes from solution when line AE is intersected. This occurs at a temperature of approximately -34°C. On the other hand, when a solution with composition given by point *w* is cooled along the dashed line *wx,* ethylene glycol crystallizes from solution at -46°C where line BE is intersected. The two melting curves meet at point E which is known as the eutectic point. It represents the lowest temperature and composition at which liquid can exist in this mixture. A solution with the eutectic composition would give the most effective antifreeze that could be made from mixtures of ethylene glycol and water, since it freezes at the lowest possible temperature.

This (solid + liquid) phase diagram shown in figure 7 is a simple eutectic binary phase diagram, and it is an example of one of the simplest and most common types that can occur. The phase diagram we obtained for (ethylene glycol + water) is shown in figure 8, and it is more complicated. Line AE_1 is the melting line for ice, and BE_2 is the melting line for ethylene glycol, with E_1 and E_2 as eutectics. A solid addition compound, containing one

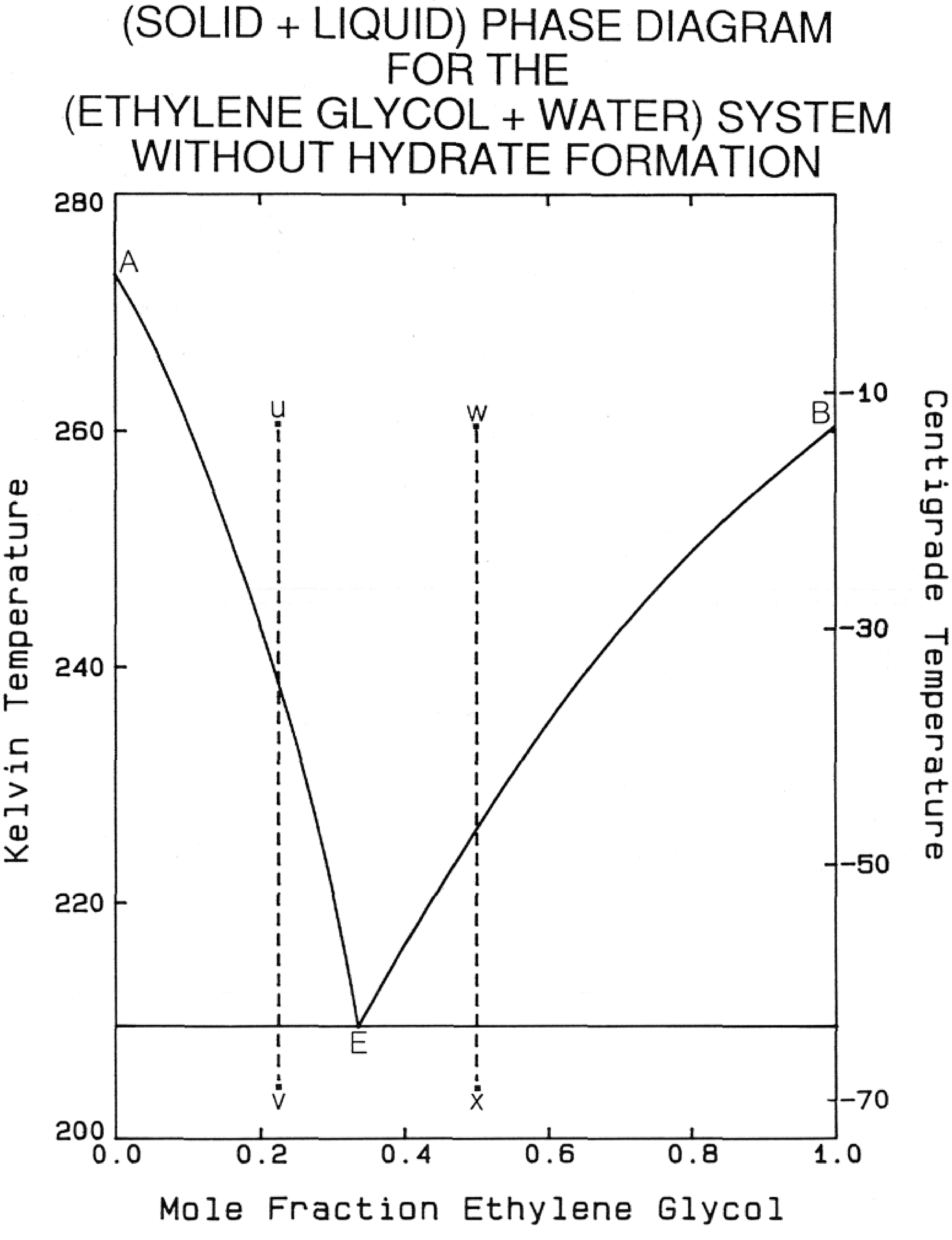


Fig. 7. (Solid + liquid) phase diagram for the (ethylene glycol + water) system without hydrate formation

ethylene glycol to one water molecule, forms in the middle region of the phase diagram. Addition compounds are called hydrates when water is one of the components. Line E_1CE_2 gives the melting curve for this hydrate. If a liquid solution at point *y* is cooled along the dashed line *yz*, solid hydrate forms when the freezing line E_1CE_2 is reached. At least in theory this is true. Actually, this hydrate supercools extensively and the mixture can be cooled well below the melting temperature of the hydrate without solid forming. Usually, the mixture supercools so much that ice freezes from solution when the dashed line E_1E_3, which is an extension of line AE_1, is reached. This happens if the composition is less than point E_3. Solid ethylene glycol would form if the dashed line E_3E_2, an extension of line BE_2, is reached instead. This occurs if the solution has a composition richer in ethylene glycol than point E_3.

Equilibrium with phases that should not exist (lines E_1E_3 and E_3E_2 in figure 8) is referred to as metastable phase equilibrium. The simple eutectic phase diagram reported by earlier workers is actually the same as the one we would obtain if we omitted the hydrate. Lines AE and BE in figure 7 and AE_1E_3 and BE_2E_3 in figure 8 are the same freezing lines for water and ethylene glycol respectively, and point E in figure 7 and E_3 in figure 8 are the same eutectic. Earlier investigators obtained an incorrect, or at least incomplete, diagram because they were not able to obtain the hydrate.

Over the past thirty years, Rex Goates and I have studied and reported in the literature approximately two hundred (solid + liquid) phase diagrams obtained from mixing components ranging from simple elemental materials to considerably more complicated organic molecules. We have found many systems that form solid addition compounds, and it is interesting and important from a chemical point of view to understand the nature of the molecular interactions that cause these compounds to form. Examples are shown in figures 9 and 10. They are the phase diagrams for (hexafluorobenzene + benzene) and (titanium tetrachloride + anisole), respectively.[7] In both of these systems, solid molecular addition compounds form containing equal numbers of moles of the components.

