

Yu.Ya.Fialkov

THE  
EXTRAORDINARY  
PROPERTIES  
OF ORDINARY  
SOLUTIONS



Mir Publishers Moscow

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Ю. Я. Фиалков

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НЕОБЫЧНЫЕ СВОЙСТВА

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ОБЫЧНЫХ РАСТВОРОВ

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*Scientists to Schoolchildren*

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Yu. Ya. Fialkov

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Translated from the Russian by  
Boris V. Kuznetsov

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*На английском языке*

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## On Dry Lemonade and About This Book

It is a hot July day. Feeling thirsty, you look around for a nearby soda fountain and find none. But your eyes catch the sign at the top of a kiosk. Styled in fanciful Old-Slavic letters, it promises Russian *kvas*, a soft drink perhaps as popular with Russians as Coca-Cola with Americans. No, there is not a drop of *kvas* left, the girl behind the counter says. Nor a bottle of *Buratino* (another Russian favourite). What she can offer is lemonade. Hopefully, I opt for two. The girl holds out – no, not the familiar paper cups full of the bubbling liquid. In her hand are two small white packages stuffed with a crackling powder. That is dry lemonade. Well, your thirst has to wait until you are back home. But that is a good point from which to start with a book about solutions – this book.

Of course, it would be more appropriate to begin by stating that the subject of solutions is extremely important, more important than anything else. For solutions are everywhere around us. Tea is a solution. A perfume is a solution. A sea wave is a solution. The pickle for cucumbers is a solution. Even cucumbers themselves are solutions. But it is not enough just to declare that solutions are vitally important. This must be proved. And this is the object of the book you are going to read.

Deep in thought about the solutions so amazingly present everywhere, you get back home, take a package of dry lemonade and, following the simple instructions stamped on it, empty its contents in a glass and fill it with tap water. In an instant, the powder dissolves, and gas bubbles stream violently to the surface. You take a sip and feel satisfied – the drink is sweet and, most important, full of fizz.

Of course, the fizz, or gas, that goes up as bubbles in the do-it-yourself lemonade is not stored in the package. It comes from a chemical reaction. The point is that the powder contains (in addition to sugar) baking soda and citric acid. The two eagerly react with each other to form the sodium salt of citric acid and gaseous carbon dioxide. Simple as that, and no tricks.

Simple? No tricks? Why is it then, you may ask, that the soda and the acid do not react when the powder is dry? Why is it that the mixture has to be dissolved for the reaction to take place?

The answer is, *Corpora non agunt soluta*, which is the Latin for "Bodies (substances) do not react unless dissolved". Alchemists discovered this rule many centuries ago.

We take it for granted that chemical reactions take place in solutions, but hold this fact at the back of our minds or even completely forget about it. To prove the point, I challenge you to take what might pass for a psychological test. Describe in words what you see with your mind's eye when you are told: "When caustic soda and hydrochloric acid are brought together, a neutralization reaction occurs according to the equation:  $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ ".

I'm prepared to bet against any odds that what you see in your mind is a flask of alkali from which a sample is poured into a test tube to which an amount of acid is added from another flask. That's all, and nothing more. But, unless you know already, any reference book on chemistry will tell you that caustic soda, NaOH, is a crystalline solid melting at 318°C, and hydrogen chloride, HCl, is a gas which turns to liquid at -84°C. Now you can see for yourself that the reactants are no liquids.

In our hypothetical test we poured together solutions of the reactants in water, rather than the substances

themselves. That's obvious. But it is not so obvious what water has to do with the reaction and why. In fact, some water is produced when the alkali reacts with the acid (so, in accord with the laws of chemical reactions the added water should only meddle with the reaction). Moreover, as is clearly seen from the reaction equation, the reactants do not need water. Yet, although they do not need water, nothing can happen without it. In some mysterious way (to be explained later), water takes part in our reaction and, indeed, in an overwhelming majority of other chemical reactions. As chemists well know, 199 reactions out of 200 can only take place in solution.

This fact alone could well support our statement that solutions are very important. And we could add many more such facts.

The title of this book promises to take up some extraordinary properties of solutions. Some readers may disagree with the choice of the word. They may argue, for example, that there is nothing extraordinary in the fact that salt solutions can conduct electricity or that a solution would freeze at a lower temperature than a pure solvent. Science has explanations for everything, they may add, what is unclear today will be clarified tomorrow.

Nothing extraordinary? Well, it depends. It depends on how you look at things. Here is a tree, an ordinary tree. But if you stop to think of how its luxuriant foliage has grown out of carbon dioxide and water, you will feel it is a wonder.

One sagacious man has once said that science begins by seeing unusual in the usual. Everyone had seen things fall when let go from one's hand, but only Galileo was intrigued by what he saw. A good many people had admired bright sun rays, but only Newton saw something striking in sunlight. Everyone had seen water freeze, but only Lomonosov treated this as a wonder.

That is why every book on science is always an invitation to see unusual in the usual. I, too, invite you to share my amazement at the extraordinary, extremely extraordinary properties of ordinary solutions.

## What is a Solution?

Well, you might say, that's obvious. A solution is a solution—that's all there is to it. But—

But as one adage goes, nothing is more dangerous in science than the obvious. A definition, a rigorous definition bears that out forcefully: **A SOLUTION IS A HOMOGENEOUS (formed of parts of the same kind) CHEMICAL SYSTEM (a mixture of substances) IN WHICH EVERY ELEMENT OF VOLUME (the smallest fraction) HAS THE SAME CHEMICAL COMPOSITION AND THERMODYNAMIC PROPERTIES.**

The words in brackets are supplied just in case you don't happen to know what their bookish counterparts mean. Of course, "thermodynamic" must have also been explained. Unfortunately, thermodynamic is thermodynamic. If you want to know more about it, you may turn to a school text on physics or "Thermodynamics for Everybody" by I. R. Krichevsky and I. V. Petryanov in this same "Scientists to School-children" series as this book.

Let's go through the definition again. Note that it does not include the word "liquid" as a noun or an adjective. Does that mean that a solution can be a gas or—just think of it!—a solid? Yes, it does. Air is a veritable solution—it is a homogeneous mixture of gases. A gold ring, too, is a solution or, rather, a solid solution—it is a homogeneous alloy of gold and copper in which every minutest part is the same in properties.

Quite logically, solutions are classed into gaseous,

liquid, and solid. Of course, liquid solutions are far more frequent in nature, science and technology than their gaseous or solid opposite numbers. That is why this book will be solely concerned with liquid solutions, and the reader will not be forced to change his habitual view of solutions as liquids. Still, it is important to remember that solutions may sometimes scratch and not only flow.

### Midway Between Gases and Crystalline Solids

**What Textbooks Say.** Thus we'll be concerned with the liquid state of matter. It is therefore worth while to define more accurately what a liquid is. As I hope, the reader is now well aware that "obvious" definitions like "A liquid is that which flows" will not do.

So let's turn to textbooks. One reads: "A liquid is a state intermediate between a solid and a gas". It's correct to the last word, but still—what is a liquid?

In another textbook we find: "Crystalline substances (solids) have a well-defined structure (which means that the constituent particles take up fixed positions relative to one another), whereas no structure exists in gases; liquids stand midway between both in that respect". This, I'm afraid, has not cleared the matter a bit.

Now we try our luck with a third textbook. This is what it says: "In crystalline solids the molecules strongly interact with one another. In gases, the interaction is so small as to be negligible. As to liquids, they stand midway between solids and gases in terms of molecular interaction".

That's how matters stand with textbooks. The only thing we've learned is that a liquid is something which is rather distant from gases but does not come anywhere near solids in properties.

We've quoted textbooks not to ridicule their authors. Far from that. We've used quotations to show how

uncertain they are about the concept of liquid. This uncertainty stems from the fact that it has taken physicists a very long time to find out the specific features of the liquid state of matter.

**A Crystalline Solid or a Gas?** Probably already in ancient times scientists had a fairly clear idea about the structure of crystalline solids (complete order) and of gases (complete disorder). Things were different with liquids. It was simple to say that liquids stood midway between crystalline solids and gases – that fact lay on the surface, so to speak, but it was far more difficult to get deep insight into the matter. It was not until the 20th century (in fact, not until its 30's) that some clarity – a relative clarity – was achieved in regard to liquids. In any case, we're in a position today to place liquids in a well-defined and not in an indistinct "midway" niche in the theory of matter.

For all this knowledge, however, we must begin by comparing the liquid state with the other two states of aggregation – solid and gaseous. For everything is learned by and from comparison, and the nature of the liquid state is no exception in that sense.

A major distinction of a solid is that it has a definite shape which it retains unless acted upon by external forces. A liquid conforms to the shape of the containing vessel and seeks to occupy the smallest possible volume. A gas, when left to itself, tends to expand without bound.

In any substance, be it a gas, a liquid or a solid, the molecules are in a constant motion. We know that the manner in which they move about is related in a most definitive way to the state of aggregation in which the sample of matter is present. The particles that make up a solid sample do not leave their sites – they only swing, like a pendulum, about some position of equilibrium. In a gas, the molecules are free to move about at random

and, in doing so, they collide with one another. The distance they travel between collisions is called the mean free path and is equal to  $10^{-5}$  cm. This is a large distance—about a thousand times the diameter of a molecule. If you happen to live in a locality where your nearest neighbour is a kilometre or two away, certainly that is not a densely populated area. In a liquid, molecules can only move on step—the distance equal to the diameter of a molecule ( $10^{-8}$  cm). This looks like a crowd.

From books on the structure of liquids you'd realize very soon that their authors do not see eye to eye with one another. Some believe that liquids are almost the same as crystalline solids because they have a regular structure and the energy involved in the interaction of their molecules is about the same as it is in solids, but is substantially greater than in gases. Others insist that liquids are more related to gases than to solids. They argue that the particles in a liquid move as randomly as they do in a gas and when the temperature is high enough (it's then called critical and is different for different substances), the difference between liquids and gases disappears altogether—physicists know that all too well.

Who's right, then? Everybody is. It does happen sometimes (and not only in science) that either side is right.

**Neighbours in a Liquid.** It was John Bernal, a British chemist, who threw a bridge between the “crystalline” and the “gaseous” theories of liquids. In the 30's he made an experiment which could pass, at least outwardly, for a child's play. He took a metal tray with its surface roughened haphazardly, poured onto it a handful of steel balls which were to imitate liquid molecules, and covered them with paint generously. When the paint had hardened, the experimenter carefully detached the balls

one by one and examined them in a magnifying glass. Where the balls had touched one another, he saw unpainted marks. By counting the marks, he found the number of closest neighbours each "molecule" had. And here came a surprise.

Before we go any further, it should be clarified how matters stand with neighbours in solids. An ordinary crystal is in effect a large single molecule. The sketch in Fig. 1 shows a fragment (of course, magnified) of a sodium chloride ( $\text{NaCl}$ ) crystal. As is seen, it is both a very simple and a very regular structure. In it, each ion is surrounded by eight neighbours. There are exactly eight (and no more)  $\text{Cl}^-$  anions around each  $\text{Na}^+$  cation, and there are exactly eight (and no more)  $\text{Na}^+$  cations around each  $\text{Cl}^-$  anion. In the crystals of other solids the number of neighbours may be four or six – what is important is that the number is always the same for a particular substance.

In a gas, there are no neighbours to speak about – they are practically nonexistent.

In a liquid, according to Bernal, the number of neighbours varies from molecule to molecule. Although the maximum number is as small as it is in a solid (not more than 10), one molecule may have five neighbours and another seven in the same liquid. Yet, there is every sign of structural order because we can easily count – and do that with sufficient accuracy – how many liquid molecules have six neighbours and how many eight at a given instant. Because of this, liquids may be called crystal-like, as if consisting of a conglomerate of tiny crystals. But to be crystal-like is not the same as to be a crystal. This is convincingly proved by changes in the properties of liquids on heating. As the temperature is raised, the liquid molecules move ever more energetically, and the microscopic crystals lose more and more of their

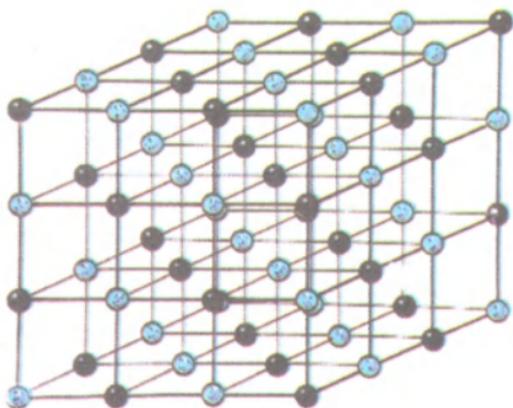


Fig. 1. Crystal lattice of sodium chloride, NaCl

stability. As this happens, the liquid behaves increasingly more like a gas.

**Both a Crystalline Solid and a Gas.** From what we've learned it's safe to draw a very important conclusion about the structure of liquids: At temperatures close to their freezing point, liquids come very nearly to solids in properties; at temperatures close to their boiling point, they come very nearly to gases.

One way or another, a liquid is not a chaotic entity. This has been proved beyond any shade of doubt by the manner in which liquids scatter X-rays. When the molecules in a specimen of a substance are arranged at random, they scatter the incident X-rays as randomly, and no definite pattern can be observed in the scattered radiation.

Quite obviously, there can be no regular pattern in the X-rays scattered by gases. As obviously, the X-rays scattered by a crystalline specimen show a distinct pattern. This pattern is closely related to the structure of

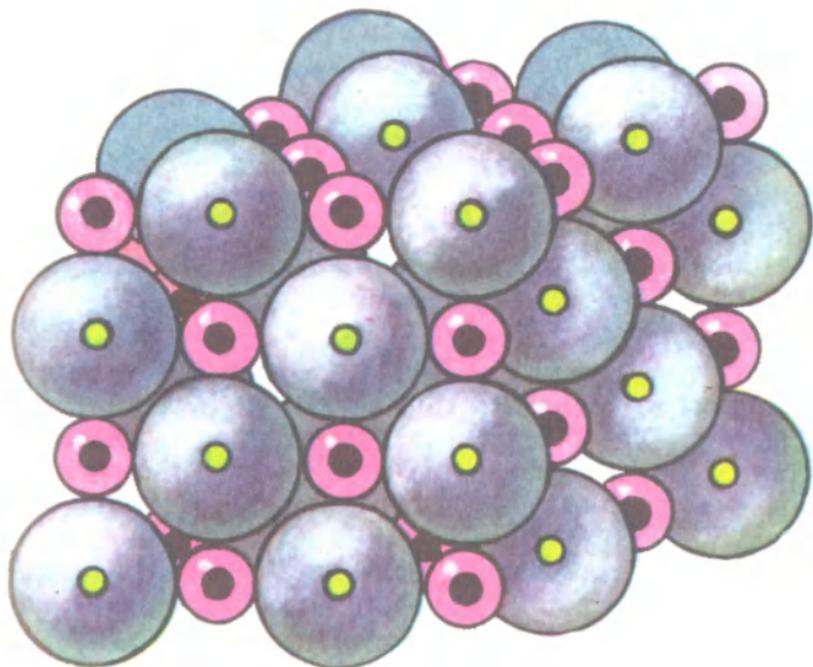


Fig. 2. Structure of sodium chloride

the crystal. That is why X-rays have come to be a powerful tool of research in crystallography.

There is a pattern in the X-rays scattered by liquids. Although it is not so well-defined as with crystals, it is distinct enough for us to state that liquids do possess a definite structure. A good deal in this field has been done by Danilov of the Soviet Union who has been investigating the scattering of X-rays by a wide range of liquids since the 30s.

The literature on liquids abounds in the terms "short-range order" and "long-range order". Now that we've developed at least a rough idea about the structure of liquids, it is easy to grasp the meaning of those words. Crystals possess long-range order, for at any distance

from a crystal cell we will find an exactly similar cell. This is not so with liquids—they show a very short-range order—the regular arrangement is retained over a distance about the diameter of a molecule. Gases possess neither short-range nor long-range order—no order at all.

Well, now we see that liquids do stand midway between crystalline solids and gases. But we can also see a good deal what stands behind those words.

**The Property of Liquids Only.** At one time, newspapers in almost all countries throughout the world carried a photograph of a large water sphere hanging at rest in front of an astronaut in the cabin of his space vehicle. Physicists had postulated well before space flight that any liquid including water, if left to itself (that is, placed outside any gravitational field or a confining vessel), would contract to a sphere because among all conceivable shapes of the same volume it has the smallest surface area. Now they were surely pleased to see their postulate come true.

The tendency of a liquid to contract in surface area as much as possible is related to what is called surface tension—a feature peculiar to liquids only. Look at Figure 3. It shows a tremendously enlarged elementary volume of a liquid drop. The arrows radiating from each molecule represent forces of attraction (adhesion) between the molecules. As is seen, in the body of the liquid these forces balance one another so their average value is zero. At the surface the situation is quite different: beyond the free surface there are no molecules to counteract the forces of attraction exerted by molecules in the interior for molecules in the surface. In consequence, molecules in the surface experience a net attraction toward the interior of the drop. These forces cause the droplet to assume a spherical shape. That is how surface

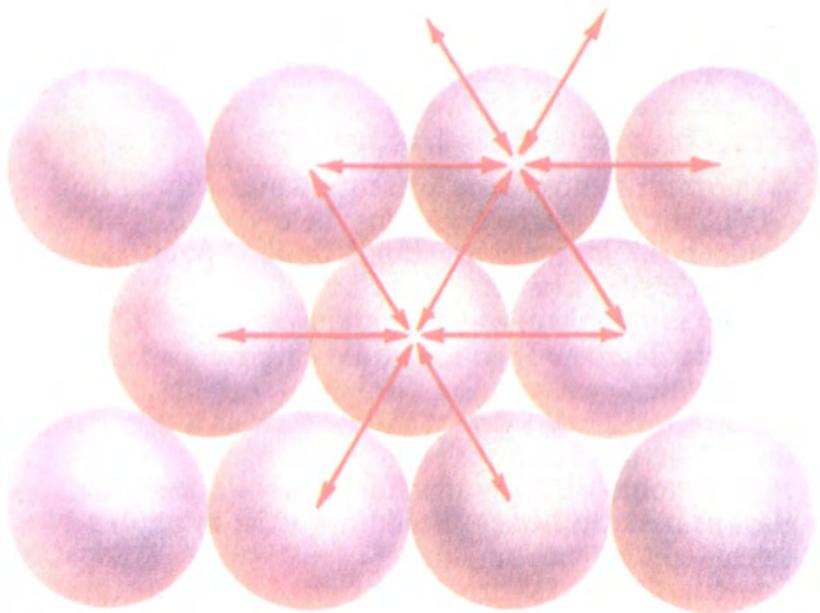


Fig. 3. Explaining the origin of surface tension

tension works. With it, a liquid molecule seems to be covered with a self-contracting film one molecule deep.

It is because of surface tension that a steel needle much denser than water will float on the water surface when carefully placed. It is because of surface tension that a water bug can step on the water surface as if it were dry land. And it is because of surface tension that a drop of water contracts to a sphere of the least possible surface area in the cabin of a space vehicle.

So far we've been talking about the properties common to all liquids. Now let's turn to water. It's quite legitimate to single it out of the huge number of liquids. For one thing, although any solvent, any liquid can be used to make a solution (that will be dealt with in the chapters that follow), solutions in water come our way far more

frequently. For another,—well, this is where the most important thing lies.

### Water—Puzzling and Extraordinary

At normal atmospheric pressure water should boil at  $-70^{\circ}\text{C}$ , or 70 degrees Celsius below zero. I've said "should boil" because its actual boiling point lies 170 degrees Celsius higher.

By the same token, water should freeze at  $-90^{\circ}\text{C}$  and not at zero degrees. Then ice would sink rather than float on the water surface.

Water from a leaky faucet should flow as a thin stream rather than fall in drops.

Sugar should dissolve in water poorly—a few grains in a glass at best. So honey should not exist in nature. Nor a sweat cup of tea or jam.

So many "should's" are only a sign of the puzzlement at the unusual, truly unusual behaviour of water. No more than puzzlement, because (as, I hope, the reader's guessed), by using all these "should's", the author is not at all bent on making Nature conform to his tastes (that would be a vain attempt to say the least).

Now it remains to prove why water should behave differently than it does actually.

In physics and chemistry there is an almost endless number of relationships deduced by using similarity. We, too, shall use it. Now I'll try to explain what I mean.

