Chemical Process Intensification
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Lecture 18
Parametric effects on Cavitation

Welcome to massive open online course on Chemical Process Intensification. So, we are to be discussing the module 6, which is about process intensification by cavitation. We have discussed under this module regarding cavitational mechanisms and also what are the different configurations of cavitation reactor. In this lecture under this module we will discuss something about the parametric effects on cavitation.

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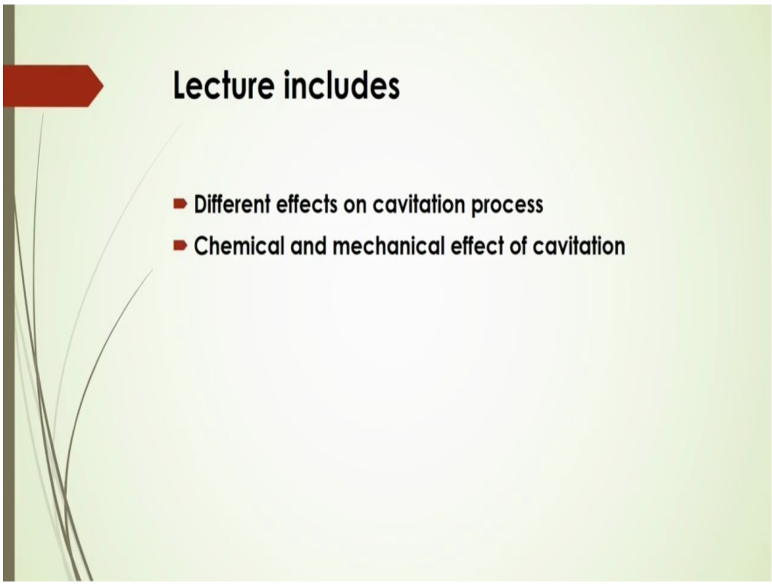

Lecture includes

- Different effects on cavitation process
- Chemical and mechanical effect of cavitation

Now, this lecture will be included about the different effects on cavitation process, chemical and mechanical effects on cavitation, all those things and also what are the cavitational effect on chemical and mechanical processes that also will be discussed. Now, before going to discuss about the effect we are actually trying to remember that what is actually that cavitation?

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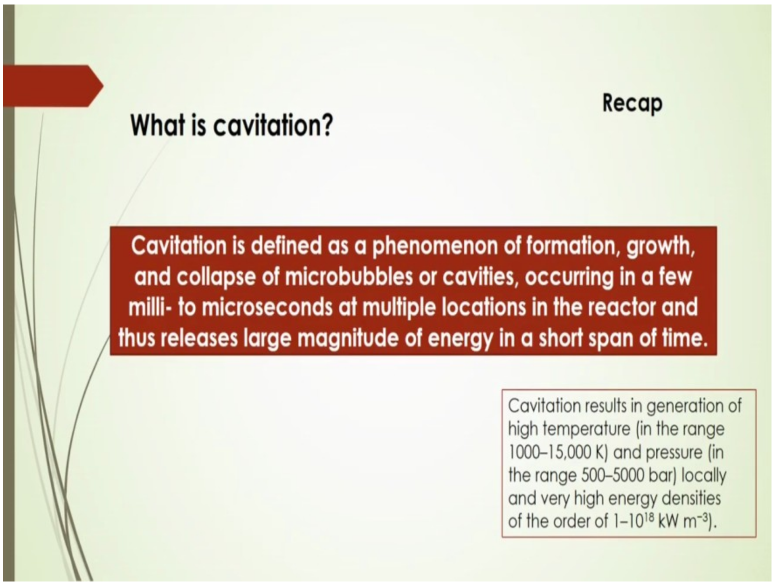

What is cavitation?

Recap

Cavitation is defined as a phenomenon of formation, growth, and collapse of microbubbles or cavities, occurring in a few milli- to microseconds at multiple locations in the reactor and thus releases large magnitude of energy in a short span of time.

Cavitation results in generation of high temperature (in the range 1000–15,000 K) and pressure (in the range 500–5000 bar) locally and very high energy densities of the order of 1–10^{18} kW m^{-3}).