An important clue from thermodynamics that helps us understand the nature of the molecular interactions that cause the formation of the addition compounds is the heat effect for the process in which the solid addition compound forms from the solid components. The reaction is

$$\text{Solid A} + \text{Solid B} = \text{Solid Addition Compound}$$
$$\Delta H = ?$$

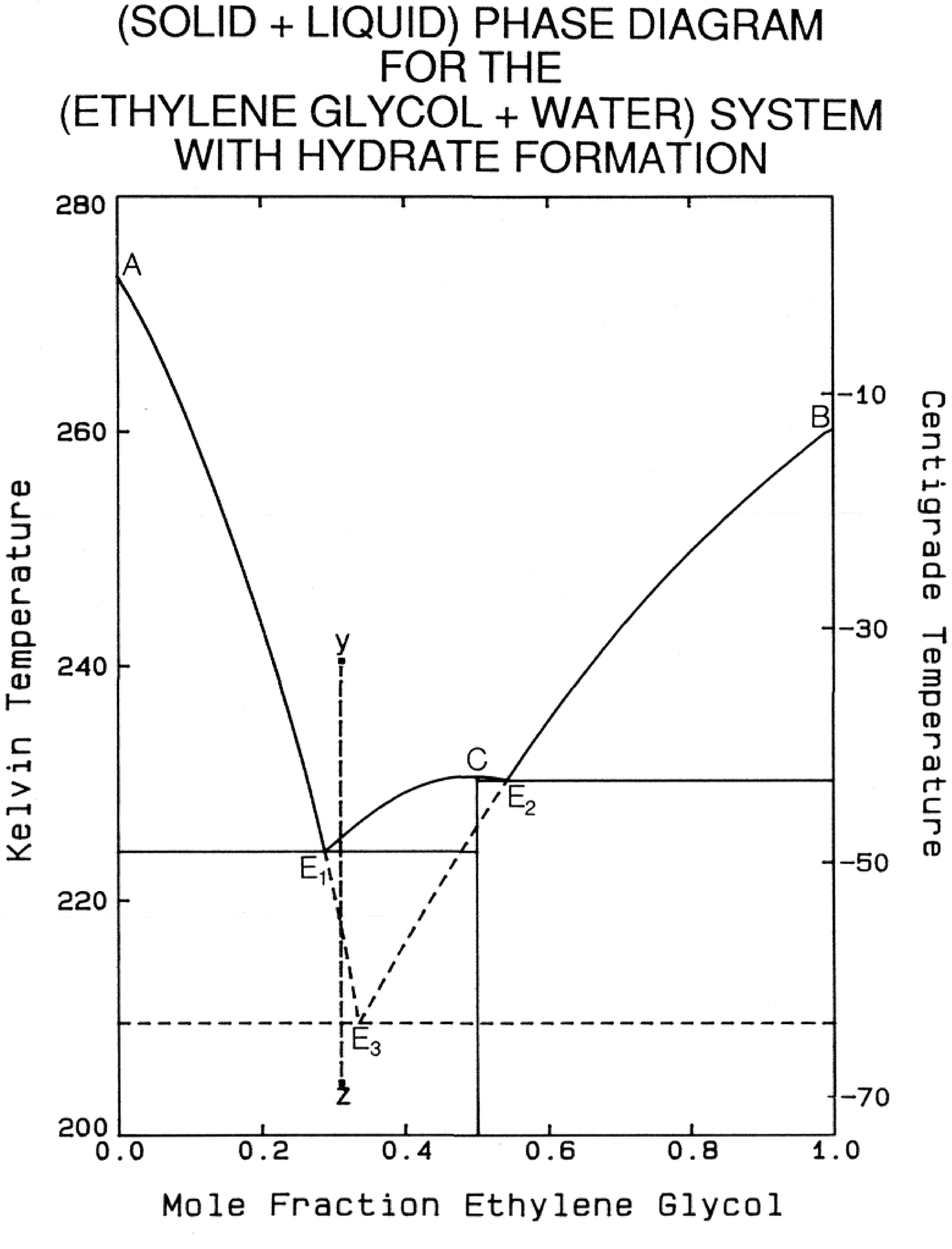


Fig. 8. (Solid + liquid) phase diagram for the (ethylene glycol + water) system with hydrate formation

where A and B are the components. The heat absorbed or liberated in this reaction is represented as ΔH, and it very nearly equals the energy change for the process. It can be calculated from heats of fusion and heats of mixing obtained from calorimetric measurements, but the calculation requires detailed thermodynamic data, and these data are usually not available. Fortunately, we have developed a method based on thermodynamic relationships for calculating this heat change directly from the experimental melting points. Most of the credit for the development of this process must go to Rex Goates along with Steven Goates and Juliana Boerio-Goates, all members of our chemistry faculty.[8]

Before applying this technique, it is interesting to quote from Auguste Comte, whom many of you recognize as a nineteenth-century French philosopher and the founder of the social science discipline of sociology:

> Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. . . . If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science.

Any of the students who made it through my upper division course in physical chemistry can testify that chemistry has changed dramatically since the days of Comte. Application of the mathematics used in disciplines such as thermodynamics, quantum mechanics, group theory, and statistics now play an important part in chemistry.

To see how the results of the ΔH calculation help in understanding the molecular interaction that causes solid compound formation, we will return to the (hexafluorobenzene + benzene) phase diagram and describe the molecular arrangement that leads to the formation of the solid addition compound.

Benzene and hexafluorobenzene consist of flat hexagonal shaped molecules of almost equal size. Representations of their structures are shown in figure 11. In each molecule, the six carbon atoms are in a hexagonal ring, and each carbon atom is attached to a hydrogen or fluorine atom, depending on whether the molecule is benzene or hexafluorobenzene. In each instance, the molecule is flat with all the carbons and (hydrogens or fluorines) in the same plane. As shown in the top representations, donut-shaped rings of high electron density are present above and below the plane of the molecule. Organic chemists usually use the more simplified representations shown in the figure. The circle inside the hexagon