Imagine for an instant a hypothetical—no, fantastic—situation: Water is unknown to chemists, indeed, it hasn't been synthesized yet. And some chemist plans to produce a compound consisting of hydrogen and oxygen. And he should draw up a forecast of the most important properties of this "oxygen-hydrogen" compound.

Let's trace his reasoning. Oxygen is in Group VI of the

Periodic Table. That same group (or, rather, subgroup) is shared by sulphur, selenium and tellurium. It's necessary to see how the boiling and freezing points of the compounds of all these elements with hydrogen vary. The pattern can then be extrapolated to the yet nonexistent compound  $\text{H}_2\text{O}$ .

The chemist takes a bulky reference book from his book-shelf, runs through its pages, and draws up the table that follows.

Compound	Formula	Molecular mass	Boiling point	Freezing point
Hydrogen telluride	$\text{H}_2\text{Te}$	129	- 4	- 51
Hydrogen selenide	$\text{H}_2\text{Se}$	80	- 42	- 61
Hydrogen sulphide	$\text{H}_2\text{S}$	34	- 61	- 82
Hydrogen oxide (water)	$\text{H}_2\text{O}$	18	?	?

The next step is to construct a plot of temperature against molecular mass. The chemist lays off the molecular masses along the  $x$ -axis and the boiling and freezing points as ordinates, and draws smooth curves through the points thus obtained. Here it is, this plot (Fig. 4). How he extends the curves until they cross the ordinate for "hydrogen oxide" so as to locate its boiling and freezing points. As you can see from the plot, the boiling curve cuts the ordinate for  $\text{H}_2\text{O}$  at  $-70^\circ$  and the freezing curve does so at  $-90^\circ\text{C}$ . From this, our chemist rightfully expects that water should (presumably!) boil and freeze at the temperatures which, as you and I know, are a long way below the actual ones.

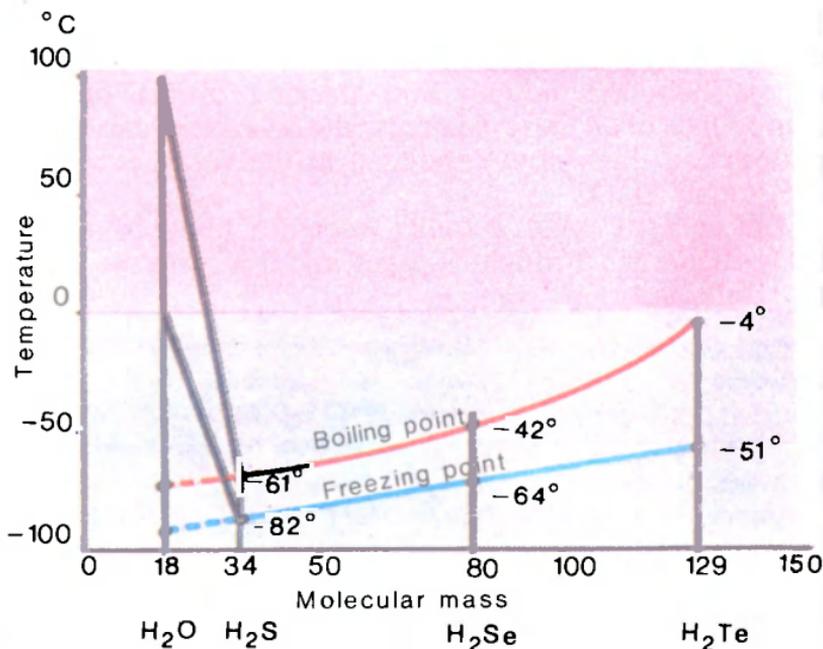


Fig. 4. Boiling and freezing points of Group VI hydrides as functions of molecular mass

Because of these “false” expectations the chemist goes a considerable length to avoid the troubles that could never happen all the same. For one thing, he places his reaction flask in dry ice (solid carbon dioxide) or even liquid air so that the “hydrogen oxide” could not go off (as he expects) in a whiff of vapour. He is happy when the reaction produces crystals, but he is certainly bewildered (not very much at first) when the crystals refuse to melt at  $-90^{\circ}\text{C}$ . His bewilderment grows as he keeps heating the crystals to  $-70^{\circ}\text{C}$  (when “hydrogen oxide” should have long melted or even boiled), then to  $-50^{\circ}\text{C}$ , and so on, with the same result. Finally, his bewilderment may well give way to grief. This mood may last for a long time

because it's not at all easy to get to the cause of these anomalies of water related to boiling and freezing—and these are only two of many other anomalies.

**The Specific Heat Capacity of Water.** This is another anomaly of water. To clarify it, let's send an inexperienced traveller to, say, the Sahara Desert. Of course, he thought it would be hot there, but not that hot. The heat streaming from the sand is so unbearable that the exposed skin seems to scorch and blister. The man can hardly wait for the Sun to set and bring with it the life-saving coolness.

At last the Sun sets, and the air turns cool at once, then cooler, still cooler, cold, very cold. Just think it can be that cold near the Equator. Now the man can hardly wait for the Sun to rise.

I'm sure the reader wonders why I should have sent my traveller to a desert in a chapter about water. For if a desert lacks anything, it's water. That's true—a desert lacks water, and here lies the climatic idiosyncrasy that drives our traveller nearly mad.

As you surely know from school, it takes a certain amount of heat to raise one gram of a material one degree in temperature. This amount differs from material to material. For mercury, it is a little more than 0.1 joule; for sulphuric acid, around 1 joule; and for ethyl alcohol, a little more than 2 joules. The all-round champion among all materials is water. It takes 4.2 joules to raise one gram of water one degree in temperature. This is known as specific heat capacity, or simply specific heat. In this respect water has a very large lead over most substances.

In localities where water is abundant, the temperature of the air rises very slowly even on a hot day, because a sizeable proportion of heat is trapped by water. After the sunset, too, the temperature of the air in such places

falls off as slowly because water is slow in giving up the heat it has stored up during the day. In a way, water acts as a climate regulator. That's why the temperature on the Baltic coast is seldom higher than  $+20^{\circ}\text{C}$  in summer and is seldom lower than  $-10^{\circ}$  in winter. The situation is different in Yakutia which is far away from the sea. There, the temperature can be as high as  $+40^{\circ}\text{C}$  in summer and as low as  $-50^{\circ}\text{C}$  in winter.

Now we're in a position to say what our traveller should have expected during his journey to the Sahara Desert. Water is scarce in Sahara, but it has heaps of sand. The specific heat of sand is one-fifth that of water. So sand grows hot very quickly in the daytime—it needs very little heat for that. For the same reason it grows cold very quickly at night—its store of heat is meagre. That's why it's cold, very cold in southern deserts at night.

**For Water to Boil.** Take any liquid (not necessarily water), dip a thermometer in it, and heat the liquid. Quite naturally, the thermometer will read a rising temperature. But just as your liquid goes simmering, that is, giving up the first bubbles (which indicates the start of the boil), the mercury column will come to a stop and remain stationary until all of the liquid has turned to vapour. Then the mercury column will resume its rise, but now it's the vapour that is being heated.

You can sum up your observations as a plot of temperature against heat input, or heat applied, as is shown in Fig. 5. If the same quantity of heat is applied every second (and this is the case most often), then time may be laid along the  $x$ -axis instead of heat units. The portion of the plot parallel to the  $x$ -axis represents boiling.

It's an easy matter to see why, as boiling goes on, the temperature of the liquid remains unchanged despite the added heat. This heat is converted to the energy that is

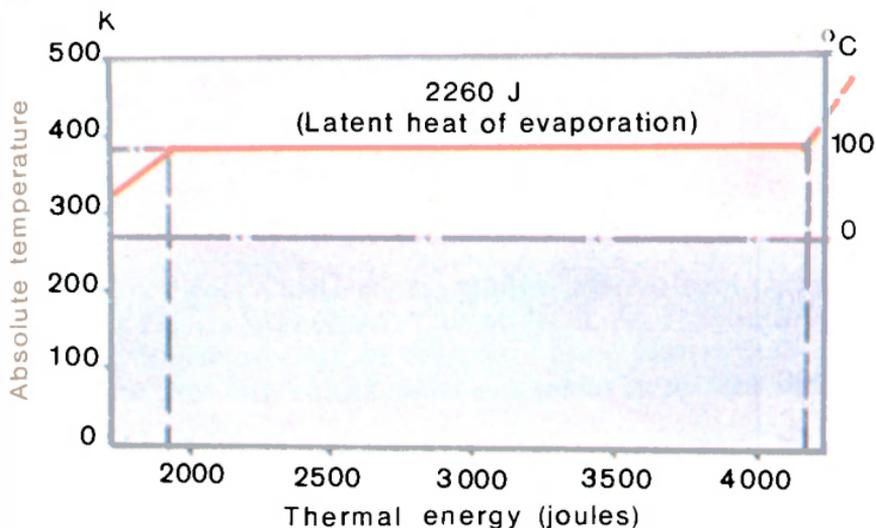


Fig. 5. Latent heat of vaporization

used up by molecules in order to break away from the bulk liquid and to pass into the vapour. The amount of heat needed for one gram of liquid at its boiling point to be converted into a vapour is called the latent heat of vaporization (or evaporation). Now every word in this definition is clear to us. Even the word “latent” is in its right place. For the effect of heat input does remain latent, or hidden, because it does not bring about any change in temperature.

The reader will, I’m sure, readily recognize water as the all-round champion in the latent heat of vaporization as well. And by a good margin at that! It takes as much as 2260 joules of heat to turn one gram of water to a vapour under normal atmospheric pressure. This figure dwarfs the mere 290 joules needed to vaporize one gram of mercury. For benzene it is 390 joules, and for ethyl alcohol, around 850 joules.

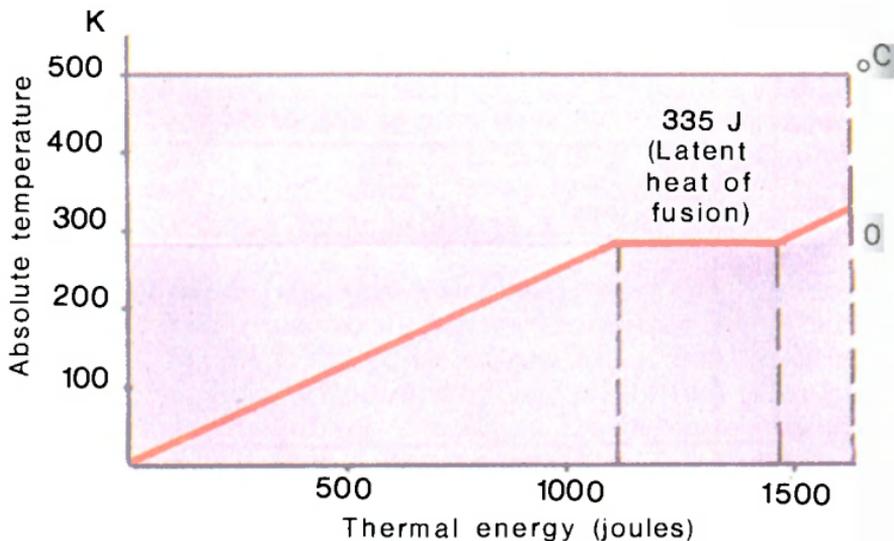


Fig. 6. Latent heat of fusion

It remains to find out why water is so special in this respect, and we'll do that shortly. For the time being it may be noted that this anomaly is undoubtedly useful. Without it, our planet would hardly have any rivers or lakes. With the oceans, too, things would be different – most of the water, if not the whole of it, would be present as vapour in the atmosphere. Stripped of liquid water but wrapped in a dense and impenetrable blanket of water vapour, the planet would look real bad.

The high latent heat of vaporization of water is also responsible for its action as a climate regulator. In turning to vapour, water cools the air; in pouring down as rains, it heats the air. If you doubt that clouds and rains have a strong effect on the Earth's climate, note that as much as 50 cubic kilometres of water is vaporizing or condensing every hour on our planet. Now calculate how many joules are needed for the job.

From what has been said it's easy to define the latent heat of fusion – the heat necessary to melt one gram of a solid at its melting (or fusion) point. By laying off the temperature of the system against heat input (or time), we shall obtain a plot, Fig. 6, which closely resembles that in Fig. 5 as if the two were twins. Look at the plot of Fig. 6, and you'll see this is true. But now the horizontal portion represents melting.

In this case, too, water stands apart from other substances. Its latent heat of fusion (which is 335 joules) is nearly 30 times that of mercury, three times that of benzene, and ethyl alcohol. This, again, cannot but have a strong effect on the Earth's climate.

I'm sure you've noticed that in most cases it becomes warmer after a heavy snowfall. The cause is obvious. In turning into beautiful snow flakes, every gram of water returns to the air the 335 joules it "borrowed" previously. If we recall that for the most part snow forms directly from water vapour, we must add the 2260 joules of the latent heat of vaporization to the total.

**More Anomalies.** Now that ice has come into the picture, it is natural to recall one more anomaly of water related to its solid state. As naturally you may picture to yourself a pair of figure-skaters performing exquisitely on the ice. For there is a close relation between the two events. A skater moves smoothly over ice because the pressure of the skates causes it to melt, and liquid water is an excellent lubricant. That's everybody's knowledge. But very few know that this should not be so. Because, except for two or three substances, those known to chemists show a rise rather than a fall in their melting point under pressure. Everything is the other way around with water – a reduction in pressure leads to a fall in the melting point of ice.

Or recall surface tension. Here, too, water is second to

none. Look up a table listing the values of surface tension for liquids, and you'll see that for most of them the figure is anywhere between 20 and 30 dynes per centimetre. Only water is rated at 73. Nature has put this anomaly to full advantage as well.

Have you ever thought of how water rises from the roots of a tall tree to its top? By the known laws of mechanics, a difference in pressure cannot raise water more than ten metres. But water does rise more than that. This happens by what is known as capillary action. Dip a capillary tube in water and you'll see it rise, and this rise will increase as the diameter of the capillary tube is decreased and the surface tension increases.

In our story of solutions, one more anomaly is important -- that of dielectric constant. Although the term is not self-explanatory (we will not go into its origin for the time being), the property it describes is fairly simple: by virtue of this property a medium modifies the mutual interaction of electrified bodies immersed in it or separated by it, as compared with their interaction in vacuum.

In tables listing the value of dielectric constant for liquids, the figure for benzene is 2.27. This means that the mutual interaction between any two charges immersed in benzene is by a factor of 2.27 weaker than it would be in vacuum. The same tables say that for most liquids the dielectric constant ranges between 2 and 10. Few (very few, indeed) have a dielectric constant of as high as 35. Even in the most detailed table of dielectric constants, we'll hardly find a dozen liquids with a dielectric constant lying between 40 and 60.

These figures bring us to realize how exceptional water is in this respect as well. Its dielectric constant is 78. Only two or three other liquids (among them, sulphuric acid) can boast a higher dielectric constant.

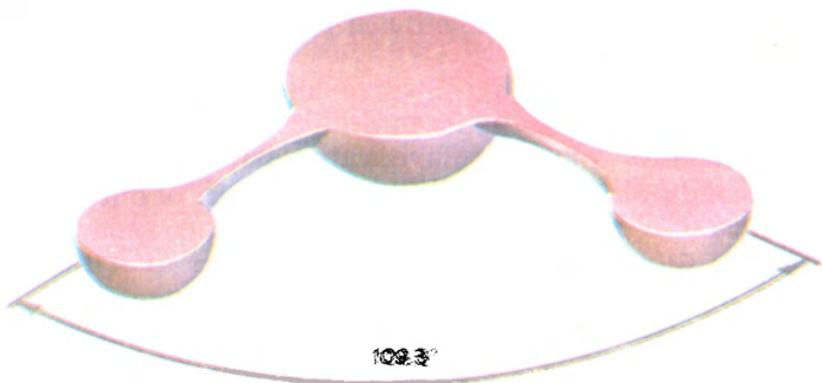


Fig. 7. Water molecule

**How a Water Molecule is Built.** We might keep on talking about the anomalies of water for a very long time. In fact, we could fill all of this book with them. But that would be a book about water, not solutions. So, it's time to get down to explaining the anomalies we've listed (and those not yet mentioned).

It should be said at the outset that many, if not all, of the unusual properties of water stem from the way its molecules are built. Geometrically, there's hardly anything that could be described as unusual. As Fig. 7 shows, there is an atom of oxygen to which two atoms of hydrogen are joined (of course, the reader should realize that the bars joining the atoms are imaginary). Naturally, the atoms of an  $H_2O$  molecule lie all in the same plane (you can always pass a plane through three points). Importantly, the angle between the O-H bars, or bonds, is  $109^\circ$ . This is important because many things hinge upon it. Notably, the negative charge of the water molecule (oxygen) and its positive charge (hydrogen) are positioned at the opposite ends of the molecule. So, the

water molecule as a whole has a positive and a negative pole.

Molecules with their positive and negative charges separated are called dipole molecules or simply dipoles. The extent to which the charges are separated is stated in terms of dipole moment, that is, the product of one of the charges of a dipole molecule by the distance separating the two dipolar charges. Small and simple as it is, the water molecule has a fairly large dipole moment: nearly twice as large as that of hydrogen sulphide (the nearest relative of water,  $\text{H}_2\text{S}$ ) and nearly seven times the figure for nitrogen oxide,  $\text{NO}_2$ .

Because water molecules have a sizeable dipole moment, they act as tiny magnets and attract one another. They can form pairs and even quartets. Such associates and the way they are produced are shown in Fig. 8. This alone suggests that liquid water is not a collection of solitary  $\text{H}_2\text{O}$  molecules. It's a mixture of molecules varying in complexity.

**The Hydrogen Bond.** Now we'll digress a little to speak about some traits of hydrogen atoms. This is not a chance subject—two atoms out of the three in a water molecule

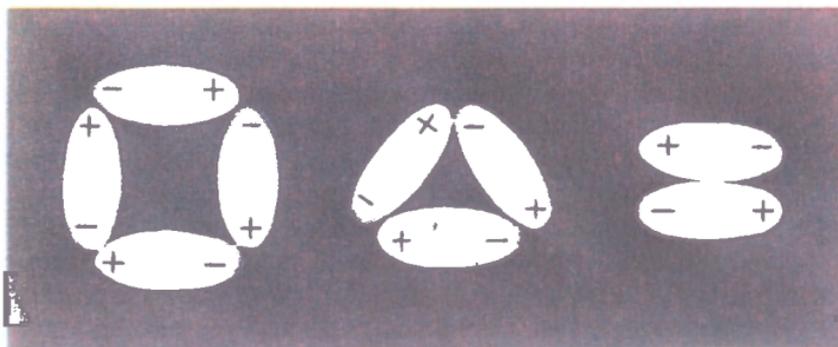


Fig. 8. Water-molecule associates

are hydrogen. In one and a very important way, hydrogen drastically (yes, drastically) differs from all the other elements in the Periodic Table. On giving up their electrons in a reaction, all chemical elements (mostly metals) do retain some. On giving up one electron in a reaction, lithium will still have two electrons remaining. On passing from the neutral state into that of a cation, sodium will retain 10 electrons, potassium 18, and so on. In short, on forming a chemical bond, any chemical element retains a number of electrons. Any, except hydrogen. Because a hydrogen atom has only one electron. On giving it up, it remains stripped of its electron shell. So, what we call the hydrogen cation,  $H^+$ , is a bare nucleus, the elementary particle proton.

The size of an atomic nucleus is a minute fraction (1/100 000th, to be exact) of that of the atom. That's why, in comparison with other single-charge cations such as  $Li^+$ ,  $Na^+$  or  $K^+$ , the  $H^+$  cation is exceedingly small. By a physical law, bodies possessing the same charge set up a field whose intensity is inversely proportional to the square of their radii. For this reason, the field due to a proton is a huge number of times stronger than that due to any other cations.

For the same reason, the hydrogen cation behaves unusually. Reacting with an oxygen anion,  $O^{2-}$ , two hydrogen cations should, it would seem, neutralize the charges\*. For example, this does happen when the cations joining an  $O^{2-}$  anion are "normal", such as  $Na^+$  or  $K^+$ , which produce the "normal" compound  $Na_2O$  or  $K_2O$ , whichever may be the case. The field set up by the proton in the  $H_2O$  compound is not neutralized, or saturated, by the negative charge of the oxygen anion. The hydrogen

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\* A simplified picture of how the bonds are formed in an  $H_2O$  molecule is, of course, given.