The cavitation is actually basically the phenomena of formation, growth and collapse of microbubbles and cavities that is actually occurred in a few milli or microseconds of you know multiple locations in a reactor. And during that cavitation we actually discussed that that will be certain amount of you know release of energy in a short span of time. So in that case this cavitation generally results in the generation of high-temperature in the range of 1000 to 15,000 Kelvin and also at a pressure in the range of 500 to 5000 bar.

So locally it is actually that the temperature generation as well as you know that very high energy densities of the order of 1 into 10 to the power 18 kilowatt per meter cube.

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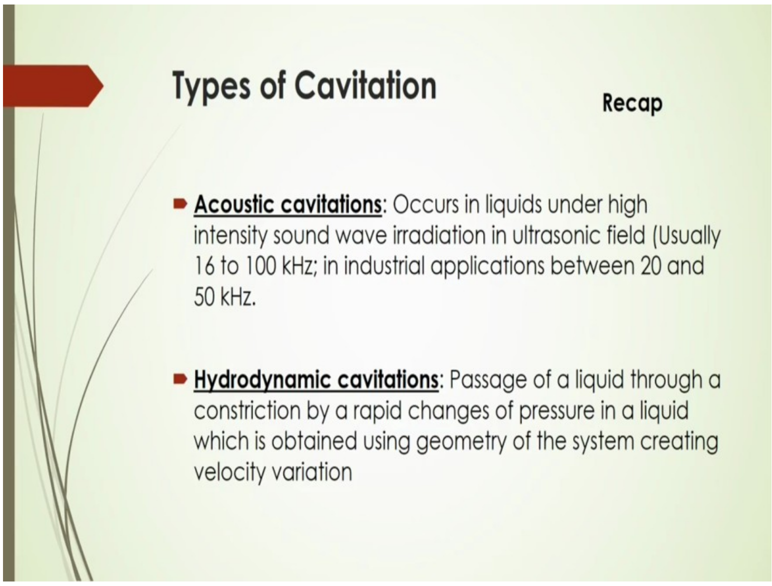

Types of Cavitation

Recap

- **Acoustic cavitations**: Occurs in liquids under high intensity sound wave irradiation in ultrasonic field (Usually 16 to 100 kHz; in industrial applications between 20 and 50 kHz.
- **Hydrodynamic cavitations**: Passage of a liquid through a constriction by a rapid changes of pressure in a liquid which is obtained using geometry of the system creating velocity variation

So this is the cavitation, so in this case we have discussed that several types of cavitation like out of which acoustic cavitation and hydrodynamic cavitation are the most useful even you can say that it is actually suitable for Chemical Engineering Processes. So acoustic cavitation what we had discussed that it occurs in a liquid under high intensity sound wave irradiation in ultrasonic field usually 16 to 1000 kilowatts; in industrial applications generally the range is in between you know that 20 to 50 kilohertz.

Whereas hydrodynamic cavitation, it is actually happened by passage of liquid through a constriction by a rapid changes of pressure in a liquid which is generally obtained using the geometry of the system that creates the velocity variation, so this is the actually that acoustic and hydrodynamic cavitation.

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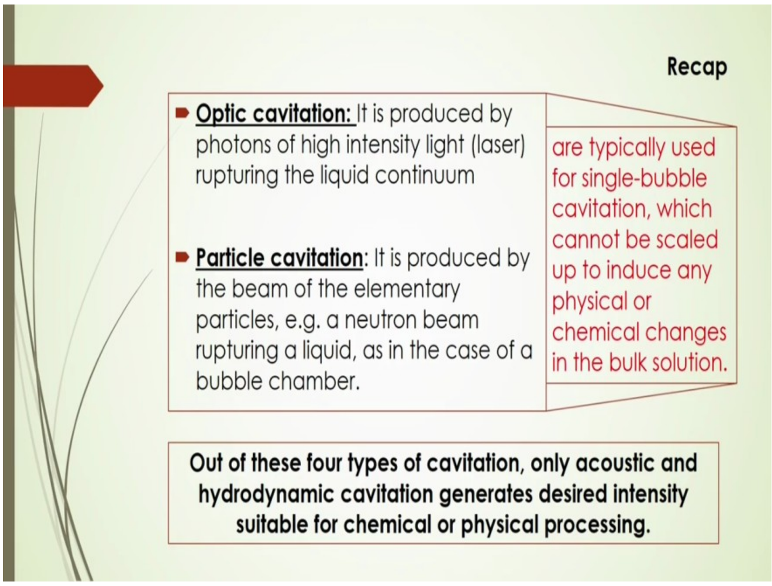

Recap

- **Optic cavitation:** It is produced by photons of high intensity light (laser) rupturing the liquid continuum
- **Particle cavitation**: It is produced by the beam of the elementary particles, e.g. a neutron beam rupturing a liquid, as in the case of a bubble chamber.

are typically used for single-bubble cavitation, which cannot be scaled up to induce any physical or chemical changes in the bulk solution.

