

Environmental Quality Monitoring Analysis
Physical and Chemical properties of interest
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Lecture – 7
Introduction to Equilibrium

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Characteristics of chemicals of concern.

1. Aqueous Solubility, mg/L
2. (Saturated) Vapor Pressure, mm Hg, ...
- 3.

The diagrams illustrate concepts of solubility and equilibrium. The first diagram shows a beaker with a substance at the bottom, labeled 'Water'. The second diagram is a graph of concentration C versus time t , showing a saturation curve with C^* marked. The third diagram is a flow diagram showing 'Pure Substance (A)' in equilibrium with 'Water'.

So now, will go back to the characteristics of some of the Chemicals. So, we are talking about physical and chemical characteristics of the chemicals now. So, so we are looking at the physical properties. From a fate and transport point of view, when we have already setup the problem, what could be what is our area of interest what is it that you are interested? We are interested in chemicals entering water, we are interested in chemicals entering air, chemicals entering plants and animals, soil, sediment and all that.

So, there are some properties of chemicals that are of interest to in this context, ok. So, which are these properties that are affected. So, straight away can you what is one of, what is what are the properties that could be of interest? If I gave if I give a name of chemical and if I ask, is it going to be health hazard in water, what is your first first question or response?

Students: solubility

Professor: What is the?

Student: solubility

Professor: what is the solubility? So aqueous solubility is usually referred see we are going to be in this class, we are going to be using absolute units.

We are we are going to be using units, no. We will try to refrain from any other we will use absolute units like this milligram per litre or gram per litre or some such things. Typically, we will use milligram per litre or unit like that even further so this is what Aqueous solubility. And then, like Aqueous solubility if corresponding to air.

Student: vaporization

Professor: what?

Student: Vaporization

Professor: vaporization. So what's the property of a chemical that indicates how vapour it is?

Student: vapour pressure? volatility? Vapour pressure?

Professor: volatility, yeah. So, vapour pressure or saturated Vapour pressure you can call whatever you want.

So vapour pressure is we will again give it as milligram per litre but you can also have other units, we can people describe it as Pascal, millimetres of Hg (mercury) whatever so on. Many units are possible for this. Then what else is important? So, what is what are these two? Aqueous Solubility and vapour pressure, these properties correspond to, correspond to something they can be classified as one particular this this measurements, when do this when how can you, how do you find solubility of a chemical?

Student: we dissolve in water.

Professor: You put it in water and then, how do you measure, because you are measuring it when you know it's reached solubility? If I am trying to find out solubility of a chemical in water is there a small experiment I can do? what what should I do?

Student: precipitate formation.

Professor: ah?

Student: with precipitate forms after certain time.

Professor: Solubility, we are talking about solubility, dissolving, you take a pure substance is put into water it will dissolve. We are trying to find out what is this aqueous solubility. What is this solubility this number how do you find out?

Student: concentration,

Professor: Ah, concentration when?

Student: till saturation

Professor: till saturation, how do you find out saturation?

Student: precipitation

Professor: precipitation

Student: before precipitation

Professor: no we are starting with pure substance if I take salt or sugar and I put it into water and I am trying to find out what is the solubility of salt and sugar. What you are talking about you are salt solid is already there. I am asking you what is the solubility limit based on that. Suppose I take a kilogram of some chemical dump it into water? What is aqueous solubility? Definition? From a lay point of view what is the aqueous solubility? It is the?

Student: till the point at which the maximum can be

Professor: maximum solubility maximum concentration that it can attain in water, which means if you want do experiment, how will you do it? So when will you when do you know that it has reached maximum? ah

Student: will try with different concentrations

Professor: no, no. it is one concentration, aqueous solubility is one number, right? it's one number. Depending on how people do it, it may vary a little bit. But it's essentially, one number.

Student: actually solubility decreases with temperature as we decrease the temperature, so when we start decreasing the temperature

Professor: No, at same temperature, I am asking about one particular temperature, pressure all conditions how would you get this number?

Student: when concentration doesn't increase

Professor: with?

Student: with addition of more

Professor: no, I think we are going off. So I am I have I have a container. I add a large amount of Solid A and I put water and I start mixing it. I stir it, I stir it. What happens to the concentration of A here,

Students: it increases

Professor: it increases with?

Student: time.

Professor: with time. The concentration increases with time and then when will you reach solubility when do you know it reached solubility?

Student: uniform concentration

Professor: Ah, it will,

Student: it won't change

Professor: so what happens to concentration with time?

Student: constant.

Professor: It will become it will do this at some point. This number is the solubility. What do you call this state?

Students: Saturation

Professor: ah?

Student: saturation

Professor: saturation, is there another word for it? Ah?

Student: Equilibrium

Professor: Equilibrium, what is this equilibrium, what is this equilibrium? Equilibrium is, equilibrium is define is defined between two states, between two particular states. So, what is this equilibrium between?

Students: vapour zone and

Professor: So we are talking about equilibrium of what, in this case? Of this particular chemical A between?