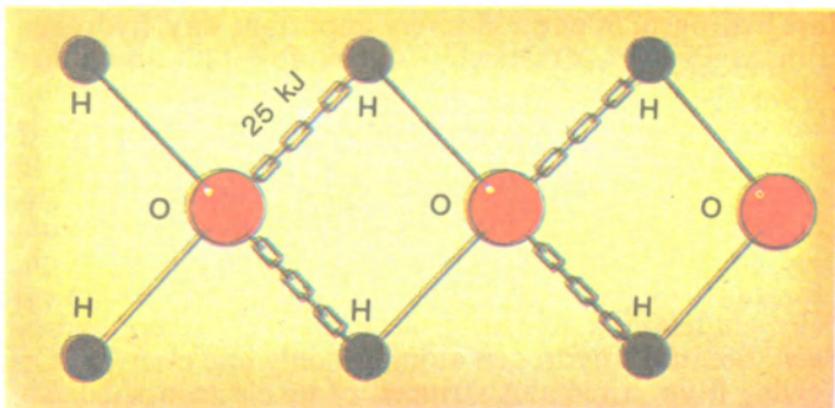


Fig. 9. Water molecules held together by the hydrogen bond

cation is still capable of forming one more bond. This is a special kind of bond—it's called the hydrogen bond. Look at Fig. 9. Each hydrogen atom is bound to two oxygen atoms. It may be said that oxygen has doubled its valence—the oxygen atom is bound to four hydrogen atoms at a time.

It's the hydrogen bond that holds water molecules strongly together. The word "strongly" is not out of place here: the total energy of the hydrogen bonds in one gram-molecule (18 grams) of water is around 25 kilojoules. Because of this, molecules in liquid water experience a very strong attraction for one another. In turn, this explains why water is practically noncompressible.

As they attract one another, water molecules develop a tremendous internal pressure—somewhere around 20 000 atmospheres.

**Anomalies Find an Explanation.** The hydrogen bond is behind many of the listed (and unlisted) anomalies of water.

Everything seems to be clear with the abnormally high boiling and freezing (or melting) temperatures—the hydrogen bond holds the molecules so strongly together that an abnormally high temperature is needed to loosen the bond. This is so clear that we have to explain why no hydrogen bond seems to exist in the hydrogen compounds of other elements in Group VI, that is,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ , and  $\text{H}_2\text{Te}$ .

Although they look alike in formula, these compounds  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$  differ a lot, especially water from the remaining three.

Oxygen attracts electrons very strongly, indeed. So in a water molecule, it may be said to be the sole possessor of electrons, and the hydrogen is left destituted—an electronless proton.

Sulphur is less energetic in attracting electrons, at least in comparison with oxygen. So in a hydrogen sulphide ( $\text{H}_2\text{S}$ ) molecule the electrons appear to be shared by the sulphur and the hydrogen. That's why the hydrogen in  $\text{H}_2\text{S}$  is not stripped of its electron shell. Because of this, it no longer displays the exceptional property it does when combined with oxygen—the property of forming the hydrogen bond. This ability is progressively weaker in hydrogen selenide,  $\text{H}_2\text{Se}$ , and hydrogen telluride,  $\text{H}_2\text{Te}$ .

With the anomalous specific heat of water, too, the root of the matter is the hydrogen bond. Any rise in temperature is in effect an increase in the velocity with which molecules are moving about. It's obvious that to accelerate the water molecules held together by the hydrogen bond takes much more heat than in a liquid whose molecules do not cling to one another so tenaciously.

I don't think we need to explain at length the anomalies associated with heats of vaporization and fusion. It's clear where these kilojoules go in either case: on top of the ordinary bonds that hold together the molecules of any liquid, we must also break the hydrogen bond.

The abnormally high surface tension in the case of water can likewise be attributed to the extremely strong attraction between water molecules arising from the hydrogen bond.

### From the Physicist's Point of View

**Concentration As a Measure of Solution.** Whenever a solution is mentioned, the first thing that is called out is its concentration, for the concentration is pivotal to most of its properties.

You can tell the concentration of salt in the pickle or of sugar in your cup of tea from the taste it leaves in your mouth. But this is hardly a dependable indicator for, as the saying goes, there's no accounting for tastes. In scientific applications it's more reliable, therefore, to determine the concentration of a solution in a more objective way. One is to state it as so-many percent, that is, as so-many grams of solute (the substance dissolved) in 100 grams of solvent (the substance able to dissolve). This approach is widely practised in everyday life. In a drug store you can buy a 30% solution of hydrogen peroxide; at a grocer's a 6% solution of acetic acid; and at a dairy shop 20% cream. In physics and chemistry, percentages are used but seldom. It's clear why—a reaction involves atoms, not grams. If we compare two solutions of different substances, but of the same concentration, we'll surely find that their equal volumes contain different numbers of molecules (gram-molecules).

Precisely for this reason, already very early in your school course in chemistry you are taught to express the concentration of solutions in moles, that is, as the number of gram-molecules of solute in one litre of solution. This is molar concentration.

Molar concentration is far more convenient to use than percent concentration: Equal volumes of different

solutions having the same molar concentration will have an equal number of moles, that is, molecules of solutes.

A third way to express concentration is in mole fractions. Now the concentration of a solution is stated as the ratio of the number of moles of solute to the sum of moles of solute and solvent. Suppose there are  $m$  moles of solute and  $m_s$  moles of solvent. Then the molar fraction of the solute,  $N$ , will be

$$N = m / (m + m_s)$$

It's obvious that the concentration in molar fractions will always be less than unity. Also, in contrast to the two previous ways of expressing concentration, the concentration in mole fractions is a dimensionless quantity.

Scientists have devised a good many ways to express the concentration of solutions—dimensional and dimensionless, objective and subjective, simple and sophisticated. It would be fruitless even to try to list all of them. We'll mention only one more, known as molal concentration which gives the number of solute moles in 1000 grams of solvent.

**On One of the General Laws.** In a way, the laws of nature may be said to be ranked in importance. There are laws which are useful and necessary, specific and general, important, very important and most important. The author doesn't insist on this largely emotional grouping. But it's beyond any doubt that laws do obey a table of ranks and classes of their own.

In the natural sciences, the fundamental law (we may say the generalissimo of laws) is the law of conservation of energy. Each of the natural sciences has laws standing one rank below (in the Army they might be called marshals). In physics, this is the law of the equivalence of mass and energy,  $E = mc^2$ . In chemistry, this is the Periodic Law

first discovered by Mendeleev. To push our analogy further, each science must have laws which are generals, colonels, and so on. In the theory of solutions, one of the laws in a general's rank undoubtedly is Raoult's law. Before we take it up in more detail, we should define several concepts.

Let's begin with the weather forecast we hear over the radio several times a day. Not all of the forecast, but the phrase, "The relative humidity of the air is (so-many) percent".

Suppose you have, before you, a water-filled glass under a bell-jar. What do you think is under the bell-jar? No, not only air, but also water vapour. If you keep the glass under the bell-jar for a long enough time, an equilibrium will be reached between the water in the glass and the water in the vapour phase.

In this context, the word "equilibrium" means that the amount of water passing from the liquid into the vapour is the same as the amount of water molecules "plunging" from the vapour back into the liquid. In this state of equilibrium, the amount of water in vapour is the largest possible at a given temperature. This will be a saturated vapour.

If we raise the temperature of the water in the glass, more water will pass into the vapour phase, and the pressure of the saturated vapour will go up in proportion. For this reason, it's convenient to describe the saturation of the vapour phase in terms of pressure.

When you hear in a weather report that to-day the relative humidity is 90%, this is not to mean that the air is 90% water vapour. That would be far too much even for a steam bath. What this actually means is that the pressure of water vapour in the air is 90% of the saturated pressure (at the temperature stated).

Usually, we can hardly stand heat at a high relative humidity. This is why it's so. Our body cools by sweating.



Fig. 10. Explaining equilibrium between liquid and vapour

It's clear that sweat will evaporate ever more slowly as the water vapour in the air approaches saturation, and cooling will be far less efficient. For this reason, you feel + 35°C differently in a humid than in an arid locality.

All that's been said about the saturated water vapour may be carried over to any other liquid. What's important is this: There's always a vapour phase above any liquid, and this vapour can reach saturation under suitable conditions.

The vapour pressure at saturation bears a well-defined relationship to temperature: The logarithm of the saturated vapour pressure is directly proportional to the inverse temperature, that is to  $1/T$ . (Here  $T$  is absolute temperature. The absolute temperature scale is used in science more widely than the Celsius scale.) Graphically, the two quantities are related as is shown in the plot of

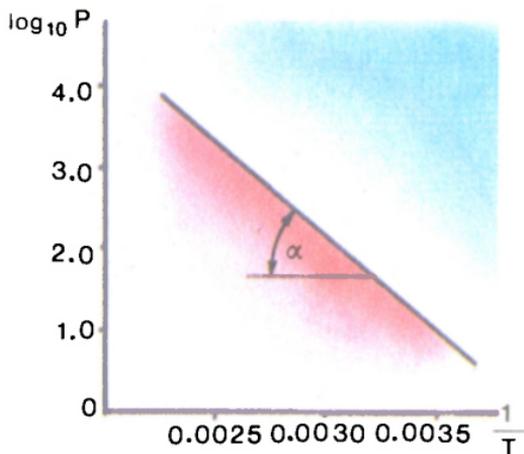


Fig. 11. Logarithm of saturated vapour pressure as a function of reciprocal temperature

Fig. 11. Such plots are very convenient in finding the saturated vapour pressure at any temperature. Interestingly, the slope of the line in the plot is proportional to the latent heat of vaporization. In fact, this quantity is mostly found like this: The experimenter determines the saturated vapour pressure at several temperatures, plots the pressure as ordinate on a log scale,  $\log_{10} P$ , and the inverse temperature,  $1/T$ , as abscissa. The plot yields a straight line, and its slope gives the sought quantity.

We've learned all the quantities that enter Raoult's law, so we're prepared to state this law in full: **THE SATURATED VAPOUR PRESSURE OF A SUBSTANCE IN SOLUTION IS EQUAL TO THE PRODUCT OF THE SATURATED VAPOUR PRESSURE OF A PURE SOLVENT BY THE MOLE FRACTION OF THE SOLVENT.**

In physics, the essence of an idea can be expressed more

succinctly by use of algebraic equations. We, too, shall use an equation to write Raoult's law. Let  $p$  stand for the saturated vapour pressure of a substance in solution,  $p_s$  for the saturated vapour pressure of a pure solvent (here and elsewhere, the subscript "s" refers to "solvent"), and  $N_s$  for the mole fraction of the solvent. Now Raoult's law takes a compact and, I'd say, elegant form:

$$p = p_s N_s$$

Now that we've turned to algebra, let's take advantage of what this beautiful science has to offer to anyone who is interested in it, and analyse the equation stating Raoult's law. It's brief and explicit: Since  $N_s < 1$ , then  $p < p_s$ . Actually, that would do because that's all we have to say. For the sake of our story, however, let's add some juice to it.

That  $N_s$  is less than unity is clear. A mole fraction (and a fraction is a part of the whole) is always less than unity by definition. If so, then  $p$  is less than  $p_s$ , that is, the saturated vapour pressure of a substance in solution is always lower than the saturated vapour pressure of the pure solvent.

When it comes to the manner in which the boiling point is connected to pressure, popular-science books (and even textbooks) always tell one and the same (and, to tell the truth, rather boring) story of an unfortunate mountain-climber who tried without success to boil an egg at the top of Mount Elbrus. I've pitied the poor devil all my life. As a child, I pitied him because he was hungry – naturally, I couldn't even imagine him eating an egg uncooked for all his bravery as a mountaineer. Later, I asked myself (as I do now) why the man should have carried a raw egg to the mountain top? And, no less important, how could he possibly do that? At best, carrying the egg in his palm all the way up. Today I know that if the mountaineer cared so much for a boiled egg, he

should have carried along a hermetic saucepan rather than humbly depend on the pressure around him, or the ambient pressure, as it's called. To learn why, let's trace how the boiling point of a solution depends on the saturated vapour pressure rather than on the ambient pressure. The saturated vapour pressure of a solution is always lower than for a pure solvent. That's why a solution must always come to the boil at a higher temperature than the solvent.

**When a Solution Boils.** From Raoult's law we can establish quantitatively how the boiling point of a solution depends on its concentration. Since each solution boils at a temperature of its own, it's convenient to relate concentration not to the boiling point itself, but to the amount by which it is elevated above the boiling point of the solvent. Mathematically, we can write that the boiling point of a solution is equal to  $T_b + \Delta T_b$ , where  $T_b$  is the boiling point of the solvent, and  $\Delta T_b$  is the boiling-point elevation of the solution. Then  $\Delta T_b$  can be connected to the concentration of the solution in a very simple way:

$$\Delta T_b = K_b C_m$$

In this simple equation,  $C_m$  is the molal concentration (we've learned about it a bit earlier), or molality. The equation is as simple to state in words: The boiling-point elevation of a solution is directly proportional to the molal concentration of the solute. That is, the higher the concentration of the solute, the higher the boiling point of the solution.

There's one more puzzling term in the equation,  $K_b$ . The way textbooks define it is terse and, undoubtedly, correct. This is a coefficient of proportionality.

Here I'll take the liberty to make a lyrical digression, so to speak. Those coefficients of proportionality—how

I hated them at school. Nor did I fall in love with them at college. And not without a reason. Suppose we are deriving a formula. Everything is based on rigorous reasoning and a still more rigorous body of mathematics. Then all of a sudden there appears a coefficient of proportionality—from some unknown place and for not yet clear a reason.

For all that I've said about coefficients of proportionality, I'll try to rehabilitate them in our esteem. The equation connecting the elevation of the boiling point of a solution to its concentration is a good occasion to do that. We may say flatly that without a coefficient of proportionality this equation, and indeed all others, would be meaningless. Let's remove for an instant (not more!) the coefficient  $K_b$  from the equation. That would leave nonsense, to say the least: degrees (the boiling-point elevation is of course expressed in degrees) would appear equal to concentration. In no case can temperature be equal to moles. Therefore, to justify the "equals" sign, we must multiply one or the other side of the equation by something that would put right at least the dimensions. This "something" is the coefficient  $K_b$  with the dimensions of degrees mole<sup>-1</sup>. As you can see, it puts right everything—now degrees are equal to degrees, and the equation has a correct physical meaning.

Now let's define the meaning of the  $K_b$  itself. That can be easily done by assigning unit values to all the quantities that keep company with it. So let's take it that the above equation applies to a solution of unit molality (1 mole of solute in 1000 grams of solvent). Then  $K_b$  will stand for the boiling-point elevation of a one-mole solution. That's all there is to it.

The coefficient of proportionality in our equation is called the ebullioscopic constant (from the Latin *ebullire* for boil). Every solvent has an ebullioscopic

constant of its own. For benzene it is 2.6 degrees per mole; for ethyl alcohol, 1.2; and for water, 0.53. Here, too, as we can see, water comes first, although from the end. There's nothing to be surprised at, though, especially when it comes to water.

What's still more intriguing is that the elevation of the boiling point of a solution is independent of what the solute actually is. Suppose we have a solution of one gram-molecule of, say, glucose (which works out to 180 grams) in 1000 grams of water, and a solution of one gram-molecule of urea (which is 60 grams) in the same quantity of water. Either solution will boil at 100.53°C which is the sum of the boiling point of the pure solvent (water) and the ebullioscopic constant. We could readily see from that same equation that if each of the two solutions contained 0.5 moles of the respective solute (that is, 90 grams of glucose and 30 grams of urea), they would boil at 100.265°C, that is,

$$\begin{aligned} & \text{Boiling point of pure water} + K_b \times 0.5 \\ & = 100 + 0.53 \times 0.5 = 100.265^\circ\text{C} \end{aligned}$$

**When a Solution Freezes.** There's an equation which looks very much like that we've just discussed. Here it is:

$$\Delta T_f = K_f C_m$$

Very much like, indeed, except the subscript—instead of “b” (for boiling) we've put in “f” (for freezing). So we may state that the depression of the freezing point of a solution is directly proportional to the molality of the solution. In other words, the higher the concentration of a solution, the lower its freezing point.

I'll leave out how it's come into being—it is derived in about the same way as the equation of the boiling point. But now the coefficient of proportionality is

called the cryoscopic constant, and its physical meaning is the depression of the freezing point of a one-molal solution or, more briefly, the molal depression of the freezing point.

The cryoscopic constant widely varies from solvent to solvent. For phenol it is 7.4 degrees mole<sup>-1</sup> which means that a one-molal solution of any solute in phenol will freeze at a point 7.4°C below the freezing point of pure phenol. For nitrobenzene the figure is 6.9 and for benzene, 4.9. Water has the lowest cryoscopic constant of all solvents, a mere 1.84 degrees mole<sup>-1</sup>.

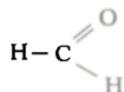
As in the previous case, the equation of the freezing point can be used to calculate the freezing point for any solution. Taking glucose and urea as examples again, their one-molal solutions will freeze at -1.84°C, and their half-molal solutions, at -0.92°C.

**Cryoscopy.** It's time to tell about the main application of the equations of boiling and freezing. For brevity, we'll take up only the "cryoscopic" equation because everything that can be said about it may be carried over to the ebullioscopic equation. Thus, we're going to talk about the use of a method based on the study of the freezing points of solutions—about the main application of cryoscopy.

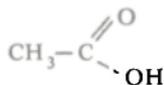
Picture to yourself a chemist busy with the synthesis of some new and not yet described substance. He's been lucky with his experiments and the new substance is here—isolated and purified. Now the chemist has to prove that this is a new substance, and this calls for qualitative analysis. Using relatively simple reactions, the chemist finds that the new compound contains carbon, hydrogen, and oxygen. From this he concludes that this is an organic compound. Now comes the turn of quantitative analysis. With it, the chemist finds that his compound consists of 40.0% carbon, 6.7% hydrogen,

and 53.3% oxygen. That is, the elements are present in the proportion  $C:H:O = 1:2:1$ .

Can the chemist now feel satisfied? Not more than a mathematician who's arrived at an equation in two unknowns. For the proportion he's found can only give a hint about the structural formula of the compound, but not the formula itself. This might be formaldehyde



the more so that its chemical formula,  $\text{CH}_2\text{O}$ , accurately fits the proportion found. Or this might be acetic acid



or  $\text{C}_2\text{H}_4\text{O}_2$ . We could add many more chemical compounds that answer the elemental proportion found. We could include, say, glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , as one more, but not the last of all possible examples. What must our chemist do? Only one thing—determine the molecular mass of his compound. All the substances we've listed have the same percentages of the constituent elements, but they differ a good deal in molecular mass which is 30 for formaldehyde, 60 for acetic acid, and 180 for glucose.

The need to determine the molecular mass of his compound does not worry the chemist because he knows only too well that the task can readily be handled with the aid of cryoscopy, a universal technique for determining molecular mass.

Let's go back to the cryoscopic equation

$$\Delta T_f = K_f C_m$$

Here,  $C_m$  is the number of gram-molecules of solute in 1000 grams of solvent. But the number of gram-molecules is, in turn, the mass of a substance divided by its molecular mass, or  $g/M$ . Now we can re-write the cryoscopic equation as

$$\Delta T_f = K_f (g/M)$$

so that

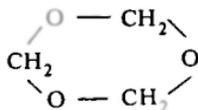
$$M = K_f (g/\Delta T_f)$$

Here is the clue for the chemist to follow. He weighs out, say, 50 grams of his compound, dissolves it in 1000 grams of water, and measures the freezing point of the solution. From the experiment he learns that the solution freezes at  $-1.02^\circ\text{C}$ . Since the pure solvent, which is water, freezes at  $0^\circ\text{C}$ , it follows that  $\Delta T_f = 1.02$ .

Now the problem is almost solved. Recalling that the cryoscopic constant of water is  $1.84^\circ$ , the chemist quickly makes simple calculations and finds that

$$M = 1.84 \times 50 \div 1.02 = 90$$

Thus, the formula of the compound he's produced is  $\text{C}_3\text{H}_6\text{O}_3$ . Its name is trioxane, and its structural formula is



(So much for the compound, I think, the more so that the chemist might have produced any other as well.)

As a technique for measuring molecular mass cryoscopy was discovered about a century ago which is a huge span of time for present-day physical chemistry. Yet, in the hundred years that have changed physical chemistry beyond recognition the cryoscopic method has remained unchanged. In its time it was so much in vogue that 80 years ago Svante Arrhenius of Sweden, one of the researchers who have made cryoscopy a powerful tool of physical chemistry, wrote with a legitimate and understandable pride: "A new glacial period has come upon Europe." Even today when the 21st century is literally round the corner cryoscopy remains the principal method for determining the molecular masses of substances in solution.