Out of these four types of cavitation, only acoustic and hydrodynamic cavitation generates desired intensity suitable for chemical or physical processing.

Other cavitations like optic cavitation, even particle cavitation that we have discussed also. Optic cavitation, it is generally produced by photons of high-intensity light laser rupturing the liquid continuum and also particle cavitation in that case there will be production of the beam of the elementary particle by which this cavitation is produced. In that case the elementary particles like neutron beam rupturing in a liquid has happened, and as in the case of bubble chamber there.

And out of these actually the different types of cavitation on the acoustic and hydrodynamic cavitation that generates desired intensity suitable for chemical and physical processing.

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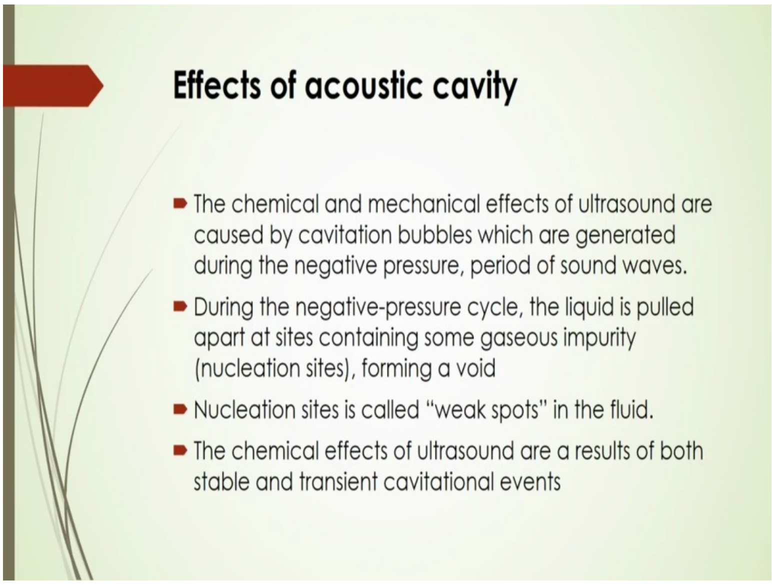

Effects of acoustic cavity

- The chemical and mechanical effects of ultrasound are caused by cavitation bubbles which are generated during the negative pressure, period of sound waves.
- During the negative-pressure cycle, the liquid is pulled apart at sites containing some gaseous impurity (nucleation sites), forming a void
- Nucleation sites is called "weak spots" in the fluid.
- The chemical effects of ultrasound are a results of both stable and transient cavitational events

Now, let us discuss what are the different effects of that cavity? Now, in case of acoustic cavity we are having that the chemical and mechanical effects of ultrasound are actually caused by that cavitation bubbles which are actually created during the negative pressure and also period of sound waves. And during the negative pressure cycle, there is a liquid which is pulled apart at sites that contain some you know gaseous impurity like nucleation sites in that case forming a void. So there will be a pressure cycle, during that pressure cycle in the negative side so there the liquid is pulled apart at sites that contains some gaseous impurities and which may form void.

Now, in that case that impurity may actually effect on that formation of void and nucleation sites is called the weak spots in the fluid and the chemical effects of that ultrasound are actually result of both stable and transient cavitational events of the forming of void. So this is the case where this we can have that chemical and mechanical effects of ultrasound that is caused by the cavitation bubbles.

