Material and Energy Balance Computations
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Lecture –56
Energy Balance with Chemical Reactions - VI

Welcome back. So, we were talking about heat of formation of ions. So, this is going to be the last lecture on energy balance with chemical reactions and we are going to talk about a very interesting case of 'heat of mixing'. And after that only one topic remains and that is 'humidity' which we will cover in sort of four lectures. So, we were continuing our discussion with the concept of heat of formation of ions. So, let us have a look into it and first finish it and then we will move on.

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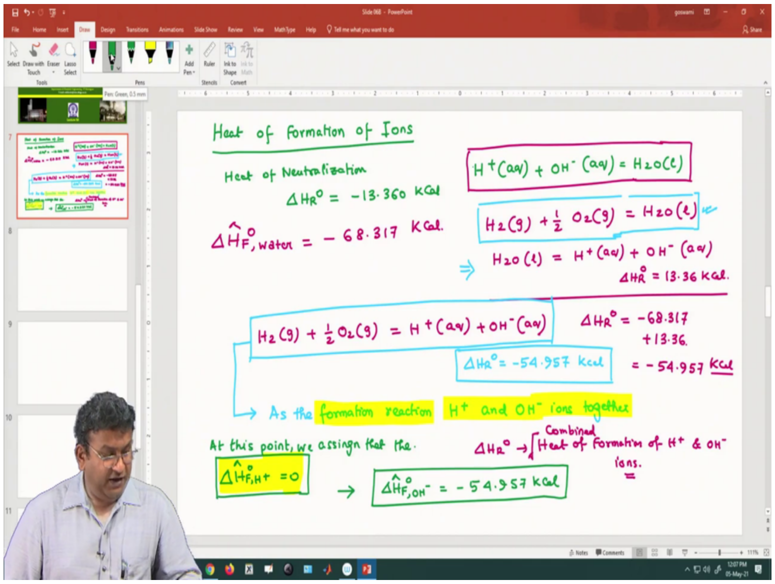

Heat of Formation of Ions

Heat of Neutralization

$\Delta H_R^0 = -13.360$ KCal

$\Delta \hat{H}^0_{F,water} = -68.317$ KCal.

$H^+(aq) + OH^-(aq) = H_2O(l)$

$H_2(g) + \frac{1}{2} O_2(g) = H_2O(l)$

$\Rightarrow H_2O(l) = H^+(aq) + OH^-(aq)$

$\Delta H_R^0 = 13.36$ KCal.

$H_2(g) + \frac{1}{2} O_2(g) = H^+(aq) + OH^-(aq)$

$\Delta H_R^0 = -68.317$
$+13.36$
$= -54.957$ KCal

$\Delta H_R^0 = -54.957$ kcal

→ As the formation reaction H+ and OH- ions together

$\Delta H_R^0 \rightarrow$ Combined Heat of Formation of H^+ & OH^- ions.

At this point, we assign that the.

$\boxed{\Delta \hat{H}^0_{F,H^+} = 0}$ → $\boxed{\Delta \hat{H}^0_{F,OH^-} = -54.957 \text{ kCal}}$

So, I think by now it is clear to everyone that the combined heat of formation of H+ and OH- ions is -54.957 kcal. Now at this point some more assumptions we assign which is the heat of formation H+ ion ($\Delta H_{F,\ H+}{}^0$ cap) = 0. So, if you make this assumption then immediately what follows is the heat of formation of OH- ion is equal to -54.957 kcal. So, again what you must remember just like the steam table had some fundamental basis, whenever you are talking about the heat of formation of any ion that actually rests on this very important fundamental assumption.