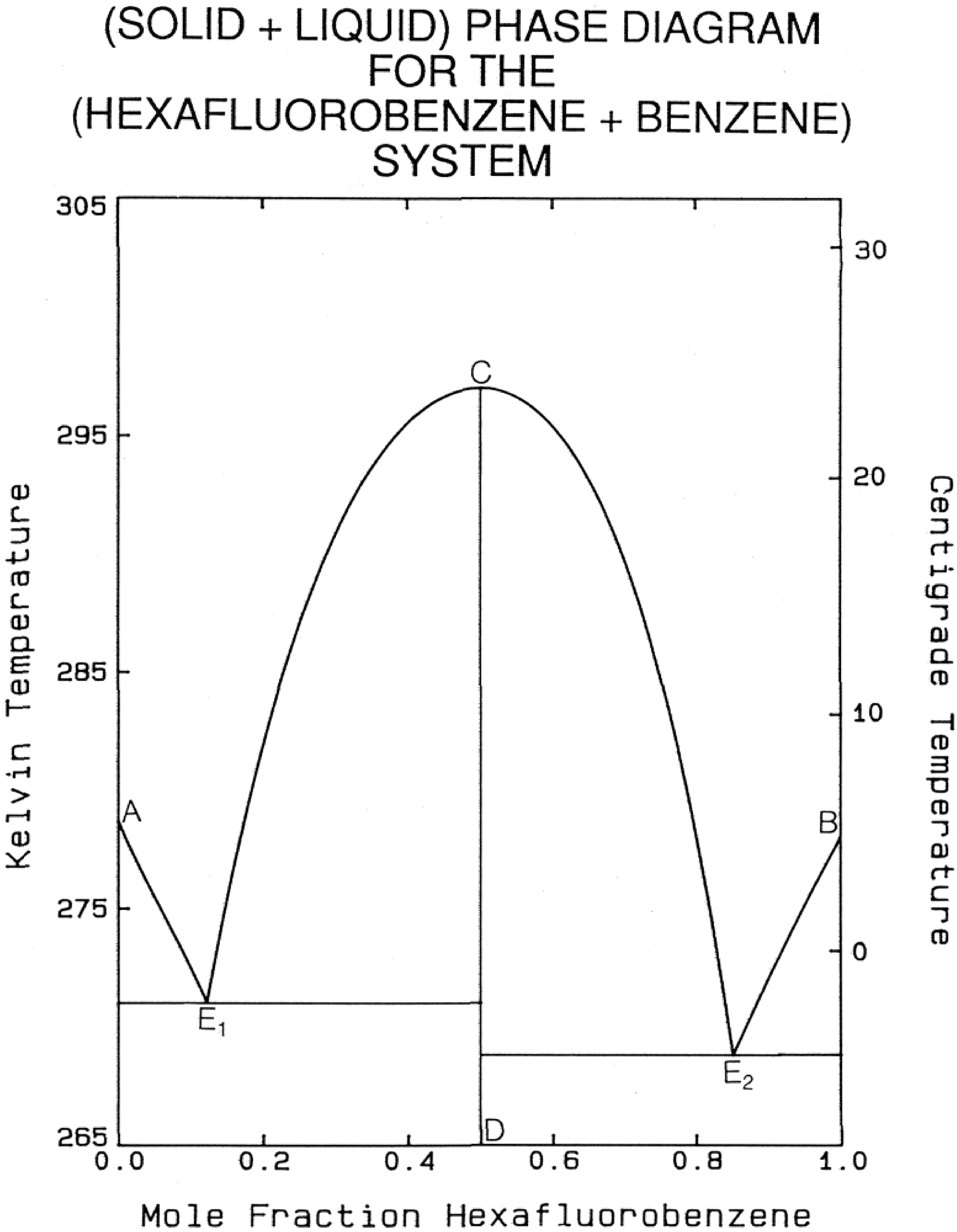


Fig. 9. (Solid + liquid) phase diagram for the (hexafluorobenzene + benzene) system. A solid molecular addition compound forms with melting temperature given by point C.

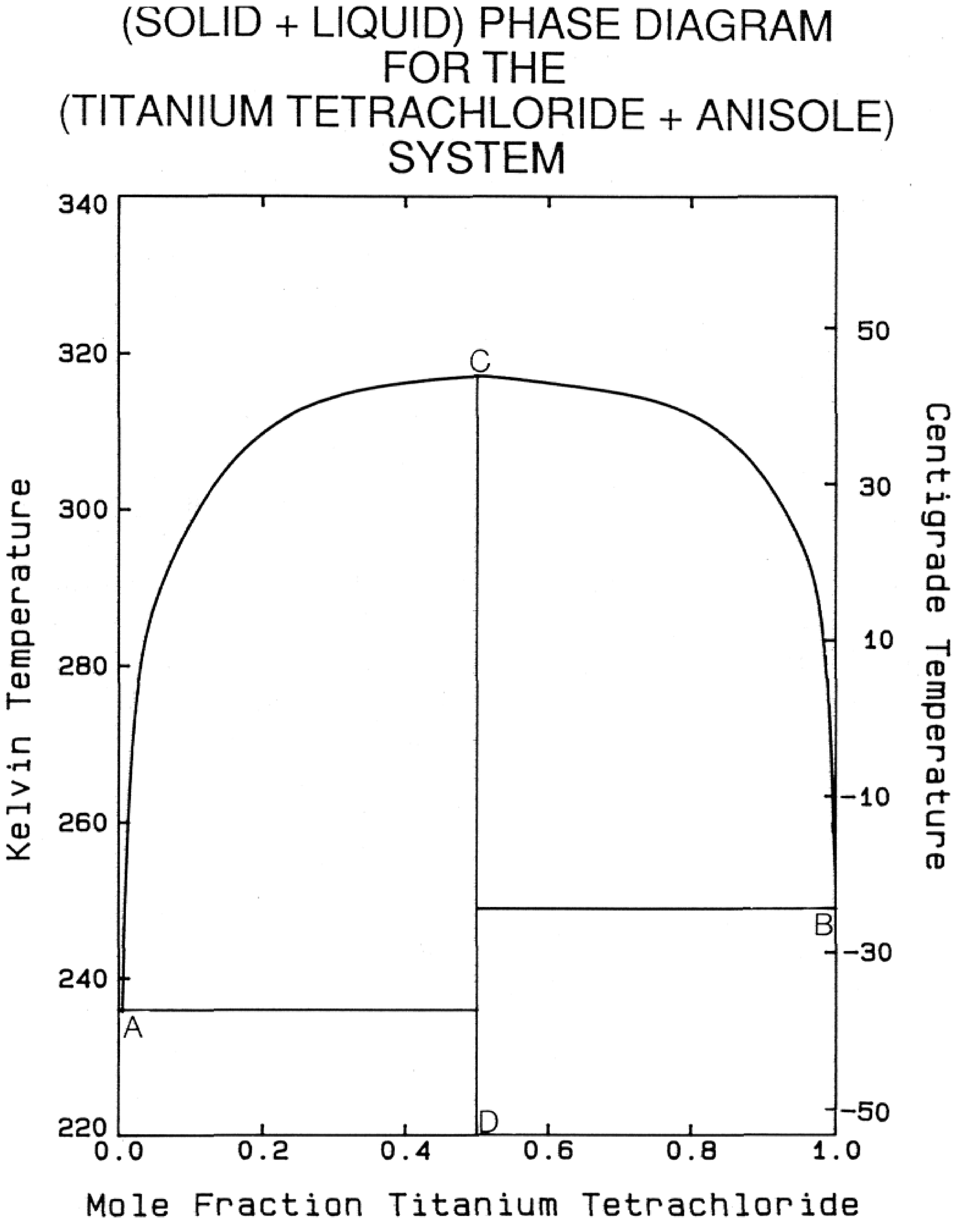


Fig. 10. (Solid + liquid) phase diagram for the (titanium tetrachloride + anisole) system. A solid molecular addition compound forms with melting temperature given by point C.

depicts the ring of high electronic charge. As we saw earlier, hydrogen attached to carbon is often omitted from the structural formula, as shown in the very bottom representation for benzene.

X-ray diffraction measurements have been made on the (hexafluorobenzene plus benzene) solid addition compound to determine its structure.[9] This is a very difficult system to study by this method and the results are not definitive, but a good interpretation is that the molecules mix in the solid to form alternate layers of benzene and hexafluorobenzene with these alternate layers rotated. This arrangement is shown in figure 12. In (a), the benzene molecules, represented as hexagons, are arranged in a flat layer. In (b), a hexafluorobenzene molecule, represented by a darker hexagon, is placed on top of the benzene layer in a rotated position. In (c), a complete layer of hexafluorobenzene is in place on top of the benzene layer.