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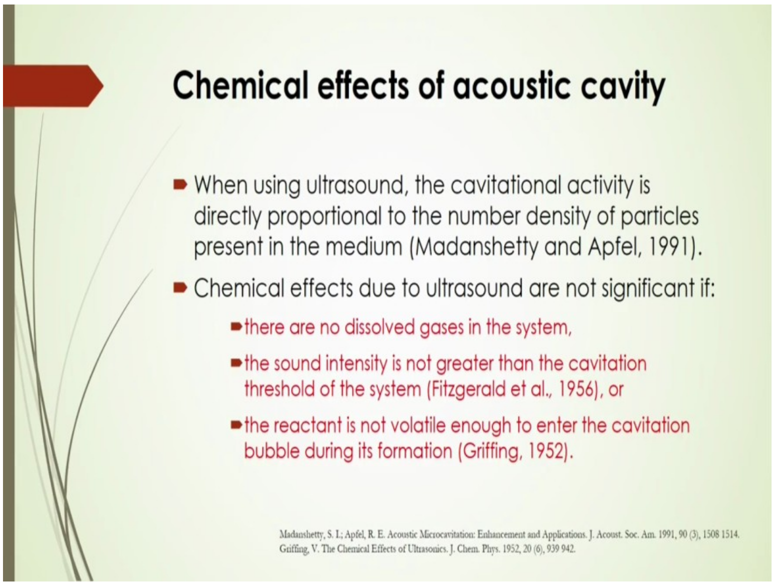

Chemical effects of acoustic cavity

- When using ultrasound, the cavitational activity is directly proportional to the number density of particles present in the medium (Madanshetty and Apfel, 1991).
- Chemical effects due to ultrasound are not significant if:
  - there are no dissolved gases in the system,
  - the sound intensity is not greater than the cavitation threshold of the system (Fitzgerald et al., 1956), or
  - the reactant is not volatile enough to enter the cavitation bubble during its formation (Griffing, 1952).

Madanshetty, S. I.; Apfel, R. E. Acoustic Microcavitation: Enhancement and Applications. J. Acoust. Soc. Am. 1991, 90 (3), 1508 1514.
Griffing, V. The Chemical Effects of Ultrasonics. J. Chem. Phys. 1952, 20 (6), 939 942.

Now, very interesting that when using ultrasound in that case you will see some chemical effects due to the ultrasounds will be happened and sometimes it may not be that much of significant if there are you know that no dissolved gases in the system will be there. And the sound intensity is not greater than the cavitation and also the chemical effects due to the ultrasound will not be significant if the reactant is not volatile enough to you know enter cavitation bubble during its formation.

Now, according to this Fitzgerald et al and also Grifting in 1956 and 1952 respectively, they actually observed this type of happenings that there are no dissolved gases in the system then chemical effects of ultrasound will not have that significant effect.

Now, when this ultrasound is being used the cavitation activity is directly proportional to the number of density of the particles that is present in the medium. So, according to this Madanshetty and Apfel 1991 actually they observed this that you know that the cavitational activity will be a function of number of density of particles that is present in the medium.

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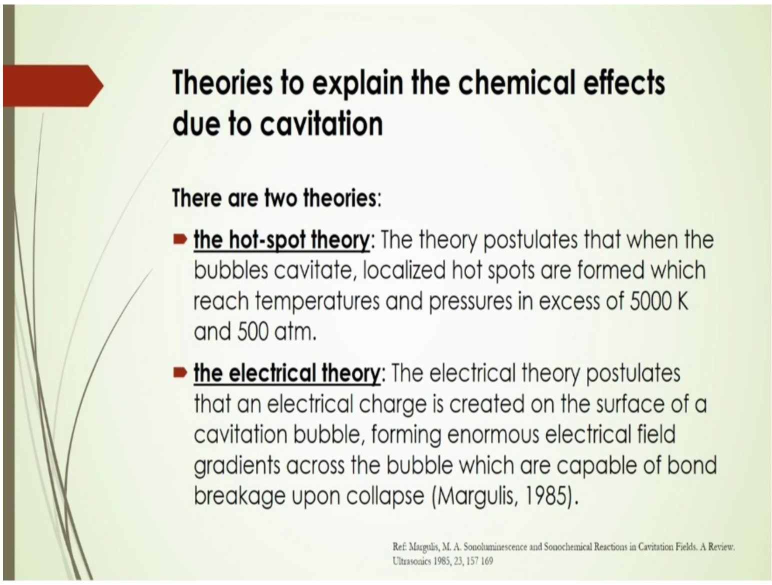

Theories to explain the chemical effects due to cavitation

There are two theories:

- **the hot-spot theory**: The theory postulates that when the bubbles cavitate, localized hot spots are formed which reach temperatures and pressures in excess of 5000 K and 500 atm.
- **the electrical theory**: The electrical theory postulates that an electrical charge is created on the surface of a cavitation bubble, forming enormous electrical field gradients across the bubble which are capable of bond breakage upon collapse (Margulis, 1985).