This is not the only use for cryoscopy. Let's turn to our chemist again. Now suppose he's going to make an experiment on a 1-molal solution of caustic soda, NaOH, in 1000 grams of water. His object is to determine the freezing temperature of the solution. What do you think it is?

"Well, that's what we've learned already," the sophisticated reader will chuckle. "There's nothing to think about. This is a 1-molal solution, so the freezing-point depression must be equal to the cryoscopic constant. The answer is, the solution must freeze at  $-1.84^{\circ}\text{C}$ ."

The course of thought is faultless. Our chemist, too, is a skilled experimenter. But he finds that the 1-molal solution of caustic soda freezes at  $-3.68^{\circ}\text{C}$ . That is, the freezing-point depression observed is exactly twice the expected value. Now we have a faultless reasoning and a perfect experiment, but there can be only one truth!

Rather than to help the reader out of this obvious contradiction, I'll tell about one more experiment our chemist is going to make. This time he takes benzene as

the solvent (the cryoscopic constant of benzene is 4.9) and dissolves 1 gram-molecule (that is, 32 grams) of methyl alcohol,  $\text{CH}_3\text{OH}$ . What do you think the depression of the freezing point will be?

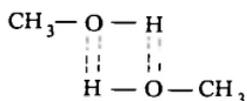
This time, I'm sure, the reader will be more cautious in giving his answer. But, however cautious he may be, he would have no option other than to say, "Yes, since this is a 1-molal solution, the freezing point of the benzene solution must be  $4.9^\circ\text{C}$ ". This time, too, the reasoning is faultless, but again the chemist finds that the actual depression of the freezing point is  $2.45^\circ\text{C}$  which is half the amount postulated by theory.

Why is it, then, that the freezing-point depression is twice the theoretical value in the first case, and half that value in the second?

The answer will turn up all by itself if we take a closer look at the cryoscopic (or ebullioscopic) relations we've dealt with earlier. The point is that the depression of the freezing point (the elevation of the boiling point) is proportional not so much to the concentration of the solution as to the number of solute particles per unit volume of solvent. "Well, isn't that the same?" you may ask. No, it isn't the same always. Let's take a solution of caustic soda in water as an example. Whereas the number of molecules in one mole of any substance is  $N_A$  (which is the Avogadro number equal to  $6.02 \times 10^{23}$ ), the number of particles left in solution by dissolving one mole of  $\text{NaOH}$  in water is  $2N_A$ , and not  $N_A$ . Yes,  $2N_A$ , because, as is well known, on dissolving in water caustic soda breaks up into  $\text{Na}^+$  and  $\text{OH}^-$  ions.

Now it's easy to guess why the solution of methyl alcohol in benzene freezes at a higher temperature than it should by Raoult's law. This is so because the 1-molal solution of methyl alcohol in benzene contains half the number  $N_A$  of particles. And this can only

happen if the  $\text{CH}_3\text{OH}$  molecules in solution combine pairwise or, as chemists say, are associated. The cause of association for methyl alcohol is well known—the molecules combine pairwise at the hydrogen bond and in doing so they make up what is known as a twice associated molecule:



As we can see, one more opportunity opens up for cryoscopy (ebullioscopy)—in the study of the molecular state of substances in solution. It's owing to cryoscopy that chemists have learned that many substances in solution may be twice associated (in which case they are known as dimers), three times associated (trimers), four times associated (tetramers), and so on.

It would be out of place to start on a special talk about the association of substances in solution. Yet we cannot but note that association was the first link in the unbelievably long chain of transformations that finally led to the origin of living matter. This thing alone underscores the importance of association. And chemists have learned about association through cryoscopy.

**Pressure in Solutions.** The theory of solutions has unraveled all of the above findings, so important and so essential for chemists, from purely physical considerations. This is not the first and not the last case where physics comes out to help chemistry. That will be clear from the story about osmotic pressure that follows.

Just to be sure I'll repeat what the reader undoubtedly knows well enough. If a vessel of 22.4 litres

capacity holds one mole of gas at a temperature of 273 kelvins (which is zero degrees on the Celsius scale), the gas exerts a pressure of one atmosphere. This may be stated differently: One mole of gas under normal conditions (a temperature of 273 kelvins and a pressure of one atmosphere) takes up a volume of 22.4 litres. We'll need both statements.

Picture to yourself a vessel such as shown at the top in Fig. 12. Its left-hand half holds a gas, and its right-hand half is exhausted to vacuum. If we uncover the openings in the wall that separates the two halves, the gas will flow from left to right and will keep doing so until the pressure is the same on either side of the partition.

Now imagine a similar vessel but with its left-hand half holding a solution of some substance and with its right-hand half full of pure water. Suppose the wall separating the two halves is only permeable to water molecules. Scientifically, a partition only permeable to a solvent is called a semipermeable membrane or diaphragm. What will happen now? Obviously, water will pass from the right-hand half into the left-hand half. This passage of a liquid or a gas from solution through a membrane is called osmosis.

I've brought in osmosis not without a reason. It has proved a dependable and, I'd say, a very convenient bridge between the molecular theory of gases and the molecular theory of solutions. It was thrown by van't Hoff, the famous Dutch physical chemist whose name is associated with a large and very important sector in the theory of solutions.

The force causing the solvent to pass through a semipermeable membrane into the solution has the same origin as the force driving a gas from a vessel where it's held under a high pressure into a vessel with a lower pressure. It's simple to grasp why this force in the case of liquid solutions is called osmotic pressure.

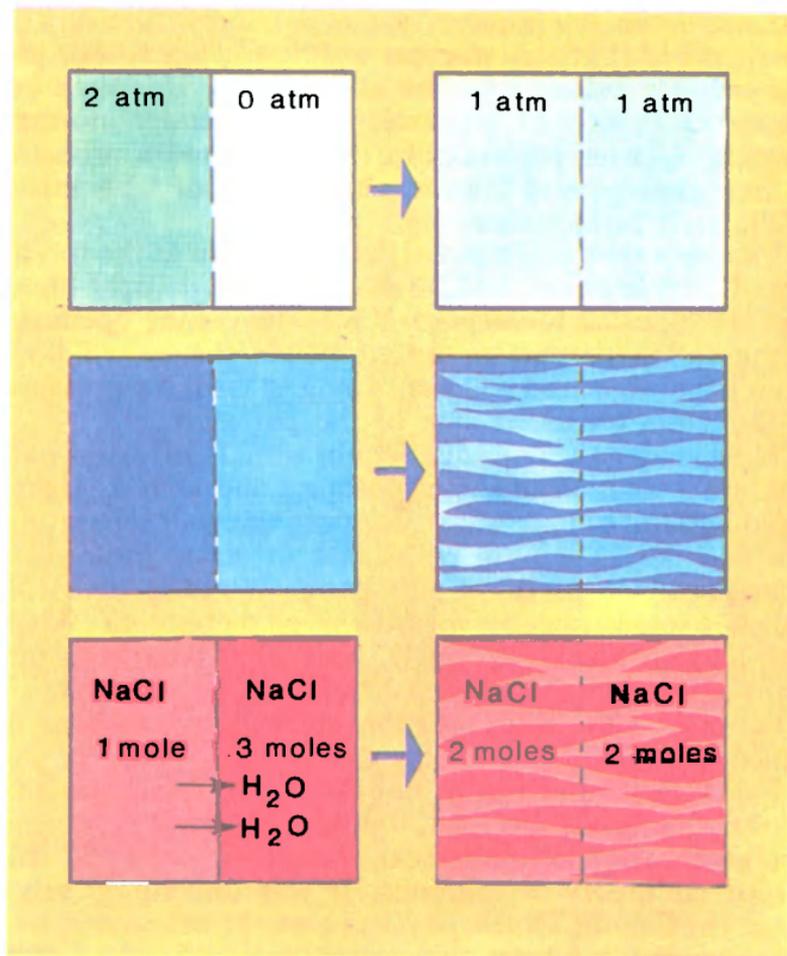


Fig. 12. Explaining the origin of osmotic pressure

Scientists were quick to learn that the osmotic pressure of a solution was equal to the pressure that would be produced by the same number of moles of the solute if it were in the gaseous state. On this ground, many of the laws deduced for gases were applied to solutions. (And it may be added that molecular physics for which the last century was one of triumph did begin with studies into gases.) By measuring osmotic pressure, researchers hoped to unravel, as they did with cryoscopy (ebullioscopy), many interesting data about the nature of solutions. They did obtain those data, and there seemed to be ground for rejoicing. But that only seemed so, for an ever stronger voice of opponents of the physical theory of solutions was rising in the chorus of its proponents. "But why?" you may ask. "Weren't the advances of the physical theory a forceful proof of its fruitfulness?" Unfortunately, absolute triumph can only happen in sports, and then for a short time only. So, before I can answer the reader's question, one more physical theory of solutions must be discussed.

### Those Dissociating into Ions

Probably already in the 18th century natural scientists knew that all solutions could be divided into two large groups: those not conducting electric current and those capable of conduction. In the 19th century, studies into conducting solutions went on with might and main, so to speak. Ohm found that conducting solutions conduct current in accord with the laws established for metals. With depth and thoroughness befitting a great scientist, Faraday investigated electrolysis and formulated its main laws. Electrolysis was used to obtain many substances, including sodium and potassium. For the first time they were produced as metals by the famous Humphry Davy. Water was decomposed into its elements by passing an

electric current through it. Many designs of galvanic cells were devised. In short, the first eight decades of the 19th century saw the discovery of many things that serve today as the basis for electrochemistry, a science which has to do with the joint action of chemical and electrical factors.

What scientists did not know was why conducting solutions were conducting.

**Arrhenius's Theory: Merits.** Strictly speaking, there was no shortage of theories put forward to explain the strange fact that solutions of some substances could conduct electric current and those of others couldn't. But that was exactly the case where the abundance of theories indicated that they were inadequate. For if one theory is true, there's no need for any other. Unfortunately, the only true theory was still nonexistent. It was nonexistent at least until the 80's of the past century when S. Arrhenius evolved a theory of electrolytic dissociation.

If we digest Arrhenius's theory to one sentence (it's hardly necessary to go in more detail, because the theory is treated at length at school), this sentence would read: **ELECTROLYTES (substances whose solutions conduct electric current) DISSOCIATE INTO IONS WHEN DISSOLVED.**

Today it may seem simple to evolve a theory based on an obvious fact (of course, it appears obvious today!). In 1884, Arrhenius was careful not to state the basic idea of his theory flatly—he had every reason to expect that his colleagues would tear it to pieces. So, in his first publication Arrhenius chose to mask the most controversial points with not too clear a terminology.

Arrhenius knew which point would come under fire—he knew and feared that, because he didn't know how to parry the criticism. Worse still, Arrhenius had not the slightest idea why, on dissolving, electrolytes decomposed into ions, and what it was that caused a positively

charged cation to part company with a negatively charged anion. On the other hand, all of his experiments as well as the experiments of his predecessors, and a wealth of knowledge about the physical and chemical properties of electrolytic solutions—everything logically brought him to conclude that ions did exist in the solutions of electrolytes.

Fortunately, the new theory was so impressive a success and its recognition (not yet general) was so inspiring that the scientist forgot all his doubts.

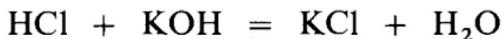
Arrhenius's theory of electrolytic dissociation convincingly explained many facts that had long been known but remained puzzling. Among other things, it explained why the specific conductance of a solution would vary with changes in its concentration. The difference in properties between the solutions of different electrolytes was plausibly explained by classing them into strong, that is, those completely dissociating into ions, and weak, that is, those which dissociate into ions only partly.

This, in turn, explained the cryoscopic behaviour of electrolytic solutions. With strong electrolytes, the depression of the freezing point was found to be much greater than it should be from theory and this naturally followed from the complete dissociation of the solute into ions. For example, the solution of NaCl was found to have a value of  $\Delta T_f$  twice the theoretical value because sodium chloride dissociates into two ions. For  $\text{CaCl}_2$ , the depression of the freezing point was found to be three times its theoretical value, because, when dissolved in water, it breaks up into three ions. With weak electrolytes, say, a solution of acetic acid in water, the freezing-point depression was found to be greater than it should be from theory, but not twice the theoretical figure, of course, because weak electrolytes dissociate into ions only partly.

Then one more fact cropped up in time and made Arrhenius and van't Hoff close allies. It was found that if the value of  $\Delta T_f$  for weak electrolytes was known, the degree of electrolytic dissociation could be determined by measuring the specific conductance of the solution. That specific conductance should be related to dissociation was clear: the higher the degree of dissociation, the greater the number of ions in the solution and, as a consequence, the higher its conductance. Now both methods yielded identical results. There could hardly be a better confirmation of the existence of ions.

By far the greatest success, however, awaited the theory of electrolytic dissociation in explaining the chemical properties of electrolytic solutions. By the time the theory was evolved, a fairly large number of strong acids (such as HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) and strong alkalis (such as NaOH, KOH, and Ba(OH)<sub>2</sub>) had been identified. In any case, there was enough of them to expect that likely reactions of neutralization must be many and diverse. But that did not happen. With any choice of an acid and an alkali, the yield of heat was practically the same, 57 kilojoules (provided an appropriate quantity of acid had been taken per mole of alkali). It turned out that for all the multitude of acids and alkalis, there was only one reaction of neutralization.

Of course, there can be only one reaction, and the theory of electrolytic dissociation explains it in a most obvious way. As an example, take the reaction of neutralization of hydrochloric acid, HCl, with potassium hydroxide, KOH. The reaction is easy to write:



On the whole, the reaction equation is correct, but it must be remembered that, by the theory of electrolytic dissociation, in the starting solutions both the HCl and

the KOH are completely dissociated into ions, as is the reaction product, KCl, in contrast to water which dissociates very little if at all, as compared with the other reactants. With this refinement, we may write the neutralization reaction this way:



On cancelling out the like terms on either side of the equation, we get



This is what should happen: The neutralization reaction does not depend on the nature of the base cation or the acid anion, as in all cases the reaction reduces to the interaction of the ions  $\text{H}^+$  and  $\text{OH}^-$ . This explains why the heat effect is the same in all cases of neutralization.

We have just scratched the top of the record listing the triumphs of the theory of electrolytic dissociation. We could recall, for example, how convincingly it explained many relations in the theory of reaction rates, how logic and simple it was in interpreting some cases of catalysis and many other things. The theory explained and predicted many happenings; it convincingly and naturally united many disjointed facts.

But that was not enough.

**Arrhenius's Theory: and Limitations.** Mendelejev was an all-out opponent of the electrolytic theory of dissociation, an opponent both militant and active. Many Russian and some foreign chemists followed his suit.

Even serious biographers often tend to describe Mendelejev's disagreement as a misconception of a great scientist or, at best, as a whim. For, they would say, eccentricities and whims are part and parcel of geniuses. Tolstoy refused to recognize Shakespeare, Verdi did not see eye to eye with Wagner and, quite naturally, Mendelejev had every right to be against Arrhenius. That

is an utterly erroneous view of the stand taken by Mendeleev and his supporters.

Let us try to state what Mendeleev put forward against the theory of electrolytic dissociation by using for simplicity present-day terminology. This is quite appropriate because by the time the proponents of the physical theory of solutions (Arrhenius) and of the chemical theory of solutions (Mendeleev) were deep in their dispute (and this occurred at the turn of the 19th century), energy concepts were well entrenched in physical chemistry.

Among other things, physical chemists had a sufficiently clear idea about the energy possessed by the crystal lattice of sodium chloride, NaCl. They knew that this energy was about 800 kilojoules. In simpler words, it would take 800 kilojoules to break the cations from the anions in one gram-molecule of NaCl, that is, in 58.5 grams of common salt. Is it much or little? Well, it depends. Look at Fig. 13. What is it? An experiment on the Magdeburg hemispheres with the use of modern machines? No. In this imaginary experiment, 20 cars are trying to pull apart the cations and anions in one gram-molecule of common salt, and it takes them a great deal to perform the act.

But what would need the power packed in twenty modern cars and involve the risk of ruining their engines (of course, this "experiment" is only a literary turn) can readily be done by simply adding a glass of water.

However, energy cannot come from nowhere. Nobody can abrogate the law of conservation of energy – and its universal truth was obvious to Mendeleev already at that time, at the turn of the 19th century. If the NaCl molecules break up into ions upon the addition of some water, they can borrow the energy necessary to overcome the attraction between cations and anions solely from the water. Obviously, the energy associated with the thermal

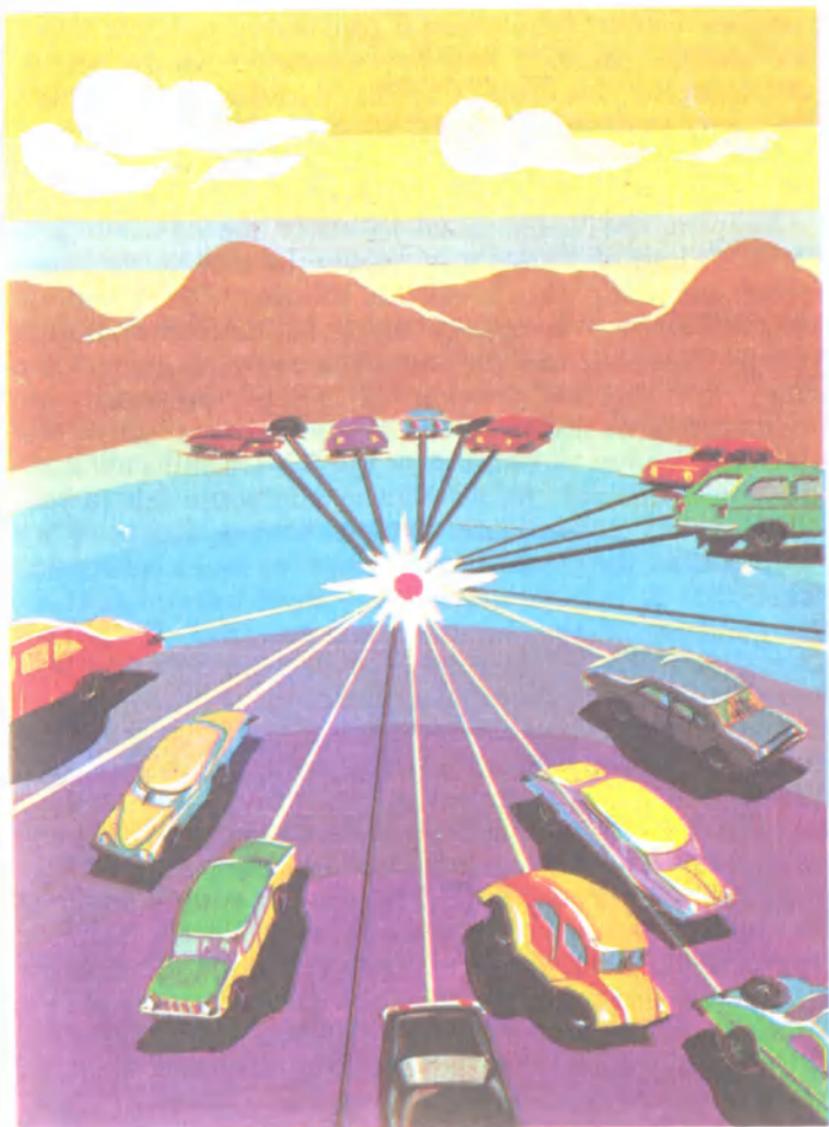


Fig. 13. Pulling apart ions in a gram-molecule of sodium chloride in an imaginary experiment

motion of solvent molecules is transferred in some way to the sodium chloride, and this enables it to decompose into ions. But this must of necessity lead to a reduction in the energy possessed by the water molecules, that is, to a slow-down in their velocity and, as a consequence, a fall in the temperature of the solution.

Suppose the water taken to make the solution is at  $20^{\circ}\text{C}$ . A loss of 4 kilojoules by one litre of water brings down the temperature of the solution by about one degree Celcius. It is an easy matter to calculate that if the energy expended to dissociate the electrolyte came solely from the thermal motion of water molecules, the temperature of the resultant solution would fall by 200 degrees Celcius to become  $-180^{\circ}\text{C}$ . Or think of it the other way around: An attempt to add some salt to your soup would immediately turn it into a lump of ice.