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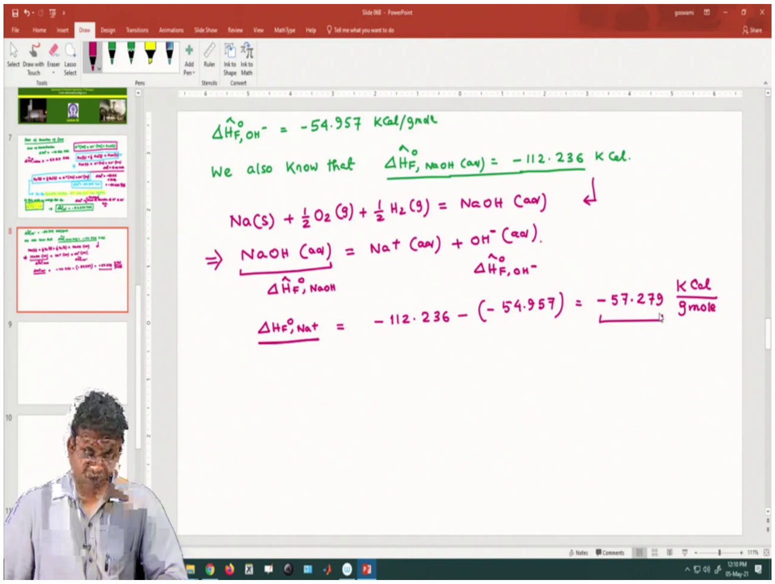

$\Delta\hat{H}^{o}_{F,OH^-} = -54.957$ Kcal/gmole

We also know that $\Delta\hat{H}^{o}_{F,NaOH(aq)} = -112.236$ K Cal.

$Na(S) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) = NaOH\ (aq)$

$\Rightarrow \underbrace{NaOH\ (aq)}_{\Delta\hat{H}^{o}_{F,NaOH}} = Na^+\ (aq) + \underset{\Delta\hat{H}^{o}_{F,OH^-}}{OH^-\ (aq)}.$

$\Delta H^{o}_{F,Na^+} = -112.236 - (-54.957) = -57.279\ \frac{KCal}{gmole}$

So, let us take an example of heat of formation of Sodium Hydroxide (NaOH) in aqueous state is -112.236 kcal. We know that the heat of formation of OH- ion is -54.957 kcal per gram mole. The formation reaction of NaOH is as follows,

$Na\ (S) + 1/2\ O_2\ (g) + 1/2\ H_2\ (g) = NaOH\ (aq)$; $[\Delta H_{F,\ NaOH(aq)}{}^{0}$ cap = -112.236 kcal/gmole]

And, $NaOH\ (aq) = Na^+\ (aq) + OH^-\ (aq)$; $[\Delta H_{F,\ OH-}{}^{0}$ cap = - 54.957 kcal/gmole; $\Delta H_{F,\ Na+(aq)}{}^{0}$ cap =?]

Now again, we know that following Hess law one can write NaOH in aqueous medium gets dissociated into Na^+ and OH^- ions. So, then what one can argue that combining the above two equations, one can argue that the heat of formation of Na+ can be calculated as shown in the above slide.

$$\Delta H_{F,\ Na+(aq)}{}^{0}\ \text{cap} = -112.236 - (-54.957) = -57.279\ \text{kcal/gmole}$$

So, this is more of a concept as I have told already that this is a hypothetical, but an important concept and you should know it. This is how you can go ahead and keep on calculating the heat of formation of more ions. So, for example if you know the heat of formation of sodium chloride and now you know the heat of formation of Na^+. Similarly, you can find out the heat of formation of Cl^- ion also but that you must remember that whatever values of heat of formation of any ion you report that actually rests on this particular assumption.

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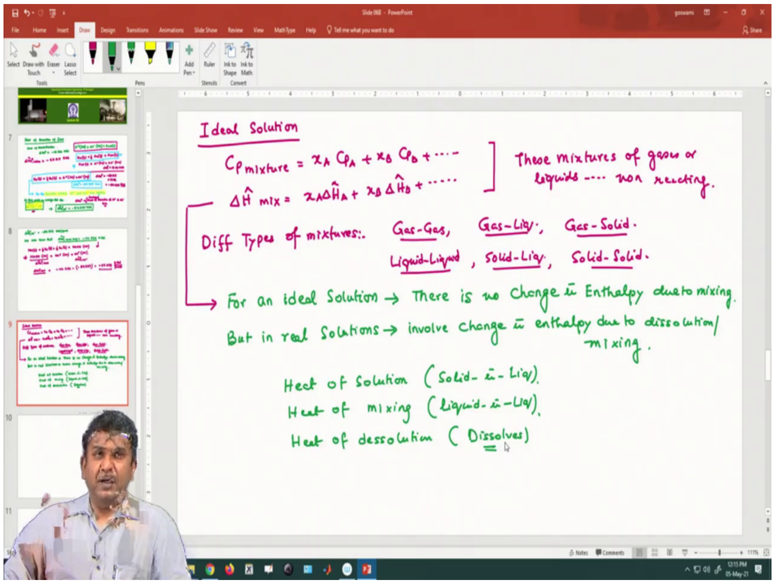