Ref: Margulis, M. A. Sonoluminescence and Sonochemical Reactions in Cavitation Fields. A Review. Ultrasonics 1985, 23, 157 169

And also in this case there are you know some theories to explain the chemical effects due to this cavitation. Generally 2 theories are available; one is the hotspot theory, another is called electrical theory. According to the hotspot theory, this actually postulates that when the bubble cavitate, localized hotspots are formed in that case the bubble cavities forms the temperature and pressure in the access of you know 5000 Kelvin and 500 atmospheres. So according to this hot-spot's theory that there will be a localized hot-spot's formation at a temperature of 5000 K and 500 atmospheric pressure.

And in the case of electrical theory, the electrical theory in that case it will predict that then electrical charges created on the you know the surface of a cavitation bubble which forms you know that electrical field and also due to this electrical field gradients across the bubble that will be capable of bond breakage upon collapse. So this is actually observed by Margullis in 1985 based on this electrical field application during that you know cavitation bubble formation.

So we are having that based on these 2 theories; one is that there will be formation of hot-spots and another is called that there will be an electrical field gradients across the bubble there.

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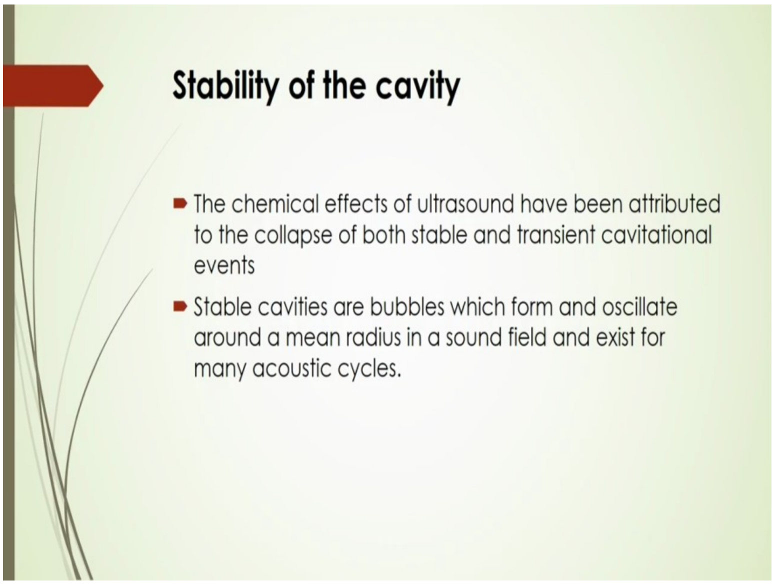

Stability of the cavity

- The chemical effects of ultrasound have been attributed to the collapse of both stable and transient cavitational events
- Stable cavities are bubbles which form and oscillate around a mean radius in a sound field and exist for many acoustic cycles.

Now, what are the stability of the cavity? The chemical effects of ultrasound have been attributed to the collapse of both stable and transient cavitational events, so it is very important that during the collapse of that bubble after it you will see there will be of formation of may be a smaller bubble and also sometimes may be bigger bubbles after coalescence of those smaller bubble.

Now, during that cavitation process simultaneously smaller and bigger bubbles or bigger cavities will be forming. Now, there will be a certain condition that in the ultrasound case that whatever cavities are forming that the collapsing of this both stable and transient cavitation events will be there at a certain condition. Now, stable cavities in that case are bubbles which form and oscillates around the mean radius in you know that in sound field and exists for many acoustic cycles there.