Of course, the reader has happened to make solution at least once in his life, and he may have noticed that the temperature of the solution changes. But, firstly, the change is seldom more than a few degrees. Secondly, and most importantly, the temperature of the solution in most cases goes up. In some rare cases, the rise is large enough to make the solution hot. An enterprising individual used this property in a chemical "hot bottle". When he went out hunting in winter, he would take along a flask of solid caustic and a flask of concentrated sulphuric acid. At first, he would prepare a solution of caustic: adding water to its crystals would rise the temperature of the solution appreciably. Then he would make a solution of sulphuric acid: this again would rise the temperature of the solution. At last, he would pour the two solutions together, and the ensuing reaction of neutralization – as we already know – would liberate a sizeable quantity of heat. Of course this quantity was not large enough to cook a meal, but large enough to warm the hunter's hands for several hours.

**The Chemical Theory of Solutions.** Mendeleev came out with his chemical theory of solutions in contradiction –no, not in contradiction, but in addition—to the electrolytic theory of solutions. By this theory, the formation of a solution is always a chemical reaction between the solute and the solvent, and the energy required to break up the neutral molecules of the electrolyte into ions comes exactly from that reaction.

The chemical theory explained many things. An example is the rise of temperature in the formation of solutions (as with the chemical “hot bottle”) which could not be explained by the physical theory of solutions. But everything logically fits together if we assume that the formation of an alkaline or acid solution is above all the reaction of KOH or  $\text{H}_2\text{SO}_4$  molecules with water, that is, an exothermic reaction—a chemical process liberating heat.

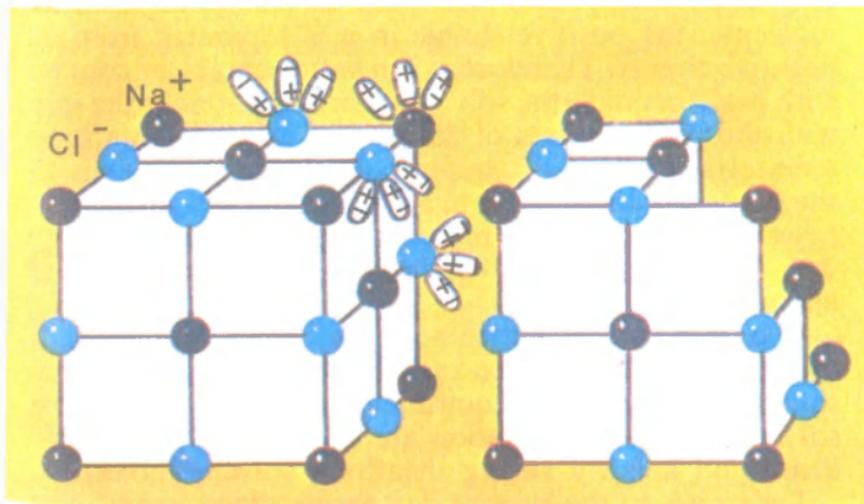


Fig. 14. Dissolution of a NaCl crystal

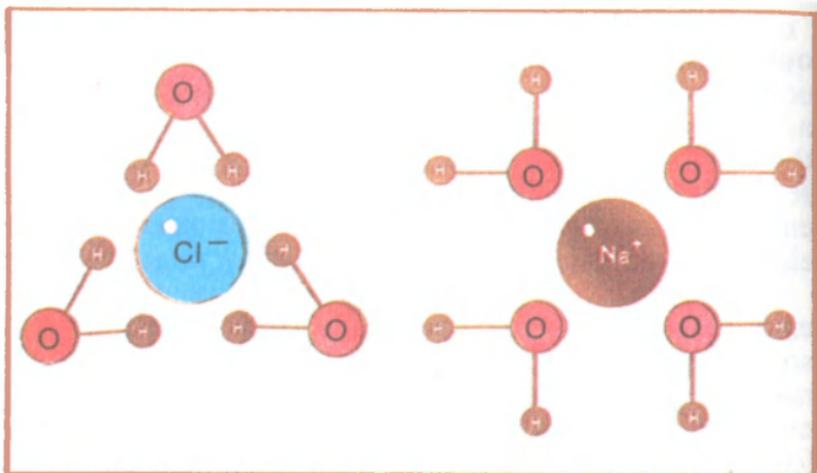


Fig. 15. Sodium and chloride ions in solution

Let's skip a few decades and stop at the time when the mechanism of electrolytic dissociation had already been fully elucidated. Let's recall the structure of a water molecule: the positive charge in it is separated from its negative charge. Therefore, when water comes in contact with  $\text{NaCl}$  crystals, the solvent vigorously attacks the salt, with the positive ends of the water molecules attaching themselves to the  $\text{Cl}^-$  anions, and the negative ends to the  $\text{Na}^+$  cations. This interaction, as indeed any other, between unlike charges releases energy – it is this energy that goes to break the bonds between the cations and anions.

The interaction between solute ions and solvent molecules has come to be known as solvation (where the solvent is water it is known as hydration). Owing to solvation, ions in a solution are surrounded by a fairly dense and a fairly strong sheath of solvent molecules.

Let's turn to the present-day terminology again. The heat of hydration for a  $\text{Na}^+$  ion, that is, the heat released from the chemical reaction by which a water molecule is

attached to a sodium cation is 425 kilojoules (and 350 kilojoules for the  $\text{Cl}^-$  anion).\* Taken together, the heat of hydration for the ions that form when common salt dissociates is 775 kilojoules. This is only slightly less than the bond energy, or the energy required to break the bond between the ions that make up a NaCl crystal (800 kilojoules). That is why when NaCl dissolves in water, the temperature goes down a bit—the system makes up for the deficiency by taking away the lacking 25 kilojoules from the water molecules.

Now we shall try and give a similar energy-wise or, more correctly, thermodynamic description of what happens when hydrogen chloride is dissolved in water to produce what we know as hydrochloric acid. The bond energy for the hydrogen and the chlorine in an HCl molecule is 1360 kilojoules. The heat of hydration of an  $\text{H}^+$  ion is 1100 kilojoules. If we add to this the heat of hydration for a  $\text{Cl}^-$  ion (350 kilojoules), the total will be 1450 kilojoules which is markedly in excess of the bond energy in a HCl molecule. That is why when hydrogen chloride dissolves in water, the temperature of the solution goes up—the energy released by the interaction between the solute ions and water molecules exceeds the bond energy, and the excess heats the solution.

As we can see, both sides in the heated dispute between the proponents of the physical and chemical theories of solutions finally emerged right. The “physics-oriented” party was right in insisting that ions do exist in electrolytic solutions. The “chemistry-oriented” party was right in insisting that the chemical interaction between the solute and the solvent is a necessary condition for an electrolyte to break up into ions.

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\* The quantity of heat released or absorbed in a process is usually referred to 1 gram-atom, 1 gram-molecule, or 1 gram-ion of the substance involved.

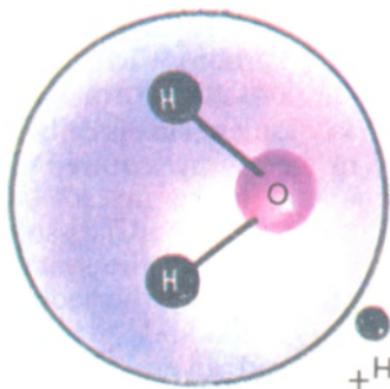


Fig. 16. Solvated proton

To sum up, the properties of a solution depend in a most decisive way on the nature of the chemical interaction between solute and solvent. This alone brings us to take a closer look at the nature of this interaction.

### Acids and Bases – is This Simple as That?

**The Classical Definitions – Limitations and Refinements.** We shall begin by describing acid-base interaction, that is, reactions between acids and bases. “Well, any one knows that”, the reader may wonder. “This is among the first things learned at school. What can be simpler than a reaction between an acid and a base?”

Let’s see if this is that simple. To begin with, we shall recall how a school book on chemistry defines acids and bases. “An acid is any substance that yields hydrogen cations in water. A base is any substance that yields hydroxyl ions in water.” Of course, those are correct definitions. But, as scientists like to qualify, they are correct only to a first approximation. And this approximation often needs refinements.

The first refinement is that the  $H^+$  cation whose yield in water is a major distinction in accord with the above definition simply cannot stand alone in solution. As already noted (p. 29), the hydrogen cation is simply a proton, a positively charged particle having a negligibly small radius and, therefore, setting up an extremely strong electrostatic field. In this field, polar water molecules are of course pulled towards and join the proton. It is a safe guess that at least one water molecule in solution is strongly bound to an  $H^+$  cation to form an  $H_3O^+$  cation, known as the hydronium ion. (Actually, more water molecules attach themselves to the proton, and we limit the process to the hydronium ion only for simplicity.)

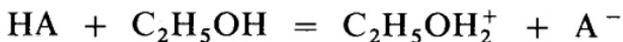
Another refinement is that the interaction with a solvent is generally mandatory for ions to appear in solution. Therefore, for any acid  $HA$  (where  $A$  is any anion, such as  $Cl^-$ ,  $NO_3^-$ , or  $CH_3COO^-$ ), the process that leads to the formation of ions in solution may be written as



The next refinement has to do with the solvent mentioned in the definitions. To believe them, acid-base reactions can only take place in water or that only water is suitable for them to form solutions. We've seen more than once that water is an exception. But is it so exceptional that it's the sole solvent for acids and bases?

No, of course not. If we dissolve, say, nitric acid in a solvent other than water, for example, ethyl alcohol,  $C_2H_5OH$ , we shall see that the resultant solution differs very little from an aqueous solution of nitric acid. (The principal difference is that when it is dissolved in alcohol nitric acid is a weak electrolyte, whereas it is a strong one when dissolved in water.) No "bare" proton can stand alone in this solution, either, so it will duly accept an

alcohol molecule. All in all, the manner in which ions come into being in an alcohol solution of some HA acid may be written as



Now re-read the definition of an acid given earlier. What has left of it? I'm afraid, not much. Firstly, it is not mandatory for an acid to be dissolved in water only. Secondly, instead of a hydrogen cation, a far more complex species is yielded in solution. To complicate the matter still more, one and the same acid will yield different cations in different solvents. So we must look for a better definition. Which is a pity, because the old one is so familiar and easy to remember.

Do not grieve over the old definition. As they say, truth comes before everything else. On the other hand, it would be wrong to say that by disproving the old definition we have only suffered a loss and have gained nothing in exchange. Quite the opposite is true. As if in passing, it might be said, we have grasped two extremely important traits of acids within the framework of the theory of electrolytic dissociation. For one thing, we have learned that an acid can display its properties in solution only. For another, the role of the solvent is above all to interact chemically with the acid molecule.\*

**The Theory of Solvated Systems.** Now it's time to introduce the reader to a theory of acids and bases which has come to be known as the theory of solvated systems.

This theory is based on the fact that – No, before we go on any further, it is worth while to recall the courageous Captain Yone Tikhy whose journeys are vividly described in “Star Diaries” by the talented sci-fi writer Stanislav

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\* All that has been said about acids fully applies to bases.

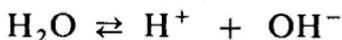


Fig. 17. The planet Fiery from S. Lem's "Star Diaries"

Lem of Poland. During his twenty-fifth space flight, this famous astronaut whose glory totally eclipses that of Baron Munchhausen, another brave man of fiction, visits a far-away planet, Fiery. It might be just another planet, very much alike Earth, except that liquid ammonia replaces water.

Not only do its inhabitants drink liquid  $\text{NH}_3$  to quench their thirst. The rivers, the seas, and the oceans of Fiery are, too, liquid ammonia. Everything on Fiery goes on in ammonium solutions. Just as the living things on Earth consist basically of water, so their counterparts on Fiery are made up of ammonia. Indeed, during one of his walks on that planet, Captain Tikhy overhears them discussing the prospects of the crop of salammoniac.

The theory of solvated system is based on the fact that many (it may be said, all) solvents are capable, like water, of self-dissociation (autoionization). I'll recall a few things. As you have probably learned at school, water can, even though on a limited scale, break up into ions of its own accord:



Now it is obvious – this equation needs an important refinement. As already noted, a bare proton cannot exist alone in solution – by accepting a water molecule it turns into a hydronium ion



Therefore, it will be correct to write the autoionization of water as



Now look at the equation for the electrolytic

dissociation of acids on p. 61. You will immediately see that, on dissociating, an acid yields exactly the same cation as appears from the autoionization of water. So, we could say that an acid in aqueous solution is a substance which, on dissolving, produces a cation identical with that produced by the dissociation of water. By the same token, a base is a substance which, on dissociating, produces an anion identical with that produced by the self-dissociation of water. Although a bit bulky, these definitions are undoubtedly correct.

Since acids and bases may exist not only in aqueous solutions and also since all other solvents are subject to autoionization, we may couch the definitions of acids and bases in terms of the theory of solvated systems as follows.

An acid is a substance which, when dissolved, produces a cation identical with that of the solvent. A base is a substance which, when dissolved, produces an anion identical with that of the solvent.

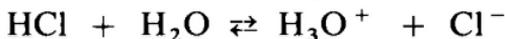
Now that we have grasped the gist of the theory of solvated systems, we could, like Captain Tikhy, make a journey to the planet Fiery if we wished so. Fortunately, experiments with liquid ammonia can be done here, on our home planet Earth. In fact, quite a number of experiments have already been done with this solvent (it turns to liquid at  $-33^{\circ}\text{C}$ ), and quite a number of interesting things have been learned about it. Among other things, it has been found that liquid ammonia undergoes autoionization according to the equation



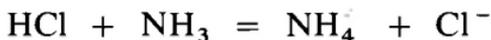
Note that the autoionization of water and that of ammonia look alike. Actually, why "look alike"? Basically, the same mechanism is at work in either case: one molecule of the solvent donates a proton which is immediately attached to the other. The molecule

donating the proton charges negatively, so it is an anion ( $\text{OH}^-$ ,  $\text{NH}_2^-$ ), whereas the molecule accepting the proton charges positively to become a cation ( $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ ).

When hydrogen chloride dissolves in water, it produces hydrochloric acid as a result of chemical interaction

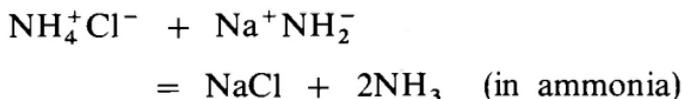
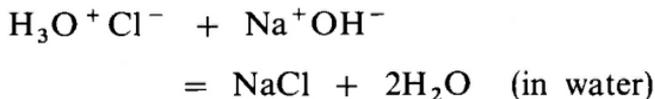


An acid solution in ammonia is produced in a similar way:



It follows then that ammoniac,  $\text{NH}_4\text{Cl}$ , when dissolved in liquid ammonia, is an acid much as hydrogen chloride, when dissolved in water.

Now we have learned that each solvent has its own system (solvated system) of acids and bases. By looking at the equation describing the autoionization of ammonia, we can say right away which compound will behave like a base in this solvent. Yes, sodium amide,  $\text{NaNH}_2$ , will act as a base in liquid ammonia, just as  $\text{NaOH}$  acts as a base in water. Compare two neutralization reactions and see this for yourself:



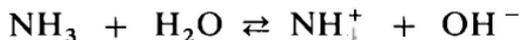
The theory of solvated systems suggests one more intriguing idea. Since chemical processes, notably acid-base interactions, can proceed not only in water, but also in any other solvent, we may ask if water is actually

a necessary condition for the origin and existence of life as is frequently stressed in books? Is it not possible for other forms of life to exist in other solvents, in liquid ammonia for that matter, for, to believe astronomers, there are planets covered with oceans of liquid ammonia (or liquid methane)?

In this book, we will still have one more chance to discuss whether “non-water” forms of life can exist. That is how a talk about solutions can lead to such lofty ideas as life itself. Now we dwell on one more theory of acids and bases. This is the chemical theory of acids and bases.

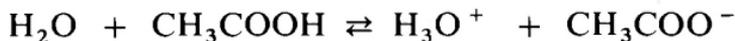
**The Chemical Theory of Acids and Bases.** The very name of the theory gives immediate insight into it—acids and bases display their properties solely through a chemical interaction with one another. In short, this theory directly connects the formation of ions in solution to chemical interaction. But there is a more important point about this theory. It argues that every chemical compound can be both an acid and a base.

If we pass a stream of ammonia through water, a well-known reaction will take place:



It is an easy matter to tell which of the reactants here is an acid and which is a base. Of course, the water donates a proton, so it acts as an acid in this reaction. Similarly, the ammonia accepts the proton, so it acts as a base.

In another reaction, water is added to acetic acid,  $\text{CH}_3\text{COOH}$ , and, as is clearly seen from the equation of the reaction



the water acts as a base, and the acetic acid lives up to its name and acts as an acid.

Now let us take an amount of absolute (that is, 100%) acetic acid and add to it an amount of likewise absolute nitric acid,  $\text{HNO}_3$ . The reaction will then proceed according to the equation



As is seen, the nitric acid in this reaction donates a hydrogen cation, so it acts as a true acid. In contrast, the acetic acid accepts the  $\text{H}^+$  cation, so it must be a base. "Acetic acid is a base" sounds like a pun. But we can do nothing about it, because in the above reaction it does act as a base.

If we wish so, we can do a similar trick with nitric acid. Suppose we add some sulphuric acid to it. The interaction that occurs when the two acids are mixed together has been well investigated:



Yes, the nitric acid in the reaction is a base. But the reader is no longer surprised. For one thing, he has already realized that in accord with the chemical theory of acids and bases just any compound can be both an acid and a base, that is, it can be amphoteric—everything depends on existing conditions. For another, he guesses that it is possible to choose pairs so that an acid will act as a base towards its partner. (Such compounds do exist, and there is quite a number of them.)

But the crucial point of this theory, because of which we have actually taken it up, is that substances act as acids or bases only in an interaction. Taken alone, a chemical compound can be neither an acid nor a base. It becomes either an acid or a base only when it interacts with another substance.

Thus, taken alone (in pure or absolute form),  $\text{CH}_3\text{COOH}$ ,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  are neither acids nor bases, but simply  $\text{CH}_3\text{COOH}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ .

This might well serve as the closing sentence to the chapter about acids and bases. All the same, we would not be able to cover all existing theories of acid-base interaction – this would fill a book of its own. But I feel an apprehension that some overzealous reader might declare at school tomorrow that the term nitric (acetic, sulphuric or any other) acid is a misnomer and that we ought to call it nitric (acetic, sulphuric, etc.) base.

No, he ought not to do that. Firstly, to stress the thing again, chemical compounds when taken alone do not show any acidic or basic property. Secondly, it would be wrong to stick new names of one's own accord. The more so that in our case the old names do their job well: all of the acids listed above are mostly produced and used as aqueous solutions. Water, too, acts as a base towards all the listed compounds, and they are true acids in most cases.

## Ions in Solutions

**Necessary and Sufficient.** If you want to be a cyclist, you will need two things. One is to know how to use a bicycle, the other is to have one.

If you want to be a college student, you will need two things. One is to finish your school; the other is to pass entrance examinations.

If you want a solute to break up into ions, you will need two things. One is that the solute should interact chemically with the solvent; the other is that the solvent should have sufficiently high dielectric constant.

You may ask, “What is there in common between cycling, going to college and making a solution?” The thing common to the three “wishes” is that each contains a necessary and a sufficient condition. Yes, before you can travel to a forest on a Sunday morning on a bicycle, you must first learn how to pedal it – this is a necessary

condition. Also, you must have a bicycle—that is a sufficient condition. To finish school is a necessary condition for being able to go to college, but that is not a sufficient condition. That one will be if you pass entrance exams successfully. With the formation of ions in a solution, too, a necessary condition is that the solute should interact chemically with the solvent—this interaction is the only source of the energy that goes to produce ions, but this is not a sufficient condition for free ions to appear in the solution.

In the chapter on water we spoke at length about dielectric constant. Now we will need it again. Even if we didn't recall it, we would run into it all the same, speaking about the causes of electrolytic dissociation. Where does it come in and why? Indeed, the interaction of a solute and a solvent produces a cation and an anion. They are unlike charges and should attract each other, and we even can find the force of attraction by Coulomb's law

$$E = e^2 Z_1 Z_2 / r \epsilon$$

Here,  $E$  is the energy of interaction,  $Z_1$  and  $Z_2$  are the charges on the cation and the anion,  $e$  is the charge on an electron,  $r$  is the spacing between ions, and  $\epsilon$  is the dielectric constant.