To build the crystal, a third layer of benzene molecules is added, which is a repeat of the first layer, followed by a fourth layer of hexafluorobenzene, which is a repeat of the second layer. The result of this stacking, which continues both horizontally and vertically, is a solid containing equal amounts of the two components, which forms simply as a result of favorable packing. No strong energy of interaction is required to hold the molecules together. The energy calculation supports this conclusion. The reaction, an example of the general reaction given earlier, is

Solid Hexafluorobenzene + Solid Benzene =
Solid Addition Compound.

For this reaction, we calculate that $\Delta H = 0.88$ kjoules/mole, which is nearly zero.[10] Since ΔH nearly equals the change in energy, there is essentially no energy stabilization.

Chemical reactions such as this one for the formation of the (benzene + hexafluorobenzene) molecular addition compound are often described as entropy driven. The reasons for this description are as follows. The free energy change ΔG for any reaction is given by the equation

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the heat, ΔS is the entropy change and T is the Kelvin temperature. From thermodynamics we know that ΔG must be negative for a reaction to take place. In our process, ΔH is nearly zero and hence does not contribute significantly to ΔG. But ΔS is positive because entropy is a measure of the disorder in a system, and the mixing of the components in forming the addition compound increases the disorder and hence the entropy. Since ΔS is

STRUCTURES OF BENZENE AND HEXAFLUOROBENZENE

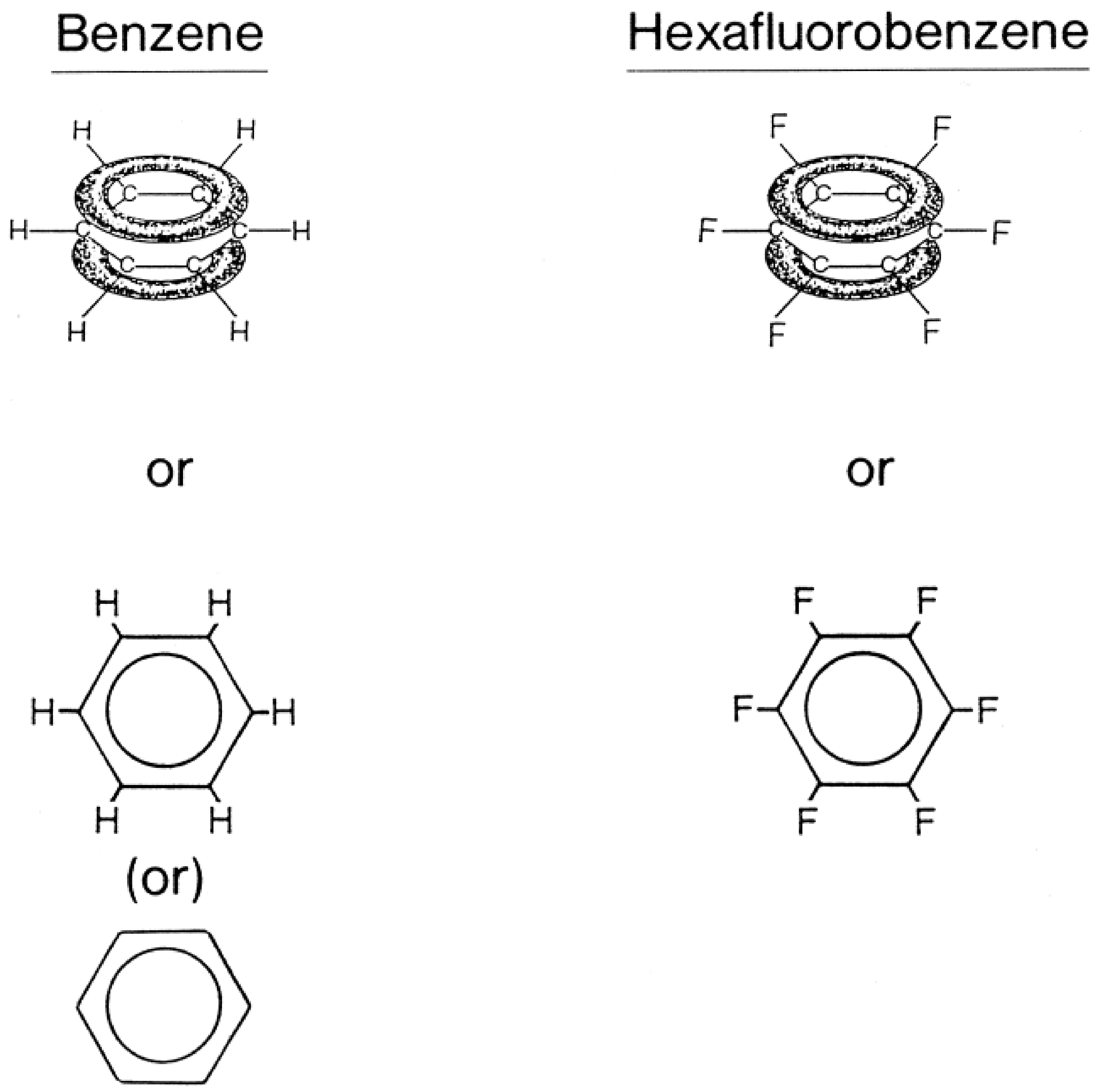


Fig. 11. Molecular structure of benzene and hexafluorobenzene. Both are flat hexagonal shaped molecules.