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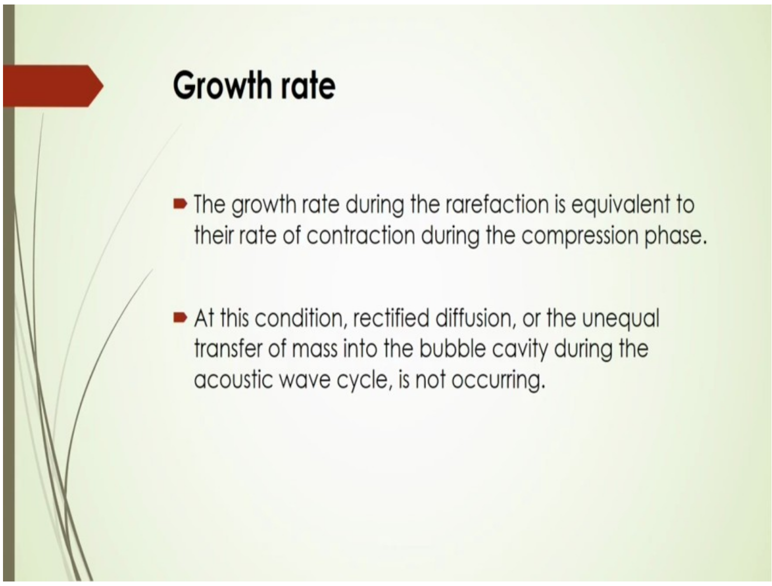

Growth rate

- The growth rate during the rarefaction is equivalent to their rate of contraction during the compression phase.
- At this condition, rectified diffusion, or the unequal transfer of mass into the bubble cavity during the acoustic wave cycle, is not occurring.

And after that you will see that there will be a certain growth rate of that cavitation, the growth rate during the rare fraction is equivalent to their rate of contraction during the compression phase. We have discussed the mechanism of formation of you know the cavity during that acoustic mechanism where that rare fraction and compressions will be there, compression will be there.

So in that case during the rare fraction this growth rate will be equivalent to their rate of contraction during the compression phase. Now at this condition the rectified diffusion or the unequal transfer of mass into the bubble cavity during the acoustic wave cycle that is not happened, so that should be noted down that the unequal transfer of mass into the bubble cavity during the acoustic wave cycle is not occurred.

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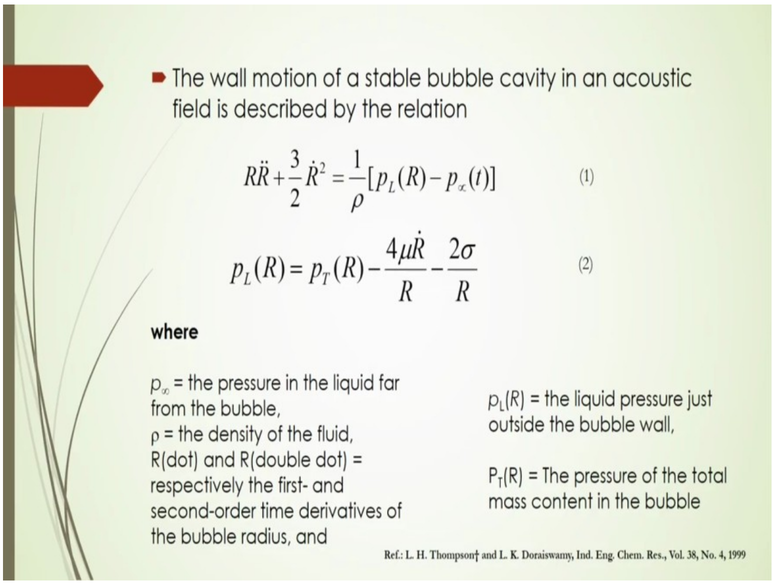

- The wall motion of a stable bubble cavity in an acoustic field is described by the relation

$$R\ddot{R}+\frac{3}{2}\dot{R}^2=\frac{1}{\rho}[p_L(R)-p_{\propto}(t)] \qquad (1)$$

$$p_L(R)=p_T(R)-\frac{4\mu\dot{R}}{R}-\frac{2\sigma}{R} \qquad (2)$$

where

p_{∞} = the pressure in the liquid far from the bubble,
ρ = the density of the fluid,
R(dot) and R(double dot) = respectively the first- and second-order time derivatives of the bubble radius, and