But instead of pulling towards each other, the cation and anion are forced apart. What is it that causes them to do so? This cause is the dielectric constant, a measure of that property that weakens the energy of electrostatic interaction between ions (the larger the value of  $\epsilon$ , the smaller the value of  $E$ ). For example, ammonia and hydrogen chloride interact in benzene about as eagerly as they do in water:



Benzene, however (as was noted in the chapter on water),

has a dielectric constant of only two. This implies that the  $\text{NH}_4^+$  cation and the  $\text{Cl}^-$  anion are attracted to each other with a force which is only half as strong as it is in vacuum. That is why there are no free ions of ammonia and chlorine in a benzene solution. In water, the energy of interaction is about one-eightieth of its value in vacuum. Now, the ion pair is free to separate, and free ions appear in water. In this way, an aqueous solution of ammonium chloride, in contrast to its benzene solution, acquires the ability to conduct electric current.

To sum up, the high dielectric constant of the solvent is that same sufficient condition for an electrolytic solution to form, about which we spoke at the beginning.

**A Measure of Acidity.** The laws of electrolytic dissociation give insight into many properties of electrolytic solutions, including one which decreases as the concentration of ions (to which it owes its existence) increases. The statement is fairly brief, but obscure—as befits riddles. But the author has not the slightest intention to speak in riddles, so let us take up logarithms. No, I'm not going to test the soundness of what you've learned about logarithms at school. But what I know for sure is that recapitulation has never done any harm to anyone.

So, the logarithm of a fraction is a negative number. In using common logarithms it is customary in such cases to leave the characteristic of the logarithm negative, and its mantissa, positive. For example, the logarithm of 0.2, or  $2 \times 10^{-1}$ , is equal to 1.301. It is more convenient, however, to add the positive mantissa to the negative characteristic and obtain

$$(-1) + (+0.301) = -0.699$$

To sum up,  $\log_{10} 0.2 = -0.699$ .

Now the reader will see why in a book on solutions a need has arisen to step aside and discuss logarithms.

Suppose we have an aqueous solution of a strong acid, such as HCl. The concentration of the solution is 0.01M, which means that one litre of solution contains one-hundredth of a gram-molecule of HCl. Because, in breaking up into ions, each molecule of HCl produces one  $\text{H}^+$  ion (of course,  $\text{H}_3\text{O}^+$ , and not  $\text{H}^+$ , but that's immaterial), the concentration of  $\text{H}^+$  ions in a 0.01M solution of HCl will be 0.01 gram-ions per litre.

In the chemical literature it is customary to denote the concentration of molecules or ions in a solution with the respective chemical symbol in square brackets. So, scientifically, the concentration of hydrogen ions in our solution will look like this:  $[\text{H}^+] = 0.01$ . Or, in logarithmic form  $\log_{10} [0.01] = 2.0$ , or  $-2.0$ .

The concentration of hydrogen ions in aqueous solutions is customarily stated in terms of what is known as the pH number. Mathematically, it is defined as

$$\text{pH} = -\log_{10} [\text{H}^+]$$

A few remarks are in order. One is about why it is convenient to designate the concentration of hydrogen ions by a logarithm and not by an appropriate number. The reason is both simple and convincing. For the most part, chemists (and not only they alone) have to deal with solutions in which the concentration of hydrogen ions is very low, say, 0.000 001, or one part in a million. Numbers with so many zeros are not easy to handle. Nor is the so-called scientific notation any more helpful ( $0.000\ 001 = 10^{-6}$ ). You must admit, therefore, that the logarithmic notation offers a good deal in brevity without losing anything in expressiveness. Look for yourself:  $\log_{10} 10^{-6} = -6$ .

The other remark is about why pH is a negative logarithm. As already noted, this number is used to designate

the concentration of hydrogen ions which is a quantitative description of the acidity (or alkalinity) of a solution. Because it is mostly very small and nearly always less than unity, the respective logarithm is always negative. If so, why should we keep the “-” sign ahead? It has been agreed, therefore, that pH will be the negative value of a negative quantity, that is, always positive.

The short table that follows puts on record what we have been talking about.

Concentration of H <sup>+</sup> ions in solution	pH
1 gram-ion per litre	0
0.1	1
0.01	2
0.001	3
0.0001	4
0.00001	5
0.000001	6

Now we are well equipped to solve the problem of finding the pH value of an aqueous solution. These problems are very simple to handle. Suppose we are to find the pH value of an aqueous solution of sulphuric acid with a concentration of 0.0005 mole per litre. This acid dissociates according to the equation



One gram-molecule of the acid produces 2 gram-ions of H<sup>+</sup>. Hence, the concentration of hydrogen ions in our solution is

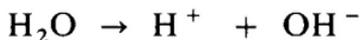
$$0.0005 \times 2 = 0.001$$

So,

$$\text{pH} = -\log_{10} 10^{-3} = 3$$

In order to calculate the pH value of solutions in which the concentration of hydrogen ions is  $10^{-7}$  gram-ion per litre and lower, we will have to recall the 19th-century German scientist Kohlrausch who spent several years distilling water from one vessel to another. His chief was afraid of taking guests to Kohlrausch's laboratory. He was sure that after the guests had been told what the honorable professor was busy with, some cute person would inevitably allude to the Laputian Academy of Sciences from Gulliver's travels.

But the ridicule would be undeserved. For Kohlrausch was doing a very important thing—he was trying to make water as pure as possible (at his time). Of course, extra-pure water was not an aim in itself. By measuring the electric conductivity of such water, Kohlrausch wanted to calculate the concentration of ions in water. In other words, his objective was to determine how active the self-dissociation of water was:



(In more detail, this is discussed on p. 64.)

**The Ion Product.** The extent to which water dissociates itself into  $\text{H}^+$  cations and  $\text{OH}^-$  anions is stated in terms of the ion product of water. This is the product of the concentration of hydrogen ions,  $[\text{H}^+]$ , by the concentration of hydroxyl ions,  $[\text{OH}^-]$ . By measuring the electric conductivity of pure water it has been found that

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

The ion product is an all-important characteristic of water as a solvent.

Everything is important here. For one thing, the ion product of water is a constant quantity. Hydrogen ions,  $H^+$ , and hydroxyl ions,  $OH^-$ , are always present in any aqueous solution. Let's go back to the solution of sulphuric acid we spoke about a few lines earlier. As we learned at that time, the concentration of  $H^+$  ions in the solution was  $10^{-3}$ . Knowing the ion product of water we can calculate the concentration of hydroxyl ions in the same solution:

$$[10^{-3}][OH^-] = 10^{-14}$$

Hence,

$$10^{-14} \div 10^{-3} = 10^{-11}$$

Hydroxyl ions are usually associated with alkaline solutions, but they are likewise present in acid solutions. In fact, we can accurately determine their concentration. By the same token, we may speak of the concentration of  $H^+$  ions in an alkaline solution.

Let's do simple calculations. We set out to find the value of  $[H^+]$  for, say, a 0.0001M solution of KOH. Obviously, for this solution  $[OH^-] = 10^{-4}$ . Therefore,  $[H^+] \times 10^{-4} = 10^{-14}$ , and

$$[H^+] = 10^{-14} \div 10^{-4} = 10^{-10}$$

So, the pH value of a 0.0001M alkaline solution is 10. In a slightly different way, we may say that a 0.0001M alkaline solution has a pH value of 10.

So, pH is a truly versatile quantity – it is equally useful in describing both acidic solutions (for them pH will be less than 7), neutral solutions (for them pH will be exactly equal to 7), and, finally, alkaline solutions (for them pH is in excess of 7). It turns out that we may (and should) speak of the acidity of alkaline solutions, and the value of pH is a very convenient way to express it.

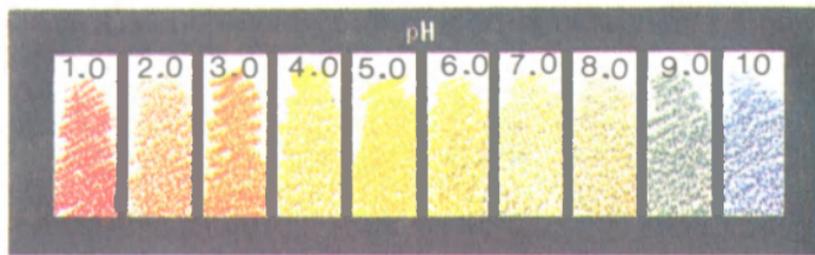


Fig. 18. The pH scale

There is hardly a single chemical, pharmaceutical or biochemical manufacture which would not use pH as a most important quality indicator for end or intermediate products. In fact, technologists are not alone in using this characteristic. As has been found, the pH value of cell matter is an extremely sensitive indicator of the condition of the organism. It is therefore very probable that before long your physician will take not only your temperature, but also your pH (which, it may be added, differs from organ to organ and even from cell to cell in the same organ).

Experimentally, pH can be measured in many ways. We shall only mention one as it is most commonly used. Strips of blotting paper are impregnated with a range of indicators – organic substances which change their colour in a well-defined way at a particular pH value. Just dip one of the strips in your solution, and the paper will take on the colour associated with the pH value of the solution. How such a set of pH-indicator paper may look like can be seen from Fig. 18. The method is not very accurate, but quite sufficient for many practical applications.

## Flow of Current Through a Solution

At first everything may seem simple; very simple, indeed. We know two kinds of electric conductors, metallic and electrolytic. In metallic conductors, the current is constituted by electrons, in electrolytic conductors by ions.

Since we are interested in solutions of electrolytes, or ion conductors, we shall take a closer look at them.

**A Humped Curve.** The first thing to do is to make an experiment, because everything in the natural sciences is based on experiments. We set out to measure how the specific conductance of a solution varies with the concentration of the electrolyte.\* This can be done by consecutively adding small amounts of common salt to the same quantity of water and noting its conductance each time.

At first, the specific conductance rises as the concentration of salt is increased. The explanation is so natural that you might regret doing an experiment whose outcome is so obvious. For, as the concentration of NaCl in solution goes up, the number of ions increases. As the number of ions increases, a larger number of charge carriers move through the solution.

Before long, however, the addition of more salt begins to bring about not so marked an increase in conductance as before. At last, it begins to go down, although we keep adding more salt. Graphically, this result appears as a humped curve. Very few curves may be said to have caused so much thought, disputes, and discussions as this one.

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\* The specific conductance of a substance is the conductance of a centimetre cube. It is the reciprocal of specific resistance, or resistivity. Some authors designate specific conductance by the Greek letter "kappa" ( $\kappa$ ).

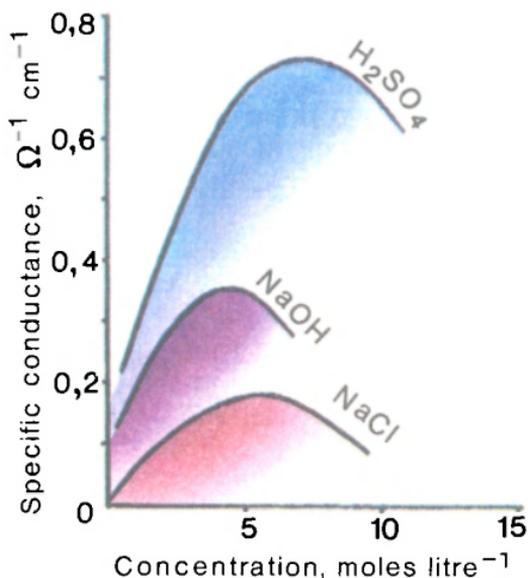


Fig. 19. Specific conductance as a function of concentration

At first sight, the classical theory of electrolytic dissociation (Arrhenius's theory) seems to give a very convincing explanation why the humped curve should have a hump. In diluted solutions, electrolytes dissociate completely, so an increase in concentration should bring about a decrease in the degree of dissociation of the electrolyte and, as a consequence, a decrease in the number of particles that carry current. Quite naturally, the specific conductance rises first and falls off afterwards.

The above explanation is a good example of the well-proven rule that you must be cautious in giving statements based on "first sight". In science, caution must be augmented ten-fold. Although Arrhenius advanced a seemingly sound explanation, it has been found that in the case of sodium chloride and, indeed, other strong electrolytes, non-dissociated molecules are non-

existent – all of the electrolyte, whatever its concentration, dissociates into ions.

The unusual trait of specific conductance stems from the fact that each ion in solution has a suite of its own. Although the term “suite” sounds a bit strange in any theory, that of solutions included, it is a legitimate and widely used term in the literature of the subject.

For decades, the theory of solutions believed that the molecules of a solute behaved in solution in much the same way as gas molecules do, that is, moving in a haphazard manner and without affecting one another. Such views seemed to be sound, the more so that they served as the basis for such brilliant findings as cryoscopy and ebullioscopy (see p. 41). But these sound views collapsed under the weight of the humped curve.

**Solution as a Crystal.** Ions in a solution cannot but affect one another because like charges are bound to attract and unlike charges to repel each other. So in a solution the ions arrange themselves so as to minimize mutual interference. If we translate this rather loose definition into one couched in more rigorous physical terms, we may say that ions in a solution take up relative positions such that their potential energy is a minimum. This arrangement corresponds to a strict order or, as the same physicists say, a particular structure.

That’s the word to which I’ve been leading the reader all the time. In contrast to solutions of nonelectrolytes, electrolytic solutions have been found to possess a well defined structure. In the case of sodium chloride, this structure bears an amazingly close resemblance to a crystal of common salt.

Look at Fig. 20. It shows an elementary volume of a NaCl solution. Compare it with Fig. 1 which shows a NaCl crystal. The two are so much alike that we might use any one instead of two. As in the crystal, each cation

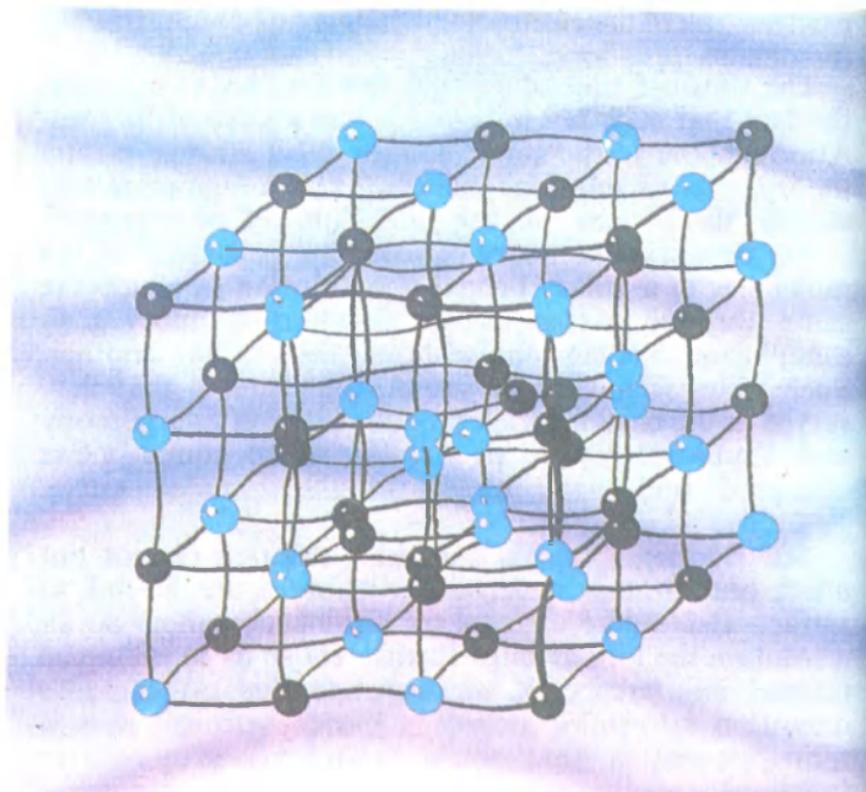


Fig. 20. Arrangement of electrolyte ions in solution

in the NaCl solution is surrounded by eight  $\text{Cl}^-$  anions, and each anion is surrounded by a suite of eight  $\text{Na}^+$  cations. Exactly this arrangement of ions corresponds to the minimal potential energy of the NaCl solution (and of many other electrolytes) in water.

It takes time for such a structure to grow in a solution. When the salt concentration in the solution is low, the ions are spaced widely apart and, naturally, their interaction is weak. The energy with which water molecules strike ions exceeds the energy of electrostatic

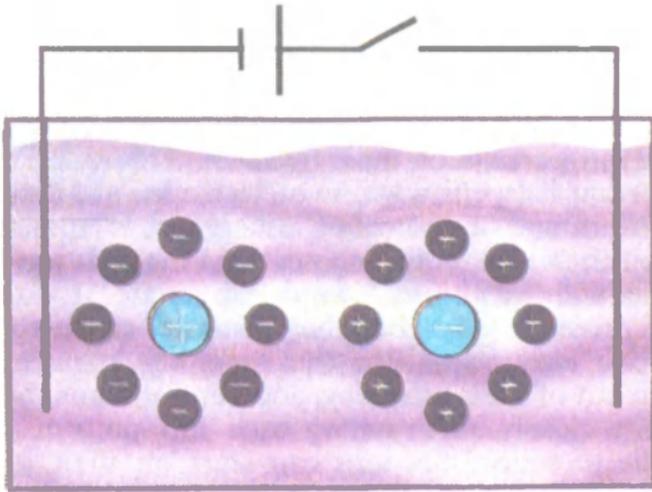


Fig. 21. Cataphoretic effect

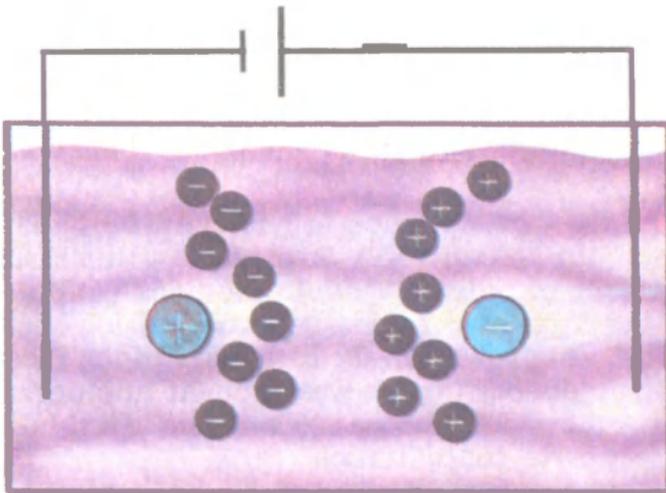


Fig. 22. Relaxation effect

interaction. Therefore, ions in a diluted solution travel independently of one another. As the concentration rises, the structure takes on a progressively well defined shape, ionic interaction gains in strength, and the ions lose a good proportion of their freedom. Figure 22 clearly shows what happens when two electrodes are dipped in a solution and a potential difference is maintained between them. Naturally, the cations move towards the cathode, and the anions towards the anode. It would be more correct to say that they tend to move to their respective electrodes. For the time being, nothing is coming out of their tendency, and cannot come, because the suite closely surrounding each ion pulls it in the opposite direction. So, ions can start on their journey towards "their" electrodes only after the force of attraction towards the respective electrode exceeds the retarding effect of the suite, and the sheath of oppositely charged ions is destroyed.

The higher the concentration of the electrolyte, the stronger the sheath of oppositely charged ions surrounding each ion in the solution, and the harder it is for ions to move to their respective electrodes. This is the principal cause of the fall in specific conductance when the concentration is high.

**When the Concentration is Nil.** Until now, physical chemists can satisfactorily explain variations in the conductance of only very dilute solutions—solutions in which the effect of the oppositely charged ion sheath is negligible. That is why, in the early days of the theory of electrolytic dissociation, it was thought appropriate to introduce the concept of the conductance of a solution at zero electrolyte concentration.

This conductance ought not to be confused with specific conductance. To tell one from the other, it has come to be known as the equivalent conductance. It is

perhaps of more theoretical significance to the physical chemistry of solutions than specific conductance. To grasp its physical meaning, imagine to yourself a cylinder one square centimetre in area at the base. Fill the cylinder with so much of your solution that it will contain 1 gram-molecule of solute. The reciprocal of the electric resistance offered by this column of solution is the equivalent conductance, designated by the Greek letter "lambda" ( $\lambda$ ). If we know the specific conductance of a solution, we can readily determine its equivalent conductance from a very simple equation

$$\lambda = 1000\kappa/c$$

where  $c$  is the concentration of the solution in moles per litre.

