

Solutions

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In chemistry, we often take a lot of random things for granted. For example, I'm sure you've seen a test paper with questions like "Bauxite of 10g in a rock" or "10 ml of Benzene in a beaker". Unfortunately, we don't see too many examples of these chemicals sitting around in this isolated fashion. The water in our taps have impurities and even commonly used metals don't have pure iron. Typically we use steel, which is an alloy of iron and other metals and sometimes even non-metals. And this can be good or bad. We may want some pure compound and be left with impurities or we may purposefully engineer this mixture to be this way for some particular purpose. For example, if we want to make a drill bit or a power saw, I wouldn't use plain iron, I'd try to make an alloy that would work under high-speed conditions. I'll throw in some carbon and tungsten and vanadium and make an alloy known as High-Speed Steel. Similarly, aqua regia is another setup where you want HCl and HNO₃ thrown in together.

So, what I want to do is keep bringing up these examples because I think you know how these are useful. These, by the way are examples of solutions. And now I'm sure you kinda know what the word 'solution' is, but let's give it a formal definition so that we're on the same page, right? I'll first state the formal definition and then we'll break it down to really get a sense of what it means, all right?

Solutions are homogeneous mixtures of two or more components

So, let's try to give this meaning. Homogeneous essentially means if I take a small component of the solution, it should be representative of the entirety of the solution. And that obviously implies that if I have aqua regia, sure you have 3 parts HCl and 1 part HNO₃, but they're spread out equally. So if I take a pipette and pipette out 1 ml of this solution, That 1 ml will also have HCl and HNO₃ in 3:1 ratio. And this should be true no matter where I pipette this out from in the solution. So, that's what homogeneous means, and hopefully you get what a solution means from this. We'll primarily look at binary solutions, because they're easy to analyse and you can always extrapolate these principles to get to solutions with multiple components.

Now, as physical chemists, our first job is always to start with "what" and "why" just like any other chemist. But what really separates us from the organic and inorganic fellows is to ask the question "how much", and I'm sure you can guess that in the context of solutions you really want to see that we're looking at how much one component in the solution exceeds the other in quantity. So when you have two components, we might as well label them so that we can easily identify them. We call the component which is more abundant than the other one as a 'solvent' and the one which is comparatively less in quantity as 'solute'. Now, our goal is to define our metric for "abundance". And our metric is concentration. There are plenty of ways to express concentration.

1 Methods of Expressing Concentration

1.1 Mass Percentage

The mass percentage is something fairly easy to understand. So basically, our assumption for now is that we prepared the solution ourselves. So let's say we were methodical when we prepared this solution and we put in the effort to record how much of each substance we threw into the solution. If I did this measurement with a weighing scale, I could more easily use mass fraction or mass percentage as a good unit of concentration. So say I chucked 2g of methane and 2g of ethane into a gas chamber and I want to get a sense of how much methane is there. Sure, you can say 2g, but that doesn't tell me much. I analyse the chemicals inside the chamber and I see ethane and methane and it doesn't feel as though 2g really represents what methane's purpose is in that chamber. So what we'll do is find out what percentage of the total mass is provided by methane. So that's 2g divided by the total mass times hundred, right? Now, we can ask ourselves the question again. I analyse the components of the chamber and I use the mass percentage metric and I say 50 percent of all the mass in the chamber is provided by methane and I say "Hey! That seems to tell me what methane's actually doing there". Also, this further tells us why our homogeneous idea is so important. Because instead of having a grand total of 4g, I had a grand total of 26.89 grams, the solution will behave the same way only if "50 percent of the contents is formed by methane". So the concentration allows us to represent how much one quantity is present in the solution, which is one of the parameters which affects the properties of this solution.

1.2 Volume Percentage

Volume percentage is fairly similar to mass percentage. If we were similarly methodical to how we were in the mass percentage context but instead of measuring with a weighing scale, we measured with a beaker, we would instead consider volume percentages. So, assume I'm a chemical engineer working for Castrol and I'm trying to design a new bike fuel which gives more mileage. So I decide to throw in 2ml of ethanol and 8ml of liquified ethyne in my chemical engineering lab. So, this fuel, as you can probably guess is 20 percent volume/volume ethanol, which means that 20 percent of this solution is ethanol. Now, say I submit the results of my laboratory test and the company executives find that this is a feasible fuel. They're probably going to want to mass produce this chemical. So they tell the specifications to all the factories. Are they going to say the fuel is "2ml ethanol and 8 ml liquified acetylene"? No! They're obviously going to say 20 percent by volume ethanol and 80 percent by volume acetylene. So, now I hope you see why we use volume by volume percentages.