Ideal Solution

$C_{P\,mixture} = x_A C_{P_A} + x_B C_{P_B} + \cdots$

$\Delta\hat{H}\ mix = x_A \Delta\hat{H}_A + x_B \Delta\hat{H}_B + \cdots$

These mixtures of gases or liquids .... non reacting.

Diff Types of mixtures:. Gas-Gas, Gas-Liq., Gas-Solid. Liquid-Liquid, Solid-Liq., Solid-Solid.

For an ideal Solution → There is no Change in Enthalpy due to mixing.

But in real Solutions → involve change in enthalpy due to dissolution/mixing.

Heat of Solution (Solid-in-Liq).

Heat of mixing (Liquid-in-Liq).

Heat of dessolution (Dissolves)

Now let us move on to another interesting topic which is known as the ‘ideal solution’. So, what is an ‘ideal solution’? We have essentially up to this point implicitly assumed that any mixture has its properties as its sum of weighted properties. So, let us say we have a mixture of liquids and we have assumed that the C_p of the mixture, $C_{P\ mixture} = (x_A{*}C_{PA} + x_B{*}C_{PB} + \ldots..)$ and so on. Let us say the enthalpy of the mixture, ΔH_{mix} cap= ($x_A{*}\Delta H_A$ cap + $x_B{*}\Delta H_B$ cap + ……) and so on.

So, in all these cases of mixtures of gases or liquids, we have assumed nonreactive components. So, there can be different type of mixtures; of course, I am not going into all the details. for example, you can have gas-gas mixture, gas-liquid mixture, gas-solid mixture or liquid-liquid mixture (very common), solid-liquid mixture (very common). Solid-solid of course again very common. Stainless steel is the classic example of that. So, all these types of mixtures are possible. In fact, one can also distinguish a gas-liquid mixture and liquid-gas mixture depending on which one is the majority phase. But let us not get into all that. So, any ideal solution is when you mix different components, there is no thermal effect. It does not involve any enthalpy change. So, for an ideal solution there is no change in enthalpy, or no ‘enthalpy of mixing’ exists. But in real solutions, they involve change in enthalpy due to dissolution or mixing. So, let us understand what they are. So, you can have terms like heat of solution typically this is referred to when a solid for a solid in liquid type of a mixture you can have heat of mixing. This is liquid in liquid and heat of dissolution there is also another term it comes from the word something dissolves.

Now before I move on to what is integral heat of mixing or heat of solution. Let me just tell you something about the process of this dissolution. Let us say we all know that sugar dissolves in water and sand does not dissolve in water. So, exactly what happens? This is a question that you might have been following from your school days. When you take a cube of sugar and put it at the bottom of a container having water let us say, you see the sugar slowly dissolves. What exactly happens? Something will dissolve when the molecule of the solute prefers to remain surrounded by the molecules of the solvent. So, when you drop a cube of sugar or even a single grain of sugar which contains thousands of molecules, each molecule is now initially only in contact with sugar molecules and there is the energy of interaction between them which can be van der Waals interaction or whatever. Which is known as the 'cohesive interaction' between the similar molecules. And when these sugar molecules come in contact with the solvent (water). Now, there is another type of interaction that is happening between the sugar molecules and the water molecules. Now, this is called 'adhesive interaction', because this is dissimilar interaction. So, when the strength of the adhesive interaction between the sugar molecules and the solvent molecules become stronger than the strength of interaction between sugar molecules themselves. Then what is going to happen? The particular solute molecule is going to leave the cluster of solute molecules and simply go away with the solvent molecules. So, this is the concept of dissolution. So, when sand does not dissolve, it means that the sand molecules do not want to remain surrounded by water molecules. They would like to prefer in vicinity of other sand molecules. This is the fundamental physics of 'Dissolution'.