For diluted solutions, there is a direct relation between concentration and equivalent conductance: The lower the concentration of a solution, the higher its equivalent conductance. No, it's not a misprint: the equivalent conductance is then higher. Now let's look at the plot on the left of Fig. 23. It relates the equivalent conductance of HCl, KOH and KCl solutions to their concentration,  $c$ . As is seen, a decrease in electrolyte concentration leads to a rise (and a fairly rapid rise) in the equivalent conductance of each solution. It should be noted, though, that physical chemists prefer to deal with straightline rather than curved plots. So they lay off the square root of  $c$ , rather than  $c$  itself, as abscissa. Now the plot on the right of Fig. 23 is a family of straight lines which can readily be extended until they cut the axis of ordinates where the concentration is zero or, which is the same, the dilution is infinite. The corresponding equivalent conductance is called just that—the equivalent conductance at infinite dilution,  $\lambda_0$ .

So it turns out that a solution would conduct electricity best of all if it contained no electrolyte whatsoever.

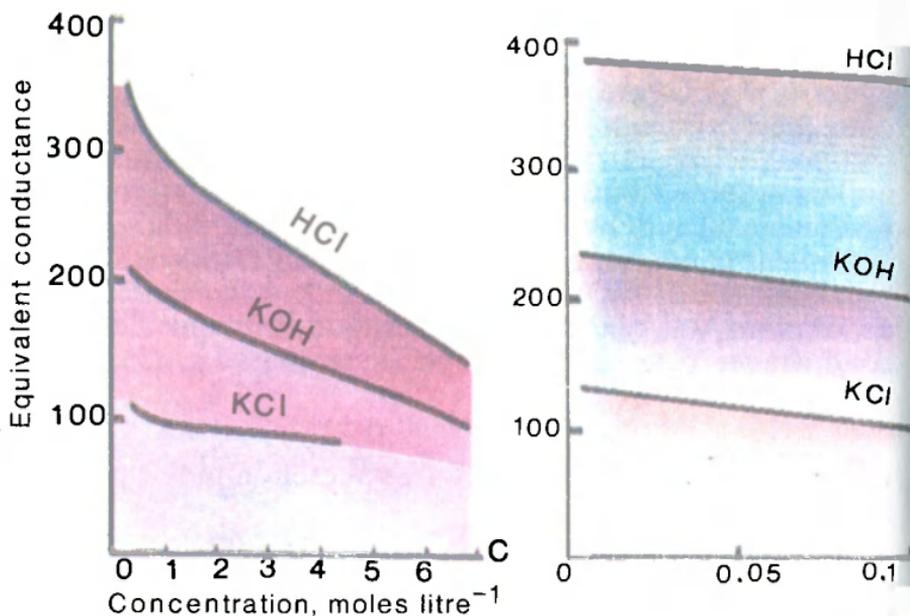


Fig. 23. Equivalent conductance as a function of concentration

Although this sounds like a paradox, there is nothing about it to cause surprise. It has been convincingly demonstrated that with a weaker ionic interaction in a solution the ions have more freedom to move and the conductance is higher. Therefore,  $\lambda_0$  is not an absurd, but a well defined quantity – it shows what the conductance of a solution would be (would be!), if (if!) there were no ionic interaction in the solution.

The value of  $\lambda_0$  referred to an ion defines the mobility of that ion. The term seems to be self-explanatory – the higher the equivalent conductance of a solution, the faster the ions move in it.

A teenager character from a recent novel says, “That’s as dull as a table”. We cannot agree with him. Looking through tables of physical or chemical properties can be

both instructive and thrilling. This fully applies to the table giving the mobilities of various ions. But before we look up the table, let us do a bit of prediction. At first sight, it will be easy to do.

So, we set out to predict how the ions from  $\text{Li}^+$  through  $\text{Na}^+$  to  $\text{K}^+$  rank in mobility. This series of cations has been chosen purposefully. They are relatives, because they belong to the same group in the Periodic Table of Elements. This is the group (or, rather, subgroup) of alkaline metals. In the top row of Fig. 24, these ions are drawn to scale so as to show their relative size when they are unsolvated (not wrapped in a sheath of solvent).

The picture seems to leave no doubts as to the outcome of our prediction. Undoubtedly, the stout potassium ion will elbow its way through the crowd of water molecules at a far slower pace than the small and, apparently, agile lithium ion. Certainly, the mobility of the lithium cation must be higher than that of the sodium cation, and that of the sodium cation higher than the mobility of the potassium cation. It only remains to bear out our obvious prediction by turning to ion mobility tables. We do so and find we've missed the point by a mile. In arbitrary units, the mobility of the lithium cation is 38.6; that of the sodium cation, 50.1; and that of the potassium cation, 73.5.

What we've learned from the table is just the opposite of what appears to be correct at first sight (that's another case where first sight turns out to be a scientific "booby-trap"). Fortunately, we've learned enough to explain why this is so—just recall that in a solution the ions are wrapped up in a sheath of solvent molecules. Any cation has a charge of  $+1$ , but the fields set up by various cations markedly differ in strength: as has already been noted, the field around a charged body increases in strength as its radius decreases. That is why the smallest

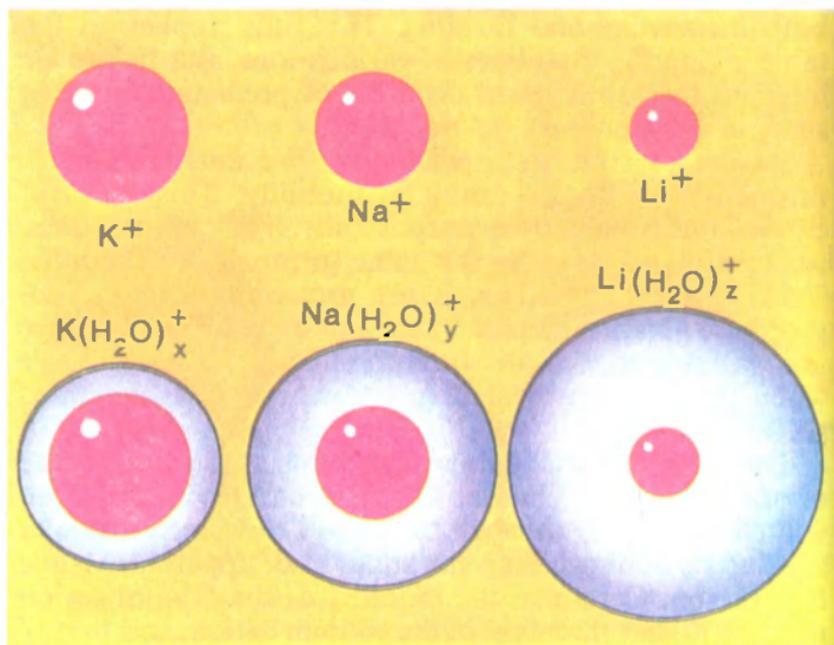


Fig. 24. Unsolvated (above) and solvated (below) cations of alkaline metals

of cations, the lithium cation, when solvated, is the largest of all; it is surrounded by several layers of water molecules. The number of water molecules around the sodium cation is somewhat smaller, and its solvated radius is shorter in proportion. The water sheath is the thinnest of all in the case of the potassium cation, so its solvated radius is the shortest of the three. Thus, the actual size of the cations of alkaline metals in aqueous solutions is opposite to what we've predicted – it is now as shown in the lower row of Fig. 24.

**A Relay Race in a Solution.** Now that we've put everything in its place, I challenge the reader to predict the mobility of  $H^+$ , the smallest of all cations. No doubt,

it must be surrounded by the densest and the thickest sheath of water molecules. It would appear, therefore, that the hydrated  $H^+$  ion should hardly be able to move in a solution. Yet, the table says it has not just a very high mobility, but a record one – it is 350, or nine times that of lithium and seven times that of sodium.

To understand why the hydrogen cation has so high a mobility, picture to yourself an overcrowded bus – overcrowded so that no room is left for anyone to move about or even to breathe. All the same, you must buy a ticket. You hand your fare to a neighbour who passes the coin on and on until it reaches the coin box and a ticket is torn off. Now the ticket has to re-trace the same route before it reaches you. Of course, you might have chosen another way to get your ticket – at the cost of strenuous effort and most of your coat buttons torn off. But what for? You've got your ticket by spending far less energy. Now I ask you a question – if you're so wise in saving energy, do you think Nature is less enterprising?

What goes on when an electric current is flowing through a solution which contains hydrogen cations, that is, an acidic solution, is not unlike the scene in our imaginary bus. The hydrogen cation is surrounded by so dense a sheath of water molecules that it cannot simply move a bit. Now, agile and extremely small in comparison with the surrounding molecules, the proton jumps over to the nearest water molecule which passes it at once to its closest neighbour, and that to a neighbour farther away, and so on, until the proton reaches the cathode.

How this relay race goes on can be clearly seen from Fig. 25. Quite aptly, this form of charge transfer through a solution is called relay (chain or prototropic) transport. Obviously, the transfer of a proton is energetically more economical than the migration of a hydrated ion through the solution. That's why the hydrogen cation has the highest mobility of all other cations.

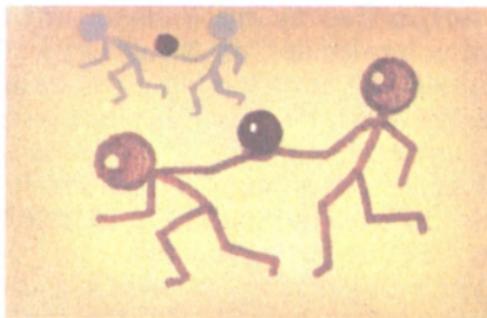


Fig. 25. Relay mechanism of charge transfer by protons

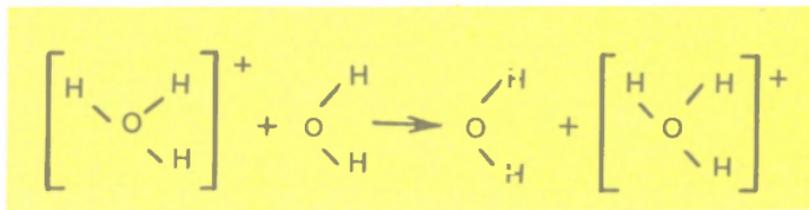
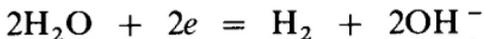


Fig. 26. Transfer of proton by water molecules

**A Flow of Electrons Through a Solution.** Now we have to dispel the somewhat outmoded concept of those readers who still believe that in solutions an electric current can only be constituted by ions. As has been found, electrons too can do the job as effectively. "Wait a moment," those readers might object. "It's been long known that what sets electrolytic solutions apart from metals is that in them the current is a flow of ions, and in metals a flow of electrons!" Well, what I'm going to tell you is another example of how Nature proves more ingenious and variegated than any classification devised

by man. It should be noted, though, that it is man that has discovered electron conduction in solutions, so we have no reason to bear Nature any grudge.

Let's begin with a question: "Is there anything that could prevent electrons from making up a flow of current through a solution?" The chemist can give a well founded answer. For a current to be made of electrons, it is essential that these electrons should exist in solution in a free state. However, once free electrons find their way into water in one way or another, they immediately react with it



The point is that an electron is a strong reducing agent, so it reduces water to free hydrogen once they come together. So free electrons cannot exist in water. (To be more precise, we should say they cannot exist free for any noticeable length of time.)

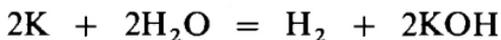
But, then, is water the only solvent suitable to make a solution? Can't we choose a solvent that will be reduced less readily than water? Yes, we can—such solvents do exist, and there is quite a number of them. Examples are amines, above all ammonia.

If we dip a piece of metallic potassium into liquid ammonia (we've already spoken about this solvent in the chapter on acids and bases), the potassium will dissolve in it like a lump of sugar in water. This, incidentally, is a well-fitting simile. For chemists use the word "dissolution" to describe two processes similar only outwardly—in their essence they may be said to be diametrically opposite.

Let's take a lump of sugar again and let it dissolve in water. If we now evaporate the solution to dryness, the residue will be crystals of the same sugar we took to make the solution.

The picture is different when we let a piece of zinc dissolve in hydrochloric acid. Although zinc eagerly dissolves in the acid, evaporating the solution to dryness will leave no trace of the original metal. We'll only find zinc chloride which in no way looks like the metal zinc.

Thus, in one case dissolution brings about no changes in the molecules of the solute; in the other it involves a chemical interaction. The same is true of potassium. It eagerly dissolves in water to form, as is well known, caustic potash:



When it dissolves in liquid ammonia, potassium remains potassium. If we drive off the water, the residue will be crystals of the metal potassium.

Nevertheless, metallic potassium dissolved in liquid ammonia does act as an electrolyte. It will dissociate electrolytically according to the equation



If we dip a pair of electrodes in such a solution and apply a potential difference across them, an electric current will flow through the solution. The bulk of the current will be electrons, and not ions of potassium. It is easy to see why this is so – energy-wise, the light (we may say, the lightest) electrons find it easier to move through the solution than the more “stout” potassium cations.

## Solubility

This only word in the heading of this chapter provokes a storm of emotions in the heart of any chemist. No less than a storm. Because the formation of a solution is

related above all to the solubility of a substance in a solvent. But chemists, to be frank, know not so much what solubility is and what it depends on. In fact, we may even say that their knowledge is poor.

Examples are at hand. Some of you probably know that, say, barium sulphate will dissolve poorly in water. In contrast, magnesium sulphate will do that eagerly—so eagerly, in fact, that if you happen to leave crystals of this salt in the air, they would greedily take in water vapour and spread into a concentrated solution.

This difference appears puzzling, because barium and magnesium belong to the same subgroup in the Periodic Table of Elements and possess similar properties. This similarity manifests itself in most chemical reactions, in many physical properties, except in solubility. But why do  $\text{MgSO}_4$  and  $\text{BaSO}_4$  differ in solubility nobody can tell definitively. Not that we lack theories trying to do that—there are at least a good dozen of them, and very few chemists can resist the temptation to add a thirteen one, of his own. This very excess of theories is an indication that there is something wrong with all of them. For if there were one good theory, there would be no need for the rest of them.

**“Likes Dissolve Likes”.** The first theory of solubility was advanced by alchemists. They discovered very soon that *Similia similibus solventur*, which is the Latin for “Likes dissolve likes”. They stumbled over this theory in their search for a solvent that would dissolve everything. In this search they were no less zealous than in their hunt for the alchemist’s stone, putting in uncommon ingenuity and imagination. They would mix any liquids that could be extracted from the human body. They would blend wines of all brands and vintages. They would combine all conceivable “caustic” liquids and finally run into *aqua*

*regia*, a mixture of nitric and hydrochloric acids. And each time they failed. Jumping a little ahead, we may say they would find nothing ever.

So, "Likes dissolve likes". That is a true observation. Indeed, hydrocarbons dissolve well in other hydrocarbons (say, hexane dissolves in benzene), but poorly in water. Hydrogen peroxide, HO—OH, is only slightly different from water, H—OH, so the two can mix in any proportion. Acetic acid, CH<sub>3</sub>COOH, can mix in any proportion with both hydrocarbons and water. This is clear why: acetic acid has a "water-like" part, or the hydroxyl OH, and a "hydrocarbon-like" part, CH<sub>3</sub>.

For all of its simplicity (or, perhaps, because of it), the alchemist's rule can predict the probability of dissolution only qualitatively. We are not so well off in regard to theories that could predict dissolution quantitatively (from, say, some properties of the solute and some properties of the solvent). We can at best speak of more or less general relationships.

**Some Relationships.** Let's begin with the effect of temperature. In most cases, a rise in temperature improves the solubility of solids in liquids. The relation between temperature and solubility is not so simple as it might seem, but it is beyond any shade of doubt. A solid passes into solution in much the same way as it melts—that's obvious, as in either case the solid turns to a liquid. For this to happen, the solid must be heated. This is the reason why a rise in temperature increases solubility. (Interestingly, in the case of gases, a rise in temperature reduces solubility. This, too, is easy to understand: by analogy with the previous case the dissolution of a gas is not unlike the condensation of a gas into a liquid, and for this to happen heat must be removed.)

There is a well defined relation between the chemical properties of the solute and the solvent. Acid solvents are better suited to dissolve substances basic in properties, and base solvents are better suited to dissolve substances acidic in properties. For example, formic acid is an excellent solvent for caustic soda (their reaction probably produces the sodium salt of formic acid), but it is a very poor solvent for  $\text{KHSO}_4$  because this substance is acidic in behaviour (actually, it is a half-acid). On the other hand, hydrazine, which is a liquid with well-defined basic properties, dissolves caustic soda very little, if at all, but it is an efficient solvent for  $\text{KHSO}_4$ .

Finally, there is a well-defined relation between solubility and the dielectric constant of the solvent. If we take four related alcohols: methanol, ethanol, propyl alcohol, and butyl alcohol, the first has a highest dielectric constant and the last one the lowest. The solubility of salts in these alcohols decreases in exactly the same order. This, incidentally, explains why on the whole some substances dissolve in water better than they do in other solvents. As will be recalled, water has a very high dielectric constant—it is much higher than for an overwhelming majority of other liquids.

### “Not in Water Alone”

I've put the heading in quotes because it is the title of one of my popular-science books (although it is written for chemists). It has to do with the unusual, truly unusual properties of non-water (nonaqueous) solutions. So that you can get an insight into the concept of nonaqueous solutions and grasp what is so unusual about the division of the theory of solutions dealing with them, I'll write the equation of a chemical reaction.

Ordinary Strange Reactions. To avoid misunder-

standings and, especially, offending remarks about this author, I ask you to take your time showing the equation I'm going to write to your chemistry teacher or any other chemist, at least for the time being. Here it is:



You needn't be a highly educated chemist to think that what I've written is an absurd thing, to say the least. For everyone knows that copper is a metal more electropositive than hydrogen. (The same thing can be stated differently: copper follows hydrogen in the electropotential series, or the metal copper is less reactive than hydrogen). What it means is that copper cannot displace hydrogen from solutions of acids.

Nevertheless, everything in my equation is correct.

It wouldn't be out of place here to use the same psychological test as we've used early in the book and to ask the reader how he pictures to himself an experiment involving this and other similar reactions. Of course, many might suspect some hidden trick in the question, but, one way or another, they would have to say that, in all probability, some hydrochloric acid is poured to a heap of copper filings and that the hydrochloric acid is obviously a solution of hydrogen chloride in water.

But who has decreed that chemists must always use only aqueous solutions, solutions of substances in water?

Nobody, for substances may well be dissolved in a multitude of other solvents and reactions may well take place in nonaqueous solutions. What is important is that this change of solvent often causes the properties of the dissolved compounds to change beyond recognition as well.

[Everything Hinges on the Solvent.](#) We know now well

enough why the absolute majority of chemical reactions prefer to take place in solutions. By attaching itself to the solute molecules (by solvating them), the solvent makes them more reactive. So, in view of solvation, the above equation can be re-written as



Here  $S$  stands for the number  $x$  or  $y$  of some solvent molecules that attach themselves to the reacting species. Now it is not at all surprising that in different solvents (different  $S$ 's) different chemical species react with one another. In consequence, the reactions themselves go on as differently.

In water, where hydrogen chloride can be present as a hydrate  $(\text{HCl})(\text{H}_2\text{O})_x$  (or more accurately, as  $\text{H}^+(\text{H}_2\text{O})_y$  and  $\text{Cl}^-(\text{H}_2\text{O})_z$ , because in water  $\text{HCl}$  dissociates into ions completely), copper, being more electropositive than hydrogen, cannot displace  $\text{H}_2$  from the acid solution. In a nonaqueous solvent, such as acetonitrile,  $\text{CH}_3\text{CN}$ , the dissolved hydrogen chloride is present as the  $(\text{HCl})(\text{CH}_3\text{CN})_x$  complex, and the properties of this complex are such that copper is now less electropositive than hydrogen. Accordingly, the reaction goes on as first written.

To sum up, there is nothing unusual in this equation, and you may show it to any one on one condition – you must explain that in this case the reaction takes place in the nonaqueous solvent acetonitrile and not in an aqueous solution as is usually implied.

I could quote a large number of examples of how the same substances yield entirely different reaction products in different solvents, and many more examples of substances which remain indifferent to each other in one solvent and react violently in another. From this difference arises a very important practical application of nonaqueous solvents.