1.3 Mole Fraction

Mole fraction is again the same thing as the last two examples. You're methodical, so you measure something and then you check how much of the given sample is present as a fraction of the total amount of sample. So, here instead of taking mass or volume, we take moles because they're a good metric of measuring amount of the reactant that's going off or the amount of product that's getting formed.

1.4 Molarity

Molarity is one of the most commonly used methods to evaluate concentration. It's defined as the number of moles of the solute per litre of the solution. So, the reason why we use molarity is because we often take things in terms of moles as they're a convenient metric for reactant decay or product formation. The point of molarity is basically to say if I take 5 ml of some solution, how many moles of each component do I really have? And that's the point of molarity here, it's to find out how many reacting packets you have in some volume of the solution.

1.5 Molality

Molality is another system where we utilised the number of moles. However, in molality the point is to try and identify the number of moles of the solute per kilogram of solvent. Not solution, but solvent. And this might seem overall confusing to you, I mean why would we take 1 kg of solvent? If we extract 1 kg of solution, we're not sure about how many moles we have. So for now, I'm not going to try and explain why we use this so much. By the end of this chapter, I hope you will come to terms with me and see why molality is enormously useful, though.

2 Vapour Pressure, Raoult's Law and Henry's Law

I'm going to quickly define Raoult's Law and then we'll try to spend some time and try to identify it by breaking the definition of Raoult's Law down into the complicated jargon that forms it.

Raoult's Law states that for a solution containing two miscible liquids, the partial vapour pressure of each component of the liquid is proportional to the mole fraction of that component, given that the solution is ideal

So, to understand this definition, we need to understand what vapour pressure means, what miscibility means and what ideal means.

2.1 Vapour Pressure

Before introducing Raoult's Law, I want to give you an introduction to the notion of vapour pressure and before doing that I want recapitulate the meaning of physical equilibrium between a liquid and a gas. A closed system containing a solution is said to be in equilibrium when the rate of evaporation of the liquid solution is equal to the rate of condensation of the gaseous phase. And Vapour pressure is defined as the pressure exerted by the vapour on the solution when the solution is in a closed system. The most important thing to understand, and let me make this clear, this is super intuitive is that when the vapour pressure of the liquid is equal to the atmospheric pressure, the solution is said to have reached boiling point. Hopefully this makes sense to you. The point is basically that the vapour being chucked out from the solution is as good as the atmospheric air and so this is essentially an upper bound on the vapour pressure.

2.2 Miscibility

Miscibility implies that two liquids can wholly mix with one another to form a homogeneous setup. So, oil and water can't be considered miscible because the oil liquid and water liquid don't integrate with one another to form one wholesome liquid setup. You can separate oil and water using a separating funnel and hence you know that they are non-miscible.

2.3 Ideal Solutions

So, let me take some time to tell you what ideal means, because essentially an entire half of the chapter will be misunderstood unless ideality is fully understood. Say I'm trying to make a binary solution with a compound A and compound B. I'm certain you're familiar with the notion of compounds interacting with one another, either by weak or strong forces of interaction. A solution is considered to be ideal if three conditions are satisfied:

1. $\Delta H_{mixing} = 0$, implying no heat change in mixing
2. $\Delta V_{mixing} = 0$, implying the sum of the volumes of the sample A before mixing and sample B before mixing is equal to the volume of the solution
3. A-A interaction = B-B interaction = A-B interaction. This means that the forces of attraction that A has with other molecules of A is similar to the forces of interaction that B has with other molecules of B, which is in turn similar to the forces of attraction that A has with molecules of B.

2.4 Raoult's Law

In the beginning of this section I already described Raoult's Law and the concepts behind it and we got to see what each part of it is like. But I'll state it again so that you can get the whole concept behind it again: Raoult's Law

states that for solutions containing two or more miscible liquids, the partial vapour pressure of each component is directly proportional to its mole fraction, given that the solution is ideal.

What ends up happening is that the proportionality constant is the total pressure. So we find out that the partial pressure of A is simply the mole fraction of A multiplied by the vapour pressure of pure A.

$$p_A = X_A P_A^o$$

I hope this makes sense. The point that we're trying to convey is that the mole fraction is the amount of the solution which is A and so, that amount of A behaves like P_A^o .