Why something dissolves and why something does not? Of course, this can be explained in terms of wettability and number of other factors which I will not cover. And dissolution is something very similar to evaporation. because what happens in evaporation is you have a liquid pool. So, you have a condensed phase and when the molecules evaporate that particular molecule which is taking part in evaporation or which is actually changes phase from the liquid state to the vapor phase. Of course, there is a distribution of energy. So, all molecules in the liquid phase does not have the same level of kinetic energy which we have talked earlier in this course. But evaporation is also aimed at breaking down of a condensed structure. So, same is dissolution. What I mean by 'breaking down of a condensed structure' is initially you take a bath of liquid where the liquid molecules are sort of interacting with each other and once it evaporates now the liquid molecules are dispersed in the vapour phase.

So, typically evaporation takes place between a liquid and a vapour and dissolution takes place either between a liquid and a liquid or a solid and a liquid. So, for example when you take even two liquids, you take in certain cases these two liquids mixture intimately alcohol and water for example. So, what does it mean? So, water molecules do not mind getting remaining surrounded by alcohol molecules or alcohol molecules do not mind remaining surrounded by water molecules. But when you take oil and water, the oil molecules do not want to be surrounded by water molecules and the oil molecules feel that they should remain together. And therefore, you see phase separation. It is very common to see if you pour some oil on water, you will see patches of oil on the water surface. So, the oil molecules remain together they do not penetrate into the bulk of the water phase and therefore they do not dissolve. I hope it is clear to all of you. Acid and water for example is a perfectly dissolvable system which means that the acid molecules prefer to remain surrounded by water molecules but there is some thermodynamic effect or thermo chemical effect associated with such mixing which we are going to talk now.

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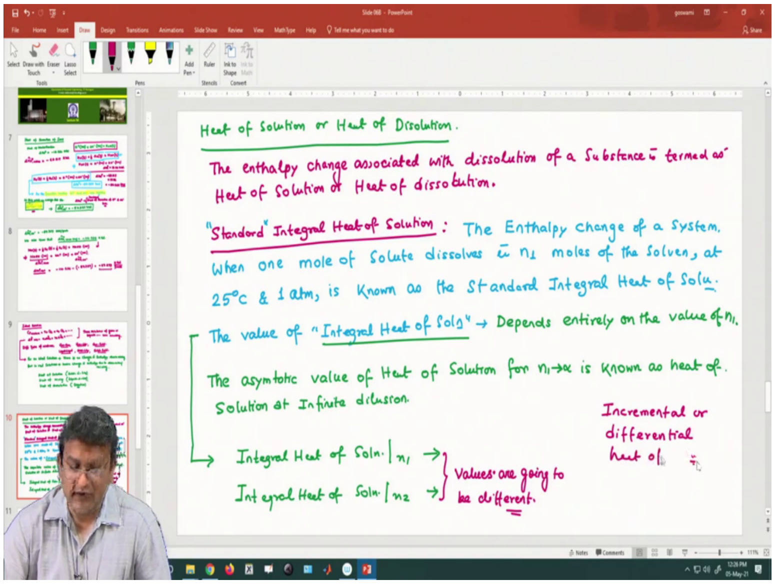

Heat of Solution or Heat of Disolution.

The enthalpy change associated with dissolution of a Substance is termed as Heat of Solution or Heat of dissolution.

"Standard" Integral Heat of Solution : The Enthalpy change of a System, when one mole of Solute dissolves in n_1 moles of the Solven, at 25°c & 1 atm, is Known as the Standard Integral Heat of Solu.

The value of "Integral Heat of Soln" → Depends entirely on the value of n_1.

The asymtotic value of Heat of Solution for $n_1 \rightarrow \infty$ is known as heat of Solution at Infinite dilusion.

Integral Heat of Soln. $|_{n_1}$ →

Integral Heat of Soln. $|_{n_2}$ →

Values are going to be different.