**How Metals Are Extracted.** I'll limit myself to only one practical application of nonaqueous solvents, but this will perhaps be a very eloquent example.

Of course, you know that most elements (about 80) in the Periodic Table are metals. It is also well known that the most convenient way to extract metals is by electrolysis. Unfortunately, about a half of the metals cannot be electrolyzed out of aqueous solutions. The cause is as simple as it is fundamental: These metals are less electropositive than hydrogen. Now, since aqueous solutions always contain some number of hydrogen (or rather, hydronium) ions, the electrolysis involving the aqueous solutions of salts of these metals yields hydrogen, or, in the best of cases, the metal along with hydrogen as gas.

The use of nonaqueous solvents for this purpose equalizes all metals: "laggards" such as gold or silver, and "activists" such as potassium, rubidium or cesium. For any metal we can select a solvent that may serve as the basis for an electrolyte for the extraction of that metal by electrolysis.

This use of nonaqueous solvents enables chemists and metallurgists to come very closely to seeing their old dream come true: electrolytic extraction of aluminium at room temperature. Today, aluminium is likewise produced by electrolysis, but the starting material is the melt of its salts at a temperature of around 1000 °C, which is obviously not an asset. On the other hand, if we dissolve, say, aluminium chloride,  $\text{AlCl}_3$ , in solvents such as nitrobenzene, esters, and the like, we can extract aluminium, by far the most important material of today's engineering, by electrolysis at room temperature.

Cesium, which excels all other chemical elements in reactivity, can likewise be extracted by electrolysis with the aid of nonaqueous solvents. You can hardly think up

a more eloquent example in favour of the practical value of nonaqueous solvents.

## Is There Life Outside Earth?

The question is, “Can life exist in other stellar worlds, in other galaxies?” If so, another question is, “Can it look like the life we know on our home planet?”

Don’t think the author has forgotten he is writing a book on solutions. In this chapter, as elsewhere in the book, our talk will be about solutions. For the origin and evolution of life is, to a very marked measure, an interplay of various matters related to the theory of solutions.

“Can life exist on other planets, in other stellar worlds, in other galaxies, or is Earth the only seat of life in all of the Universe?”

This question has intrigued man from time immemorial. The motive behind his interest is obvious: It is important and, indeed, essential for us to know if there are intelligent beings like us somewhere, or we are alone in the Universe. Even if we learn that there are no intelligent beings except on Earth, we must at least find out if there are any living creatures elsewhere however elementary, and if there are any plants, be they single-celled.

**Living Matter.** I’ve written “single-celled” and the words make me think. Is it mandatory for life in other worlds to be organized in exactly the same manner as ours? Is the cell structure a mandatory form of existence for animals and plants? Is the division of Nature into plants and animals (based on the manner in which they obtain energy for their life processes), as adopted on the Earth, mandatory for life forms in other worlds (of course, if these forms do exist at all)?

Just a few years ago everything related to the likely

forms of life outside the Earth would fall in the domain of science fiction. Of course, sci-fi writers were dead-sure: Life exists everywhere. In this, they were amazingly unanimous. They only differed on the appearance of inhabitants on other planets. Some insisted that everything must be as it is on the Earth. Others packed their books with such monsters that over-sensitive readers were afraid to read them before going to bed.

More recently, the problem of extraterrestrial forms of life has been receiving a growing interest in scientific publications, as well. As should be expected, scientists have begun by trying to answer what terrestrial life is and what the properties of living matter in general are. So as not to be tied up to cell forms of life, scientists have chosen to speak in terms of living matter—that is, molecules or, rather, a collection of molecules from which living organisms could be built.

Once the matter of molecules has cropped up, it is clear that we can't do without chemistry. Approaching the problem of life from this angle, scientists have noticed that all chemical processes underlying the life activity of both plants and animals take place in solutions, notably aqueous solutions. In short, each organism (to be more precise, I'll add "each terrestrial organism") can to a very good degree of approximation be looked upon as an aqueous solution. Hence comes the lavish stream of jokes and witticisms varying in caliber, based on the undeniable fact that three quarters of man's weight is water.

In tracing down the most general attributes of living matter, scientists have also noticed that the mandatory and indispensable condition for living matter to exist is spontaneous rejection of the excess energy accumulating in the organism. The point is that the various chemical processes (we'll limit ourselves to chemistry) occurring in

any organism need energy, and this energy comes through photosynthesis in the case of plants and with food in the case of animals. The build-up of energy in an organism must raise the velocity of molecules in living matter. If excess energy were not withdrawn, the molecules would in the final analysis be moving about with a velocity which would upset the regular structure of the organism, and the complex compositions of molecules would break up. Yet living matter is above all an embodiment of a strict order.

If we translate this semilyrical discourse into the rigorous language of science, we must say that the chemical processes taking place in the organism lead to a build-up of excess entropy (see "Thermodynamics for Everyone" by Krichevsky and Petryanov we've mentioned already). The build-up of entropy is an increase in the degree of disorder. That is why for living matter to exist it is essential and indispensable that excess entropy should be rejected spontaneously.

This statement does not run counter to what F. Engels said in defining the concept of life. In fact, it fully checks with Engels's brilliant definition. Over a century ago, Engels noted perspicaciously that metabolism is a mandatory condition for living matter to exist. Today we know that the objective of metabolism is to deliver energy to the organism and withdraw excess entropy from it.

**How Living Matter Came About.** During one of their deep-space journeys, the characters in a story by the Soviet sci-fi writer Yefremov run into a space craft whose inhabitants come from a planet where life is based on liquid hydrogen fluoride, HF, and not water. Quite naturally, the bodies of the strange creatures are made up mostly of HF. But should we call them "strange"? Perhaps, these "fluoride" beings might look strange to us,

Earthlings. But we, "Waterlings", would look no less strange to them.

The courageous Captain Yone Tikhy from Stanislav Lem's "Star Diaries" (mentioned earlier in this book) visits a planet where life is based on liquid ammonia. On that planet, the worst punishment for criminals is to be hosed with water.

If you at least thumb through the scientific books concerned with extraterrestrial forms of life, you would immediately note that scientists, much as sci-fi writers, are vividly interested in whether water is essential for living matter to come into being and evolve, or other forms of life based on nonaqueous solvents, such as liquid hydrogen fluoride or liquid ammonia, are possible. Their interest in these seemingly out-of-ordinary solvents is not without a foundation. Astronomers have a very weighty reason to suppose that there may be planets on which the rivers, seas and oceans are not water, but exactly these solvents—hydrogen fluoride or liquid ammonia.

They reason in about this way.

Whatever it may be, terrestrial or extraterrestrial, living matter must be based on complex molecules. For only complex molecules can have memory to store their responses to external stimuli, or information, and it is complex molecules alone that can get rid of excess entropy of their own accord.

Every chemist realizes that complex molecules could only be formed from simple molecules through a more or less long sequence of consecutive reactions. These reactions proceeded spontaneously. Yes, spontaneously. To admit the opposite would mean to admit the existence of some outside controlling factor (whatever it might be). In fact, there are theories according to which life on those planets where it does exist could arise not necessarily of its own accord. It is not unlikely, as these theories argue (one such theory was advanced in his time by Arrhenius),

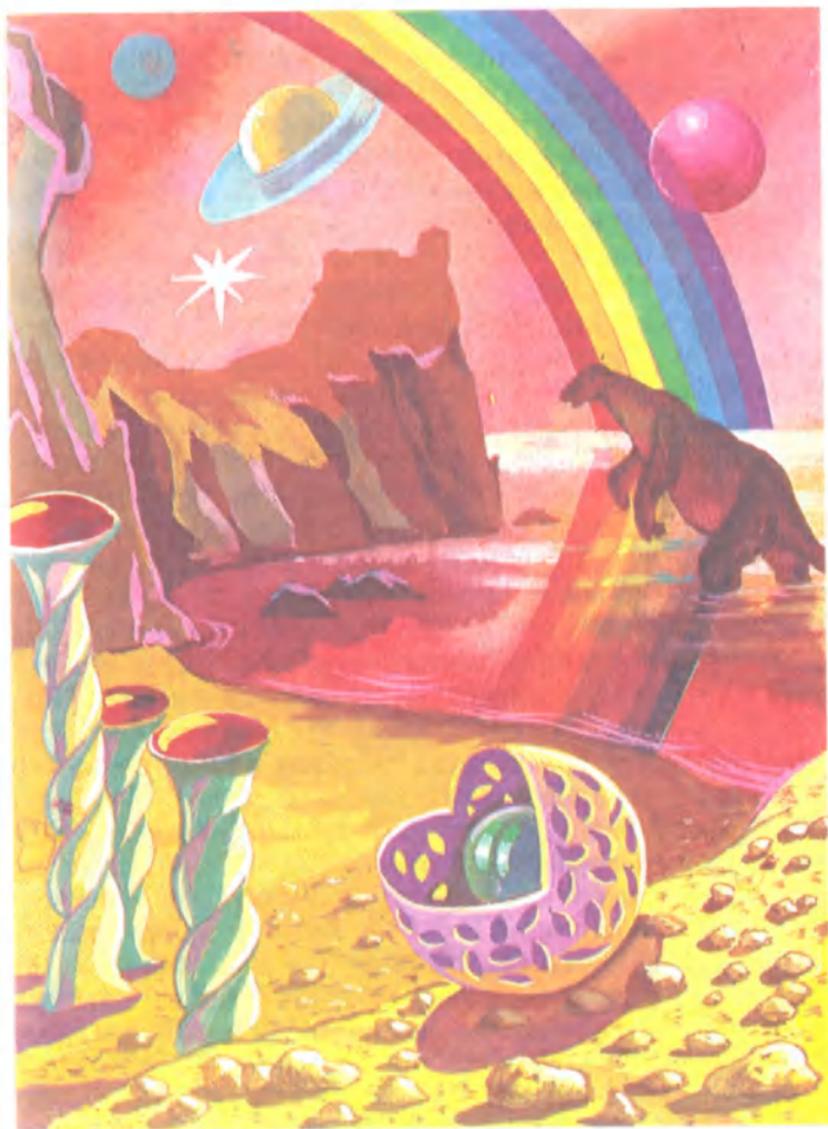


Fig. 27.

that meteorites or specks of interstellar dust could have brought with them some spores which could have given rise to life on a particular planet. But even if such theories are correct, this does not relieve us of the necessity to define the conditions that must exist for the spontaneous synthesis of living matter to take place. For it must have come into being somewhere at least once.

**Physical Conditions.** Let's explore what combination of physical conditions could favour the synthesis of living matter. We have the choice of three alternatives: reactions in a gas phase, reactions in a liquid phase, and reactions in a solid phase, that is, between solids.

Gas-phase reactions may be rejected from the outset for the simple reason that a more or less complex chemical compound cannot exist as a gas or vapour. If we want to convert some compound to a gas or vapour, we must impart to it some excess energy so as to make up for the latent heat of vaporization (see p. 23). As compounds grow in complexity, their molecular mass increases, and they must have a larger latent heat of vaporization. Finally, a limit is reached at which this energy exceeds the bonding energy between the members of the molecules, and the substance simply disintegrates rather than turns to vapour. A reduction in the external pressure can only postpone this outcome a bit, but not avert it. That's why it is an easy matter to convert to vapour the relatively light-weight acetone,  $(\text{CH}_3)_2\text{CO}$ , and this is not so easy with glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ . Nobody has ever succeeded in turning to vapour the simplest of all proteins. And we may add without running the risk of being stigmatized, that nobody will ever do that!

Solid-phase reactions, too, should be ruled out. The reason is simple: it takes a very long time for a reaction between solids to proceed. To begin with, two crystals of two different solids must first come in contact at their

surfaces. When this happens, a reaction does take place, but it lasts a very short time (whatever the rate of the reaction), because it has already used up all the molecules available—there is only one layer of them at the surface, and the reaction stops at that. For the reaction to continue, the reaction products must clear room for “fresh” molecules. This can only happen through diffusion, and diffusion is a very slow process. As slow are the reactions between solids. They are so slow that a crystal of sodium oxide,  $\text{Na}_2\text{O}$ , and a crystal of sulphuric anhydride,  $\text{SO}_3$ , each weighing about one gram, would take no less than 1 200 million years to react and form  $\text{Na}_2\text{SO}_4$ .

So, if the reactions involved in the synthesis of living matter proceeded in the solid phase, all of the time during which the Universe is in existence would not be enough even for the earliest phases in the synthesis to take place. This leaves us with the only choice: liquid-phase reactions, or, which is the same, reactions in solutions. We have derived this condition with absolute confidence.

**Chemical Conditions.** For a reaction to go on in a solution, we need a suitable solvent or a suitable mixture of solvents. “Suitable” does not sound definitively, so let’s fill it with something concrete.

To recapitulate, the molecules that are the basis of living matter are complex, very complex forms. As to their origin, they could only arise from a very long chain of diverse chemical reactions—we stress the word “diverse”.

Now let’s believe for a moment that Captain Yone Tikhy has discovered a planet where life has arisen and evolved on the basis of liquid ammonia, and not water.

Now we shall try and picture to ourselves how the chemistry textbook for the kids on that planet might look like. From our view-point, it would look very strange indeed. Almost all of its pages would describe acids, and only a few lines in small print would be devoted to bases. Strange as it might look to us, this division of the subject-matter would be only too natural – on that planet. The point is that in ammonia which is a strong base nearly all solutes would behave as acids. For any substance to act as a base in ammonia, its basicity must be in excess of that of ammonia. Such compounds are very few and far between.

For the same reason, the reactions in liquid ammonia cannot be diverse: nearly all the solutes would behave in it as acids. If so, the very complex molecules needed to serve as the basis for living matter could not form spontaneously in such a solvent.

Couldn't it then be that the right answer comes from the sci-fi writers who believe that life can arise on the basis of liquid hydrogen fluoride which, it should be recalled, is a very strong acid. Unfortunately, this case holds no more than that of liquid ammonia.

In liquid hydrogen fluoride, an absolute majority of solutes would act as bases, and the number of those acting as acids would be negligible. So, this solvent, too, must be struck out of the list of likely "life-giving" contestants. This also goes for all other strong-base and strong-acid solvents.

Now we can formulate one of the chemical conditions that a "life-giving" solvent must satisfy. It must be "bipartisan": it must have an about equal number of both acids and bases. Of course, no chemical dictionary lists the word "bipartisan" among its entries – its chemical counterpart is "amphoteric". In short, a "life-giving" solvent must be amphoteric, that is, it must be able to act as an acid or as a base, as the case may be.

This requirement to be amphoteric reduces the number of likely contestants still more. Apart from water, the most known of all amphoteric solvents, this group includes alcohols and acetone.

With a stretch of imagination, we could, of course, cover our planet with seas and oceans of ethyl alcohol, but that would be a plunge into that part of the literary art which has many adepts, but has nothing to do with science.

Another condition that a “life-giving” solvent must satisfy is to be capable of dissolving many things and of doing that well. It must be able to dissolve organic and inorganic compounds because a huge multiplicity of both had been involved in the long chain of chemical reactions that finally led to the spontaneous synthesis of living matter.

We’ve already mentioned alchemists’ futile search for a universal solvent. And that solvent was always close at their hands. Of course, that was water, the very water which can dissolve very many, if not all, things.

Water is a good solvent because it has a high dielectric constant (see p. 26). Water is a good solvent also because its molecules make up the hydrogen bond with the molecules of the solute.

Our list of likely contestants for the title of a “life-giving” solvent has now shrunk to only one entry. That’s water. Yes, water, and water alone.

We could add many more, nonchemical points in favour of water. An important one is that, to believe astrophysicists, hydrogen is among the most abundant elements in the Universe, and oxygen is among the most stable. That’s why water is highly likely to form on the surface of a cooling planet. Water, and not ethyl alcohol, because the spontaneous synthesis of water is thermodynamically more advantageous than that of ethanol.

This book would seem incomplete if we failed to touch at least in brief on the future of solutions in conclusion.

**Solutions in the Nearest Future.** A story about what the future has in store for the science of solutions and for the solutions themselves in science, technology and industry could fill a book probably as large as this one. So let's indulge a bit in wishful thinking—no, that's a wrong word. Let's picture to ourselves a few very probable scenes from not so distant a future. Let's imagine some of the uses for the main of all liquid solutions that exist on our home planet—seawater.

*Scene One.* A transoceanic liner has just reached its destination. It has cast its anchors at the roadstead, and a small, nimble motorboat pulls alongside. In quick and well-rehearsed movements, the boat's crew removes from the ship's sides some boxes immersed in the water. The boxes are then carried ashore whence they are whisked to a gold recovery factory situated nearby.

A gold recovery factory nearby? But the nearest gold fields are thousands of kilometres away. Do they bring in gold rock from away to work it here? But where do the boxes removed from ship's sides come in then?

At the factory, the boxes are emptied of their contents—a gray, cottonwool-like, rather unattractive mass which is immediately incinerated in a muffle furnace. Almost all of the mass burns to ash which is an indication that the mass is organic in origin. Buried in the ash are dull beads which are collected with utmost care and, I'd say, reverence. This is a well-deserved reverence because the beads are gold, and a very pure gold at that.

This is how gold can be extracted in a very interesting (of course, interesting) process from seawater. It has long been known that seawater contains gold and, in fact, nearly all the other elements listed in the Periodic Table.

It has also been long known that the concentration of gold in seawater is extremely low: around one hundred-thousandth of a gram per tonne of water. Of course, gold could be extracted from seawater in the usual way, but that would require to process 100 000 tonnes of seawater in order to extract one gram of gold. I won't go into detail, explaining what the word "process" means, but you can believe me that it means a lot of things.

It is for some time now that chemists have been using special substances called ion exchange resins. In an aqueous solution, they are capable of donating its cation (say, a hydrogen cation) and accepting a metal ion from the solution. The ion exchange resins known today can remove from solution any cation present there. So, if we place an ion exchange resin in seawater, it can remove metal cations from it, but only in amounts proportional to the concentration of those metals in seawater. That's why an ion exchange resin will remove from seawater only sodium and, to a smaller extent, magnesium, but gold will remain in solution.

Laboratories all over the world are working today on ion exchangers that would be selective in their action, that is, would remove from solution only one definite cation, say, gold. Such an ion exchanger is to be developed yet, but its appearance is round the corner, because there is nothing in it that would run counter to the laws of Nature. If so, it is a sure bet that seaports will certainly have gold recovery factories of their own.

*Scene Two.* The press learns the whole thing at the last press conference held by the yacht's crew just before they are to put out to sea on a round-the-world voyage.

"Not a drop of fuel, you say?" wonders a reporter.

"No, not a drop, sir", nods the captain.

“Then why these engines?” asks another reporter in half-bewilderment.

“They will propel us by burning hydrogen”, says the captain.

“Which you’re going to produce from water?” notes the reporter tauntingly.

“Right, sir”, says the captain curtly.

It remains to tell you what’s all about. To produce hydrogen from water is a simple job. But to do this, you must have a source of electricity or a supply of some substance, such as sodium, which would react with water to release hydrogen. Obviously, to supply enough hydrogen for the yacht’s engine on a round-the-globe voyage would require far more than a couple of storage batteries or a kilogram of sodium. This job needs a huge power station or a tonne of sodium. Nevertheless, the captain has told the truth.

His yacht is propelled by hydrogen produced from seawater by the traditional process of electrolysis. But the energy needed for the operation comes from the Sun. Suitable devices convert solar energy directly into electricity.

In theory and, to some extent, in experiment, such devices already exist today, and tomorrow they will do their job in earnest. Then seawater, one of the many solutions, will supply huge amounts of energy so unusually transformed from solar light.

The two imaginary scenes might be followed by a third, a seventh, and so on. Because there is no limit to the uses of solutions.

Almost every researcher working in some field of science is sincerely convinced that his problem is most important and most intriguing. This conviction is often ridiculed—unjustly. Without conviction to support you and without enthusiasm to motivate you, hardly anything—or even nothing—can be achieved in science.

Solutions, so limitlessly important in science and everyday life, deserve closest attention. That's why the science of solutions has always been, is, and will always be one of the most exciting fields of the natural sciences. Because this problem is most important and most interesting...



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Fialkov's interests are centred around the chemistry of solutions and radiochemistry. He has devoted over 200 publications, including 4 monographs, to these problems. He is a member of several Learned Councils within the USSR and Ukrainian Academies of Sciences. He also is an active popularizer of chemical sciences. His popular science books turned out by the 'Detskaya Literatura' Publishers have been translated into many languages spoken in the Soviet Union.