From Dalton's Law of partial pressures, we know that the total vapour pressure of a solution is equal to the sum of the partial pressures. This gives us the relation:

$$P_{total} = p_A + p_B$$

$$P_{total} = P_A^o X_A + P_B^o X_B$$

Mole fractions of Gas Species

If we let χ_A and χ_B are the liquid phase mole fractions and y_a and y_b be the gas phase mole fractions, we have to find out some relation to determine the relation between y_a and y_b . Well, there's a certain neat law we know which tells us a lot about gas phase partial pressures, right? It's called Dalton's Law! Which tells us that the total pressure is a sum of the partial pressures of individual components. Which means that if the partial pressures of gases A and B are p_A and p_B , then $p_{total} = p_A + p_B$. But logically, y_A represents how much of the total amount is A. So,

$$p_A = p_{total} y_A$$

And we also know what p_A is from Raoult's Law. On substituting, you would get: $y_A = \frac{\chi_A P_A^o}{\chi_A P_A^o + \chi_B P_B^o}$

2.5 Deviation from Raoult's Law

Naturally it's going to be super hard to find a bunch of compounds that really satisfy this whole ideal solutions business, so we find out how to talk about cases where A-A is stronger than A-B or A-A is weaker than A-B. In the first case, where A-A or B-B could be stronger than A-B, what happens is that the observed vapour pressure is higher than the vapour pressure in the case that the solution had been ideal. Hence, this is known as a positive deviation from Raoult's Law. Similarly, if A-B is stronger than A-A and B-B, then the vapour pressure is obviously less than the ideal case and hence this is termed as negative deviation from Raoult's Law.

Azeotropes

An azeotrope is a very simple concept to understand. Essentially, if we have high positive deviation from Raoult's Law, i.e., A-A or B-B is much greater than A-B, this sort of setup after a given temperature starts to evaporate in a manner by which both A and B vapourise together equally. So, they can only be separated by fractional distillation upto a certain extent, which is fairly high. For example, methanol and water showcases positive deviation from Raoult's law, but ethanol can be separated and forms a 95 percent pure solution of ethanol, beyond which the vapour will have the same composition as the liquid solution itself. This is known as a minimum boiling azeotropic mixture. Similarly, in an azeotrope with negative deviation, what happens is that A-B interactions are stronger than A-A and B-B and so you form what is known as a maximum boiling azeotropic mixture, where you still can't separate out the A from B by distillation alone.

Henry's Law

Henry's Law is not really too related to Raoult's Law, but I appended it to this section because there's not too much to it. Henry's law basically states that the amount of gas dissolved in a definite volume of liquid at constant temperature is directly proportional to the partial pressure of the gas at equilibrium. This law is valid if and only if the gas is non-reactive with the solvent. Mathematically:

$$p \propto C$$
$$p = K_h C$$

The units of K_h depends on the units of C. There are enough measures to determine concentration which we have already detailed essentially if you take the unit of pressure multiplied by the inverse of the concentration unit, we would get the unit for Henry's Law constant K_h .

3 Colligative Properties

Colligative Properties are properties which are determined by the number of particles sitting in a solution. For example, if I throw in a molecule of glucose into water, glucose is going to act as one particle. However, if I throw in one molecule of NaCl into water, the polar medium of water is going to allow the NaCl to break into Na⁺ and Cl⁻ ions. Now each ion can act as independent floater around the system. Here the number of particles is 2. Usually however, we assign this number 1 or 2 to one mole of NaCl or one mole of glucose, but I'll get to the formal details later.

3.1 Relative lowering of vapour pressure

Relative lowering of vapour pressure is the first on the list of colligative properties because it's fairly easy to understand and conceptualise. So, the question is what is the change in vapour pressure of the solution? Which is basically

saying what is the difference between the vapour pressure of the solution and the vapour pressure of the pure solvent? We can math this out to find our answer. Let A be the solvent and B be the solute. Note that here, the notation X_i represents the mole fraction of component i.

$p_A = P_A^o X_A$ We know this from Raoult's Law.

$p_A = P_A^o (1 - X_B)$ A simple exercise for you to prove that $X_A + X_B = 1$

$p_A = P_A^o - P_A^o X_B$

$P_A^o - p_A = P_A^o X_B$

Here, $P - p_A$ tells us the change in vapour pressure from the pure P_A^o to p_A which is the A part of the total and the total as we know is not purely A.