BUILDING THE (BENZENE + HEXAFLUOROBENZENE) ADDITION COMPOUND

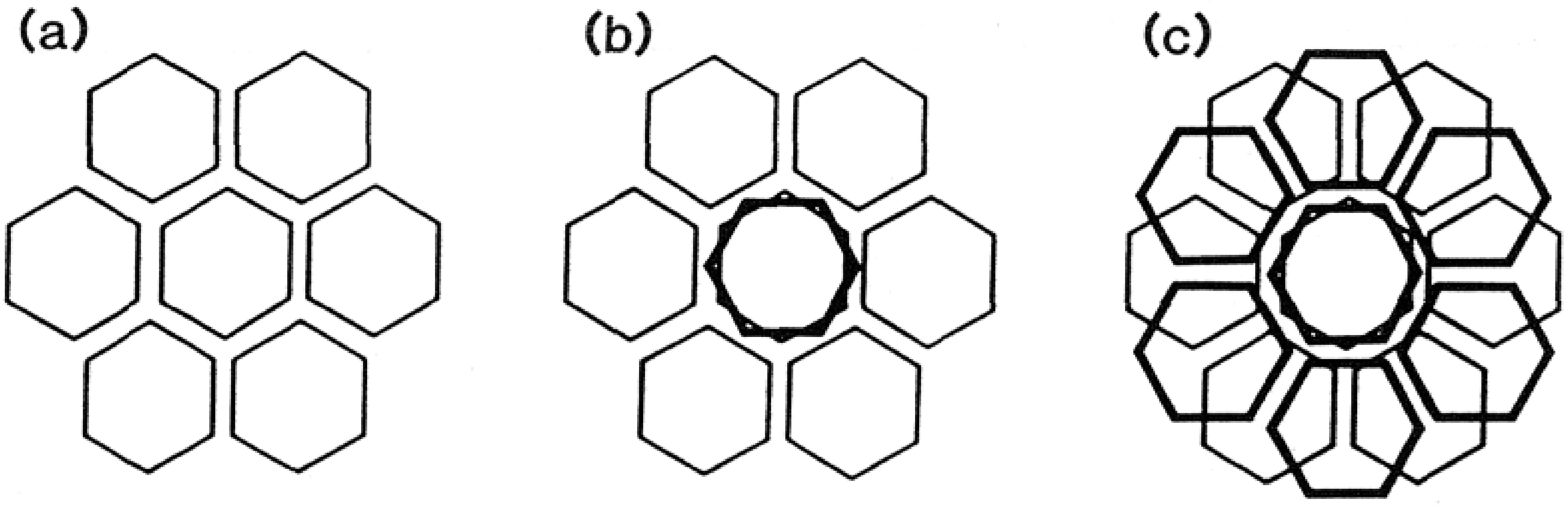


Fig. 12. Stacking of benzene and hexafluorobenzene molecules (represented by hexagons) to form the solid molecular addition compound: (a) layer of benzene molecules; (b) start of a layer of hexafluorobenzene molecules; (c) layer of hexafluorobenzene molecules on top of the benzene layer.

positive, ΔG is negative with ΔH equal to zero, and the compound forms.

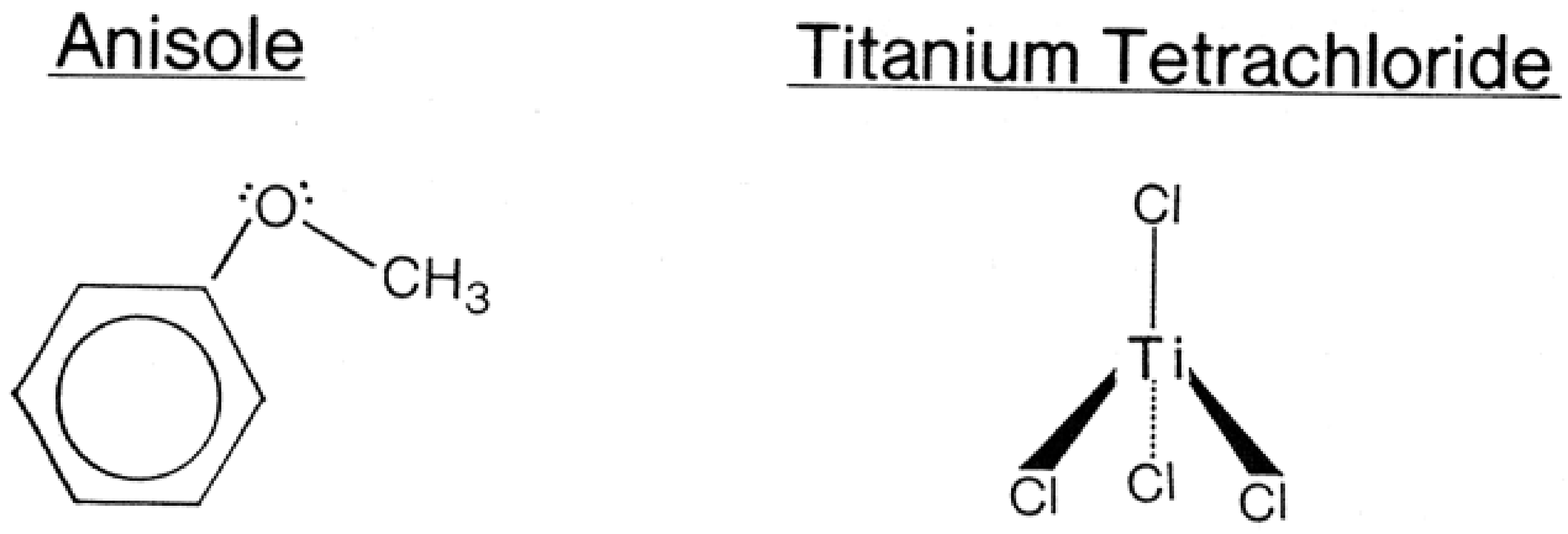
The formation of the (titanium tetrachloride + anisole) solid compound in the phase diagram shown in figure 10 results from a much stronger interaction. The structures of titanium tetrachloride and anisole are shown in figure 13. Titanium tetrachloride exists as a tetrahedral molecule. That is, the titanium atom is at the center of a four-sided pyramid with the chlorines at the four corners. The anisole molecule contains a benzene ring attached to an oxygen that in turn is attached to a carbon and three hydrogens. Electron pairs on the oxygen, which are not used in bonding within the molecule, are represented by dots. They will turn out to be important as we describe the interaction leading to the formation of the solid addition compound.

The formation of the (titanium tetrachloride + anisole) solid addition compound is interesting to observe. Both titanium tetrachloride and anisole are colorless liquids at room temperature. If an equal number of moles of titanium tetrachloride and anisole are mixed, a dark red solution forms that freezes to a dark red solid, which is the addition compound. This solidification happens at room temperature because we see from figure 10 that the addition compound freezes at about 44°C or 317 K, which is above room temperature.

The formation of the (titanium tetrachloride + anisole) solid addition compound is explained as resulting from a Lewis acid-base interaction as shown in figure 14. The tetrahedral titanium tetrachloride molecule shown on the left is a Lewis acid or electron acceptor. The molecule can accept a pair of electrons from a Lewis base or electron donor to form a complex. In our case, the oxygen in the anisole, also shown on the left in figure 14, has extra electron pairs and is the Lewis base. When the compound forms, the oxygen shares a pair of electrons with the titanium to form a titanium-oxygen bond. The structure shown on the right in figure 14 represents the addition compound. It has the titanium at the center of a trigonal bipyramid, which is a six-sided structure made by putting two three-sided pyramids base to base. The four chlorines and the oxygen from the anisole are bonded to the titanium at the five corners of the bipyramid.

In addition to the phase equilibria measurements, we also made x-ray crystallography and infrared spectral measurements on the addition compound.[11] These measurements show that the oxygen from the anisole is bonded directly to the titanium from the titanium tetrachloride, which is a necessary condition for our explanation of the bonding to be acceptable. The heat effect also

STRUCTURES OF ANISOLE AND TITANIUM TETRACHLORIDE



Anisole

Titanium Tetrachloride

Fig. 13. Molecular structures of anisole and titanium tetrachloride. Anisole contains a benzene ring with one of the hydrogen atoms replaced by an -OCH_3 group. The dots represent pairs of electrons. In titanium tetrachloride, the titanium atom and the upper chlorine atom are in the plane of the paper. The two outer chlorines below the titanium extend out of the plane of the paper while the chlorine at the end of the dotted bond extends into the plane of the paper. The result is a structure with the titanium at the center and the chlorines at the corners of a tetrahedron.