Students: liquid (solid) phase and solid (liquid) phase,

Professor: and a liquid. What is the solid phase?

Student: solid

Professor: In this case, what's the solid phase?

Students: solid A

Professor: We are looking at the equilibrium of A between water and what is the solid phase?

Student: particles

Professor: of what? There is a very specific definition of this, very important.

Student: solid solute

Professor: What is this solid phase? This is what?

Student: undissolved

Professor: ah, it is made of what? This is pure substance, it is there's nothing else, only A. All of A, your pure A in contact with water so it's equilibrium of A between pure substance and water is solubility. So, equilibrium of pure substance of A between its pure form and air is saturated vapour pressure. So, if you leave something in a in a container and it will rather vapour pressure it will evaporate and it will come to a point where it won't evaporate anymore. So that will be vapour. For example, if you put water in a jar, water will evaporate and it will reach its maximum concentration of water vapour in a jar that is the saturated water vapour pressure of water, at a given temperature and pressure. So these are all conditions for if we

change temperature and pressure this all will change, ok. Thermodynamically the all these will change.

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1. Aqueous Solubility
2. Saturated vapor pressure
3. Henry's Law constant

Diagram: A box divided into 'Air' and 'A+water' with an upward arrow.

Equation: $C_{A,air} = C_{A,water}$

Text: Vapn-Liquid Equilibrium (VLE)

Graph: A plot of y versus x showing a curve.

So we are looking at Aqueous Solubility, Saturated Vapour pressure, two things which are equilibrium of A between its pure form and water and pure form and air, yeah. What's next? What if I dump a large amount of chemical into water all of it dissolves, when it comes in contact with air how much of this will go into air? Now we don't have a pure substance, we have a solution in contact with with air, ok. So if I have a if I have a mixture with A plus water and there is air, how much of A will go to the air if I leave it long enough to go to equilibrium?

So this is the equilibrium between the concentration of A in air versus the concentration of A in water, air and water are in contact with each other and they go to equilibrium? You allow it come to equilibrium. What is that number? What is that ratio? So it is the distribution of the distribution of A between air and water at a given temperature and pressure. What is this general name and what's the specific name here?

There is a general name for this kind of relationship, relationship? It is a thermodynamic relationship. Yeah, yeah?

Student: chemical potential

Professor: Everything is chemical potential. Chemical potential is what we are discussing. What we are discussing is simpler forms of it.

Student: distribution coefficient

Professor: Distribution coefficient yeah, but is there a for this specific system of air and water is there a general name? Distribution coefficient is between any two phases that that is a generalised name, that's correct? We call it as a Partition Coefficient or Distribution Coefficient or one of those terms can be used, yeah.

So, from a Chemical engineering background there is a generalized equation, there is a generalized name this, lot of stuff lot of this thing is drilled into you in your thermodynamic course. Yeah, you look at

Students: relative volatility

Professor: ah?

Student: relative volatility

Professor: relative volatility, no no. It's equilibrium, it's some equilibrium, what equilibrium is this? It is equilibrium between what and what?

Student: Chemical potential

Professor: Chemical potential is a general term but it's equilibrium between what and what? This is called Vapour Liquid Equilibrium or VLE.

It is applied in several things but here, so generalized vapour liquid equilibrium in Chemical Engineering applications extends to a very large range of compositions. But in our case, we are not worried about that. We are worried about evaporation of component from water to air. In this case, the only components which are going to evaporate are organic compounds. Most of the inorganic compound don't evaporate that much, ok. Very few, one or two cases are there.

And there are and we also known as the solubility of organic compounds are very low. So if you look at vapour liquid equilibrium general diagram if it nonlinear also. We are now this is ah, concentration in the aqueous phase, this is the concentration in the gas phase, vapour phase. We are working in this small region here, very small region here which is a linearized version of the vapour liquid equilibrium. And this small region linear region where is the dilute portion of the liquid is known as the Henry's Law constant.

Henry's Law which says that there is this, this linear relationship is very linear. On the other hand, it is called as Raoult's law on the higher end. So, Henry's Law, the definition of Henry's Law constant is very straight forward, simple. It's a partition constant as we describe described. So, it is really the is the ratio of the concentration in air versus the concentration in water. This

is a general definition; this is how we describe. In contact with each other this is the equilibrium ratio in which the concentration in the vapour phase and the liquid phase will distribute itself.

So a compound which has a very high Henry's Law, essentially will a lot of it will go into the air and little will remain in the water, it will partition itself to that extent, ok. In some applications the Henry's Law is reversed where the concentration of water goes on top so you have to watch out for it? And will come to that one of those cases later. In literature, you will find people do all these things for convenience.

For example, if the Henry's Law is very small. Henry's Law is 0.00001 so you don't like to put 0.00001 so you want to reverse it and say Henry's Law is Henry's constant is 1000. But it is the concentration of A in A in water over that of air. It happens in cases where where does it happen, where the partitioning is favourable in water than in air. So in like places absorption where for sulphur di oxide absorption and all that, people use reverse of it.