Incremental or differential heat of

So, essentially the heat of dissolution or heat of solution is the enthalpy change associated with dissolution of a substance is termed as heat of solution or heat of dissolution. So, formally it is something very interesting and not exactly similar to heat of reaction. Let us say, you take an acid molecule in water and now you add a mole of acid and then you add another after it dissolves. So, is there a progressive thermal dissolution or something like that? So, let us first write down what it is and then I will look into some data and which will make it very clear. So, there is a concept called '***standard integral heat of solution***' and this is a very interesting concept which actually says that the enthalpy change of a system when one mole of solute dissolves in n_1 mole of the solvent at 25 degree centigrade and 1 atm pressure; it is known as the ***standard integral heat of solution***'. Important to note as we will soon see the value of integral heat of solution depends entirely on the value of n_1. The asymptotic value of heat of solution for $n_1 \rightarrow \propto$ is known as heat of solution at infinite dilution. So, we understand that ***'Integral heat of solution for n_1***' and '***Integral heat of solution for n_2'*** values are going to be different. And as these values are different, if you subtract these two values that would lead to a concept of 'incremental or differential heat of solution'. So, these are the essential concepts. now at this point let us look into the data set as shown in the following slide.

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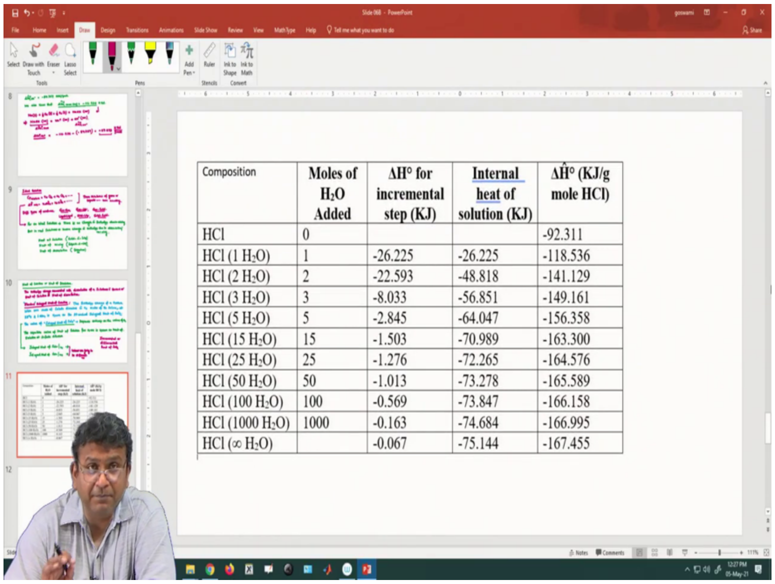

Composition	Moles of H_2O Added	ΔH^o for incremental step (KJ)	Internal heat of solution (KJ)	$\Delta\hat{H}^o$ (KJ/g mole HCl)
HCl	0			-92.311
HCl (1 H_2O)	1	-26.225	-26.225	-118.536
HCl (2 H_2O)	2	-22.593	-48.818	-141.129
HCl (3 H_2O)	3	-8.033	-56.851	-149.161
HCl (5 H_2O)	5	-2.845	-64.047	-156.358
HCl (15 H_2O)	15	-1.503	-70.989	-163.300
HCl (25 H_2O)	25	-1.276	-72.265	-164.576
HCl (50 H_2O)	50	-1.013	-73.278	-165.589
HCl (100 H_2O)	100	-0.569	-73.847	-166.158
HCl (1000 H_2O)	1000	-0.163	-74.684	-166.995
HCl (∞ H_2O)		-0.067	-75.144	-167.455

Let us look into one simple concept of dissolution of HCl in water or the aqueous solution. So, what we have; the first data is for pure HCl and this ΔH^0 is nothing but the heat of formation. Now, when you add one mole of HCl into one mole of water, you see the ΔH^0 for this incremental step is -26.225 kJ and the total incremental heat of solution for n_1= 1 mole, $\Delta H_{S,\ n1=1}$ = – 118.536 KJ/gmole.