LEWIS ACID-BASE REACTION

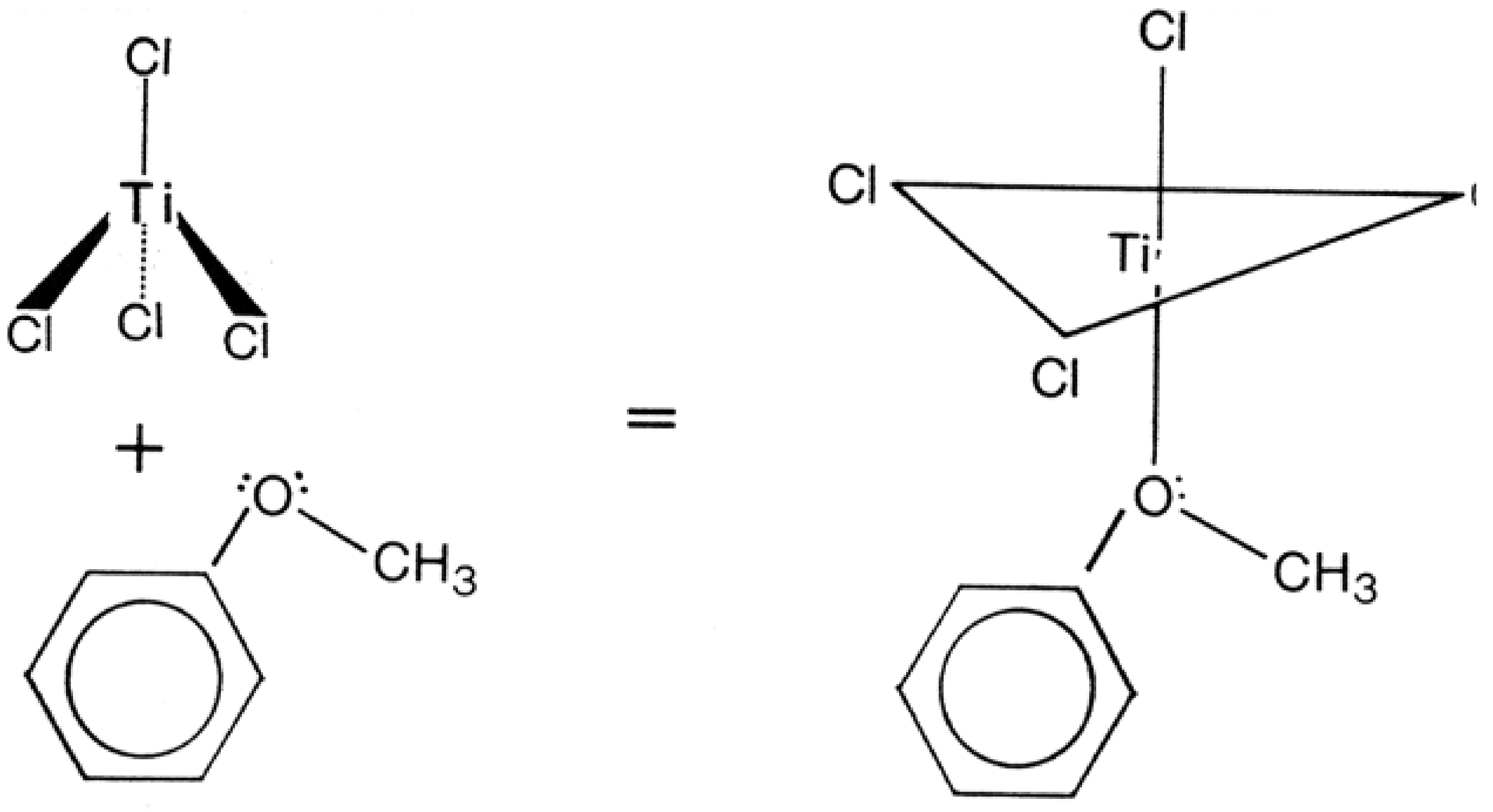


Fig. 14. Formation of the (titanium tetrachloride + anisole) solid addition compound. The titanium is at the center of a trigonal bipyramid, with four chlorines and the oxygen from the anisole at the five corners.

supports this explanation. Lewis acid-base interactions are strong, and we would expect a large lowering in energy and hence a large negative ΔH. The formation reaction for this system is as follows:

Solid Titanium Tetrachloride + Solid Anisole =
Solid Addition Compound.

The calculation of ΔH gives a value of -44.27 kjoules/mole.[12] In other words, almost 45 kjoules of heat are released when a mole of this compound forms. This is indeed a large heat effect, and the energy is lowered by almost this amount when the reaction occurs. Reactions such as this one are described as energy driven. Again, the free energy change is given by

$$\Delta G = \Delta H - T\Delta S$$

and for the reaction to occur ΔG must be less than zero. Since ΔH is a large negative number, ΔG will be negative unless ΔS, the entropy change, is large and negative, and this is very unlikely. Most spontaneous chemical reactions are energy driven. Entropy driven reactions in which ΔH is zero or positive, such as the one described earlier for the formation of the (hexafluorobenzene + benzene) solid addition compound, are unusual.

I hope I have given you a glimpse into the world of phase equilibria. Let me assure you that many of the (solid + liquid) phase diagrams we have studied are not as simple as the ones described here. Nature in her perverse way often likes to complicate things by combining together in one phase diagram, solid addition compounds, solid phase transitions, metastable equilibrium, solid solutions, and so on. In such cases, the construction of the phase diagram becomes a real challenge. We must separate all of the melting points, eutectics, and metastable equilibria, as well as other features we haven't discussed, such as transition points and peritectics, to put together a coherent diagram that explains all of the observations.

As examples, figures 15 and 16 show the (solid + liquid) phase diagrams we obtained for mixtures of the alkali metals (sodium + potassium), and [N,N-dimethylformamide (DMF) + trichlorobromomethane ($CBrCl_3$)], respectively.[13] In the (sodium + potassium) system, a solid addition compound forms, which contains twice as many sodium atoms as potassium atoms. This compound melts incongruently, that is by decomposition. When the addition compound is heated, it decomposes at the temperature given by line CD in figure 15 to a solid that is mostly sodium (composition given by point C) and a liquid with composition given by point D, which is known as the peritectic point. We will not describe this interesting intermetallic compound, which is known as a Laves Phase. Details of its structure can be found in the literature.[14] Solid solutions also occur in this system along lines AC and BF.

The (DMF + $CBrCl_3$) system (figure 16) is more complicated. An incongruently melting compound containing twice as many moles of DMF as $CBrCl_3$ forms at F, a congruently melting compound containing an equal number of moles of the two components forms at C, and a solid phase transition in the $CBrCl_3$ occurs at D. Eutectics are present at E_1 and E_2, and a peritectic occurs at F.

My research director at Berkeley many years ago was W. F. Giauque, a Nobel laureate in chemistry. He once told me that it was the unexpected that makes science exciting and that if things always came out as predicted scientific research would not be worth the effort. Each of the systems we have studied has been fun and exciting. Constructing a (solid + liquid) phase diagram is like putting together a picture puzzle without having a picture on the box to look at. Melting points are measured over the entire range of composition, along with eutectic and peritectic halts and solid phase transitions. Each piece of data adds to the picture, a picture that is not complete until the final piece is in place.

In one of my favorite "Wizard of Id" comic strips, the King asks, "Why is it that this country honors its athletes while men of science go virtually unnoticed?" The Queen then answers, "Did you ever spend an evening with a man of science?" I am grateful to those who have chosen to spend an evening with me.