If we divide on both sides by P_A^o , we get the relative lowering of vapour pressure to be the left hand side.

$$\frac{P_A^o - p_A}{P_A^o} = X_B$$

Van't Hoff Factor

Before we can move on any further, we need to introduce a new interesting term represented by i , known as Van't Hoff Factor. As we stated earlier, Colligative properties are properties which are determined by the number of particles sitting around. So we need some quantitative way of representing that. And our way of doing that is through the Van't Hoff factor. Essentially the Van't Hoff factor is the overall number of particles sitting in the place as a function of one mole of the given solute. So, essentially the point is if I'm chucking 1 mole of the solute into the solvent, i is the number that tells me the number of particles floating around. So, what might really freak you about the number i is that because of this whole "per mole" business, i doesn't necessarily have to be a whole number. I could have i be 4.20 or 0.69. And the reason that's the case is because compounds don't fully decompose all the time. What happens is that per mole, half of it becomes 2 particles and the other half remains as one particle. So, at equilibrium, you end up getting $0.5 * (2) + 0.5 * 1 = 1.5$. This is known as dissociation. Similarly, there's another thing known as association where particles bunch up together. This is where things get weird as well. So if I throw in 1 mole of a compound, half of the species gets associated to form a dimer and the other half just stays as the regular compound, what you get is $i = 0.5 * (0.5) + 0.5 * 1 = 0.75$.

3.2 Elevation in Boiling Point

So, this is a fairly easy notion to grasp. So say I toss some NaCl into water, what happens is that the Na^+ and Cl^- ions split up and swirl around in the water environment. And water is polar, so it really likes inviting these positive and negatively charged species into its house. Now, evaporation is like catching a flight. And the surface is like an airport. So, for water molecules to evaporate, they have to go all the way up to the top and then "catch the flight", which essentially means that they have to jump off from the surface and become a

molecule of vapour. But when you have guests at home, you have to make them comfortable. So, water is too busy frivolously mingling with the guests at home and kind of forgets to catch the plane. So what happens is you need to apply some extra heat to get the water molecules to jump up to the top and jump out. And naturally, had you used AlCl_3 instead of NaCl , you'd have 4 particles and with more guests at home to interact with, water needs even more incentive to catch the flight. The point is, you need to add more heat to pull water molecules apart from the guests at home and take him to the airport. So the overall average energy at the point where water is boiling, is higher, right? So this is the effect called elevation in boiling point.

And you can try to guess what the formula for this is like. It obviously is going to incorporate the Van't Hoff factor and it's obviously got something to do with the solvent itself. And on top of that it should have something to do with the batch size, right? If I have a larger setup for the same property, you want to know how much is happening.

$$\Delta T_b = iK_b m$$

m is the molality, which sort of gives you the batch size. K_b tells you the solvent property, this is calling the Ebullioscopic constant and i is the Van't Hoff factor. ΔT_b is the change in boiling point.

3.3 Depression in Freezing Point

If boiling is the process of catching a flight, you can think of freezing as going to bed. If guests are at home, you tend to stay up late and chat with them rather than going to sleep. So the point is that water spends too much time interacting with Na^+ and Cl^- and hence it's all jumpy and happy. So you have to go there and be a real killjoy and suck out even more energy from it to get it to freeze up. So at freezing point, the overall energy is lower and hence the temperature is lower. So you have to go to a lower temperature to get water to freeze. And again, you have the same effect with AlCl_3 as before, where there are 4 particles, so more guests and hence you need to really drain out the energy for water to go to sleep and freeze.

3.4 Osmotic Pressure

Osmosis is the flow of solvent into the solution when the two are separated by a semi-permeable. When there is a concentration gradient, osmosis is incentivised to occur. We represent the osmotic pressure using π because we use p for vapour pressure. Don't accidentally substitute π to be 3.14 or something, because it's not the same pi. We're using pi as a variable here. So the thing about osmotic pressure is that it behaves very similar to diffusion of gases. So, I'm going to tell you something you sort of have to take for granted, which is basically that gas laws are fairly obeyed by the solutions in the osmotic frame. By our gas laws, we know that $P \propto \frac{1}{V}$. And, additionally, we also know that the inverse of volume gives us concentration, right? Sure, you need moles, but for the most

part, we can say that we get concentration from inverse of volume. So this gives us the relation $P \propto C$. We also know that $P \propto T$ from gas laws.