Similarly, if you now keep on adding more and more moles of water, so, for example we have data for 2 we have data for 3; you see that the incremental change in enthalpy progressively reduces. Why does this happen? Because when you add the first mole of the solvent it has to actually overcome all the interactions between the HCl molecules to dissolve. Now, when subsequently more and more water is added it actually has to overcome far a smaller number of such interactions because already HCl has dissolved in water. So, for example for 1, 2, 3, or 5 moles there is some significant values; and then at 50 moles if you add more water, the value is very less, and which is even smaller at 100 moles. In fact, you keep on adding where the incremental ΔH does not change that is where you can say that this is as we argued in the previous slide, the heat of solution at infinite dilution. So, I request all of you to look into this data carefully. So, this is the heat of solution at infinite dilution. And if you are supplied with this data for example then step wise for each step incremental step you can also find out.

So, if you have the data set for the integral heat of solution for $n_1 = 1, 2, 3, 4, 5, \ldots$; then you can find out the differential or the incremental heat of solution for each step. It is very interesting because what is happening is that you are adding the same one mole of the solvent but depending on the value of n_1, the incremental value is changing. So, this is what is known as the concept of integral heat of solution.

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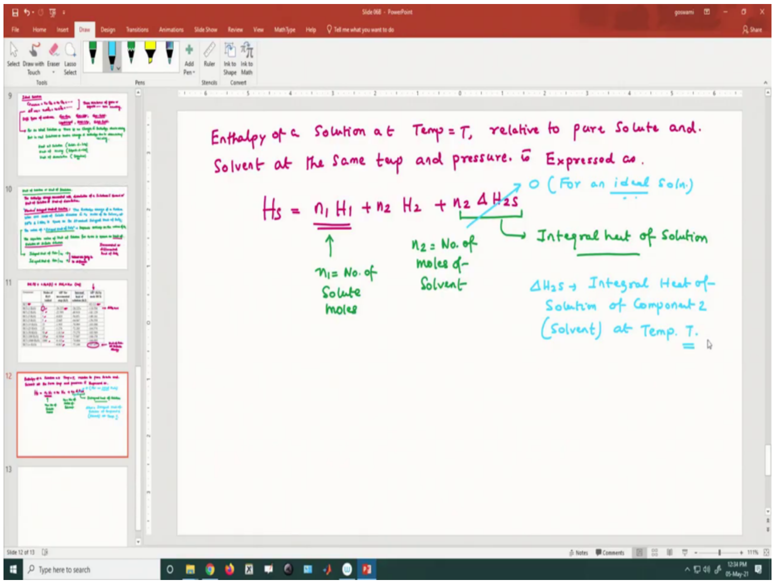

Enthalpy of a Solution at Temp = T, relative to pure Solute and. Solvent at the Same temp and pressure. is Expressed as.

$$H_S = \underline{\underline{n_1 H_1}} + n_2 H_2 + \underbrace{n_2 \Delta H_{2S}}_{\text{Integral heat of Solution}} \rightarrow 0 \text{ (For an ideal soln.)}$$

n_1 = No. of Solute moles

n_2 = No. of moles of Solvent

$\Delta H_{2S} \rightarrow$ Integral Heat of Solution of Component 2 (Solvent) at Temp. T.

So, enthalpy of a solution at temperature, T relative to pure solute and solvent at the same temperature and pressure; the enthalpy of a solution at temperature can be expressed as enthalpy of solution = $n_1H_1 + n_2H_2 + n_2\,\Delta H_{2S}$. Here n_2 = number of moles of the solvent. And this is the integral heat of solution and we now also understand that had we had an ideal solution this term would have been 0 for an ideal solution. So, it is very simple whenever you if you so you must be knowing that if you are adding acid to water there should be very careful arrangement for cooling because the reaction chamber heats up. And therefore, you must therefore straight away realize that what is happening is it is a non-ideal solution because otherwise there will be no effect of heat of solution or heat of mixing.

So, of course we write that ΔH_{2S} is the integral heat of solution of component 2 that is the solvent at temperature T. So, these values again of course you can understand that depend on the temperature but whenever you are talking about the standard heat of solution, we are essentially talking about the enthalpy effect at 25 degree centigrade and one atmospheric pressure. So, that sort of brings us to the end of our discussion whatever I wanted or intended to cover in as a part of this enthalpy balance with chemical reactions.

Thank you very much for joining and only one major topic remains and that is a discussion on humidity and where I will teach you the use of the very interesting psychometric chart, thank you very much.