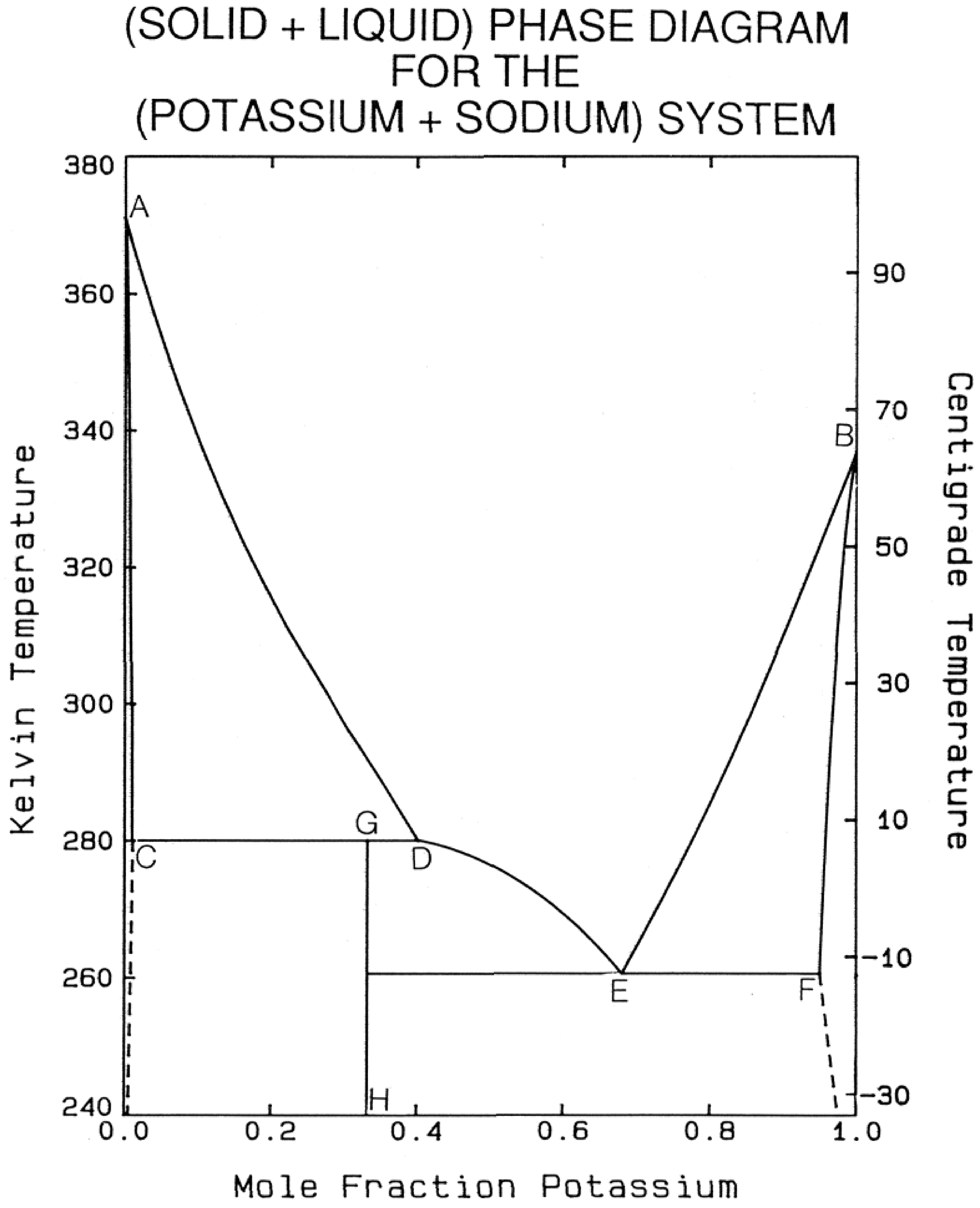


Fig. 15. (Solid + liquid) phase diagram for the (sodium + potassium) system

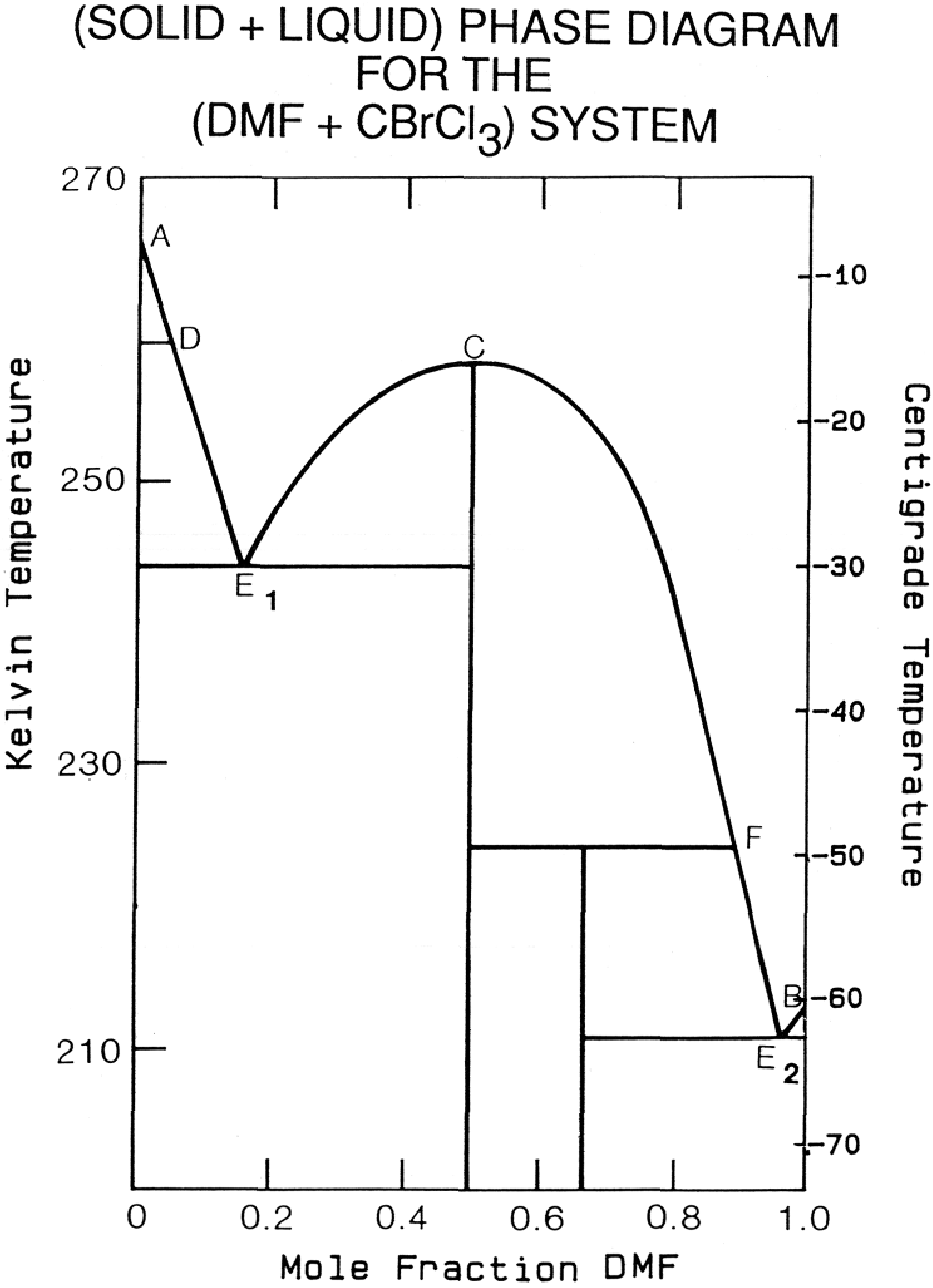


Fig. 16. (Solid + liquid) phase diagram for the [N,N-dimethylformamide (DMF) + trichlorobromomethane ($CBrCl_3$)] system