We also know from the fact that we're using colligative properties that Van't Hoff factor is going to be linked here. And our proportionality constant ends up being the gas constant R. So overall, we get:

$$\pi = iCRT$$

And this is basically all you need to know about osmotic pressure.

Problems

Ex 1. 18g of glucose ($C_6H_{12}O_6$) is added to 178.2g of water. Calculate the vapour pressure of water for this aqueous solution.

Ans. Vapour pressure of pure water = 760 mm of Hg. Relative lowering of vapour pressure = mole fraction of solute.

$$\text{Mole fraction of solute} = \frac{\text{moles of solute}}{\text{moles in solution}} = \frac{\frac{\text{mass of glucose}}{\text{molecular mass of glucose}}}{\frac{\text{mass of water}}{\text{molecular mass of water}} + \frac{\text{mass of glucose}}{\text{molecular mass of glucose}}} = 0.01$$

$$\frac{760 - p}{760} = 0.01$$

$$p = 760 - 7.6 = 752.4 \text{ mm of Hg}$$

Ex 2. Which of the following show positive deviation from Raoult's Law?
 (a) Carbon Tetrachloride + Methanol (b) Carbon Disulphide + Acetone (c) Benzene + Toluene (d) Phenol + Aniline

Ans. Positive deviation from Raoult's Law implies that A-A or B-B is stronger than the A-B interaction. In (a) we have CCl_4 and Methanol. A methanol molecule will show hydrogen bonding with another methanol molecule and hence B-B in this case is stronger than A-B as there is no hydrogen bonding between methanol and carbon tetrachloride, so it will show positive deviation. In (b), acetone has intermolecular forces of attraction due to dipole-dipole interaction. Again B-B is stronger than A-B. In (c), Toluene and benzene are fairly similar in nature and there is no reason in particular why they shouldn't form an ideal solution. One could argue that toluene-toluene interactions are stronger as toluene having one extra methyl group could probably lead to more Van Der Waal's forces of attraction or that benzene-benzene interactions are stronger because there's no methyl group hindering the molecules coming close to each other, but those are fairly loose and not concrete reasons. Benzene and toluene form an ideal solution. In (d), phenol and aniline both show hydrogen bonding. However, phenol has an acidic hydrogen and aniline has a basic N

group, so phenol aniline interactions are probalby stronger than phenol-phenol or aniline-aniline, hence A-B stronger than A-A or B-B, so this is negative deviation.

Answer is (a) and (b).

Ex 3. Acetic acid forms a dimer in benzene. If freezing pt decreases by 0.45K, when 0.2g of acetic acid is added to 20g of benzene, find the percentage association of acetic acid. K_f of Benzene = 5.12 K kg / mole

Ans. 0.2g of acetic acid corresponds to $\frac{0.2}{60} = \frac{1}{300}$ moles of acetic acid in 20g of benzene. By unitary method, this corresponds to $\frac{1}{6}$ moles of acetic acid in 1kg of benzene, which is molality. Hence, molality = 0.16667. We know that, $\Delta T_f = i K_f m$. By rearranging, we find $i = 0.527$. Assume we take the initial amount of acetic acid to be 1 (as reference) and that alpha amount of acetic acid dimerises. Since we are talking in terms of moles, if alpha amount of acetic acid gets dimerised, the right hand side will have alpha/2 moles (write the equation to see). So the total number of moles at equilibrium is $1 - \alpha/2$, which is basically i as i represents the number of particles. So $1 - \alpha/2 = 0.527$, giving us $\alpha = 0.946$. Implying 94.6 percent association.

Ex 4. If a solution of 0.1 M sodium chloride has osmotic pressure of 200 kPa, find the temperature at which measurement was made.

Ans. $\pi = iCRT$ $i = 2$, $C = 0.1$ and $\pi = 200$ Pa, $R = 8.314$. Rearrange in terms of T. $T = 120.279K$.

Challenge Problem : The vapour pressure of two miscible liquids A and B are 300 and 500 mm Hg respectively. A flask is taken and 10 moles of A and 12 moles of B are mixed. A starts polymerising into a completely insoluble liquid. Polymerisation follows first-order kinetics. After 100 mins, 0.525 moles of a solute is dissolved which arrests polymerisation completely. The final vapour pressure is 400mm Hg. Estimate rate constant of polymerisation reaction. Assume ideal behaviour of initial and final solution. (Try this problem after you learn Kinetics).