NOTES

[1] For a description of the calorimeter Iduna, see J. B. Ott et al., "Excess Enthalpies for (Ethanol + Water) at 298.15 K and Pressures of 0.4, 5, 10, and 15 MPa," *Journal of Chemical Thermodynamics* 18 (January 1986): 1–12; for a description of other flow calorimeters, see J. J. Christensen, H. D. Johnston, and R. M. Izatt, "An Isothermal Titration Calorimeter," *Review of Scientific Instruments* 39 (September 1968): 1356–59; J. J. Christensen et al., "An Isothermal Titration Microcalorimeter," *Review of Scientific Instruments* 44 (April 1973): 481–84; J. J. Christensen et al., "Isothermal High Pressure Flow Calorimeter," *Review of Scientific Instruments* 47 (June 1976): 730–34; J. J. Christensen et al., "Isothermal, Isobaric, Elevated Temperature, High-pressure, Flow Calorimeter," *Review of Scientific Instruments* 52 (August 1981): 1226–31; J. J. Christensen and R. M. Izatt, "An Isothermal Flow Calorimeter Designed for High Temperature, High Pressure Operation," *Thermochimica Acta* 73 (February 1984): 117–29; J. J. Christensen, P. R. Brown, and R. M. Izatt, "An Isothermal Flow Calorimeter for High Temperature Aqueous Solutions," *Thermochimica Acta* 99 (March 1986): 159–68.

[2] Jay Purdy and Brian Neely were the students who made the heat of mixing measurements on (cyclohexane + acetonitrile), and Robert Harris made the (liquid + liquid) phase equilibria measurements. The paper describing the results is J. B. Ott et al., "Excess Enthalpies at 323.15, 348.15, and 373.15 K and (Liquid + Liquid) Equilibria for (Cyclohexane + Acetonitrile) at 0.4 and 15 MPa," *Journal of Chemical Thermodynamics* 20 (September 1988): 1079–87.

[3] Ibid.

[4] Ibid.

[5] The temperature measuring apparatus is described in J. B. Ott et al., "(Solid + Liquid) Phase Equilibria in Acetonitrile + Tetrachloromethane, + Trichloromethane, + Trichlorofluoromethane, and + 1,1,1-Trichlorotrifluoroethane," *Journal of Chemical Thermodyamics* 19 (1987): 177–84. Brian Woodfield was the student who assembled the apparatus.

[6] The (solid + liquid) phase diagram for the (ethylene glycol + water) system is reported in J. B. Ott, J. R. Goates, and J. D. Lamb, "Solid-liquid Phase Equilibria in Water + Ethylene Glycol," *Journal of Chemical Thermodynamics* 4 (January 1972): 123–26. John Lamb, the student who made the measurements, is currently a professor of chemistry and director of research administration at Brigham Young University.

[7] The formation of the (hexafluorobenzene + benzene) addition compound is described in J. R. Goates, J. B. Ott, and J. Reeder, "Solid + Liquid Phase Equilibria and Solid Compound Formation in Hexafluorobenzene + Benzene, + Pyridine, + Furan, and + Thiophen," *Journal of Chemical Thermodynamics* 5 (January 1973): 135–41. Joan Reeder, the student who made the measurements, is currently a faculty member at Eastern Kentucky University. The (titanium tetrachloride + anisole) addition compound is described in J. R. Goates et al., "Infrared and Phase Equilibria Studies of Intermolecular Compounds of Titanium Tetrachloride with Several Aromatic Hydrocarbons and Ethers," *Journal of Physical Chemistry* 68 (September 1964): 2617–21. Nolan Mangelson and Reed Jensen were the students who performed the original experiments with titanium tetrachloride. Nolan is currently a professor of chemistry at BYU, and Reed Jensen is an associate director of the Los Alamos Scientific Laboratories.

[8] Summaries of the method for calculating ΔH for the formation of molecular addition compounds from the components along with the results of this calculation for a number of systems are given in J. R. Goates et al., "(Solid + Liquid) Phase Equilibria for (N,N-dimethylacetamide + Tetrachloromethane): Enthalpies of Melting of Pure Components and Enthalpies for Formation of Molecular Addition Compounds from Phase Equilibria," *Journal of Chemical Thermodynamics* 19 (January 1987): 103–7; and S. R. Goates et al., "Thermodynamic Stability of Solid Intermolecular Compounds," *Journal of the Chemical Society, Faraday Transactions I* 83 (1987): 1553–58.

[9] J. S. W. Overell and G. S. Pawley, "An X-Ray Single-Crystal Study of the Molecular System $C_6F_6 \cdot C_6D_6$," *Acta Crystallographia B38* 15 (July 1982): 1966–72.

[10] See J. R. Goates et al., "(Solid + Liquid) Phase Equilibria for (N,N-dimethylacetamide + Tetrachloromethane)," and S. R. Goates et al., "Thermodynamic Stability."

[11] See J. R. Goates et al., "Infrared and Phase Equilibria Studies"; and R. J. Jensen, "Thermodynamics of Charge Transfer Complexes" (Ph.D. diss., Brigham Young University, 1965).

[12] See J. R. Goates et al., "(Solid + Liquid) Phase Equilibria for (N,N-dimethylacetamide + Tetrachloromethane)"; and S. R. Goates et al., "Thermodynamic Stability."

[13] J. B. Ott et al., "Solid-liquid Phase Equilibria in the Sodium Potassium System," *Transactions of the Faraday Society* 65 (1969): 2870–78; J. R. Goates, J. B. Ott, and D. E. Oyler, "Intermolecular Compound Formation in Solutions of N,N-dimethylformamide with Carbon Tetrachloride and Several Related Substances," *Transactions of the Faraday Society* 62 (1966): 1511–18.

[14] See, for example, F. Laves, "Factors Governing Crystal Structure," in *Structure of Metals*, 3d ed., ed. C. S. Barrett and T. B. Massalski (New York: McGraw-Hill, 1966), 129–43. Other references describing the structure of this compound are R. L. Berry and G. V. Raynor, "The Crystal Chemistry of the Laves Phase," *Acta Crystallographia* 6 (1953): 178–86; C. S. Barrett and T. B. Massalski, ed., *Structure of Metals, Crystallographic Methods, Principles, and Data*, 3d ed., rev. (New York: Pergamon Press, 1980), 256–59.