$p_L(R)$ = the liquid pressure just outside the bubble wall,

$P_T(R)$ = The pressure of the total mass content in the bubble

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

Now, the wall motion of a stable bubble cavity in an acoustic field is described by the relation here as given in equation you know that 1 here. This is actually as a function of pressure that is you know the pressure in the liquid far from the bubble, and also it is you know that function of the size of the cavity or bubbles there. So what should be the motion of the wall of a stable bubble cavity in an acoustic field that is described by the relation here it is given here in equation number 1.

$$R\ddot{R}+\frac{3}{2}\dot{R}^2=\frac{1}{\rho}[p_L(R)-p_{\propto}(t)] \qquad (1)$$

$$p_L(R)=p_T(R)-\frac{4\mu\dot{R}}{R}-\frac{2\sigma}{R} \qquad (2)$$

This is basically this is or you know that second order derivative of R. Here R is called radius of the bubble and R dot means here the size that is radius is increasing with respect to time.

So this equation has come up after you know that the energy balance there, so we are not giving here the total derivation of this you know equation, it is not required, but you just see the final equation of this motion. And in this case the $p_L(R)$ is called the liquid pressure just outside the bubble wall and the $p_{\propto}(t)$ is the pressure in the liquid far from the bubble.

So and another term is called this $p_L(R)$ is actually in terms of that the pressure of the total mass contained in the bubble, so this $p_T(R)$ is the pressure of the total mass contained in the bubble. So this $p_L(R)$ is dependent on this $p_T(R)$ as well as the size of the bubble, but here one important effect that the surface tension, to stabilize the bubble you will of course consider the surface tension of the bubble at the that surface.

So, based on this equation we are having the motion equation of that stable bubble, wall motion equation and this is the function of $p_L(R)$ and $p_\propto(t)$, where $p_L(R)$ can be calculated from this equation number 2, which is a function of surface tension, size of the bubble and also the pressure of the total mass that is contained in the bubble. So this is actually by which you can calculate that how the growth of the bubbles will be there with respect to time.

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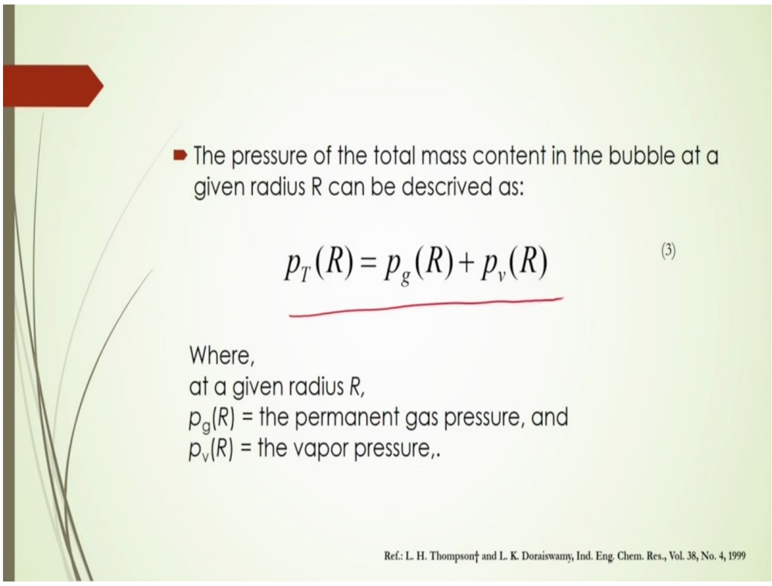

- The pressure of the total mass content in the bubble at a given radius R can be descrived as:

$$p_T(R) = p_g(R) + p_v(R) \tag{3}$$

Where,
at a given radius *R*,
$p_g(R)$ = the permanent gas pressure, and
$p_v(R)$ = the vapor pressure,.

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

Now the pressure of the total mass contained in the bubble at a given radius R that can be actually calculated by this equation number 3

$$p_T(R) = p_g(R) + p_v(R) \qquad (3)$$

here that is $p_T(R)$ as a function of R that will be equal to $p_g(R) + p_v(R)$. What is that $p_g(R)$? $p_g(R)$ is actually at a given radius the permanent gas pressure and also $p_v(R)$ is called that the vapour pressure they at that particular size of the bubble there. So by this equation you can calculate what should be the pressure of the total mass contained in the bubble.

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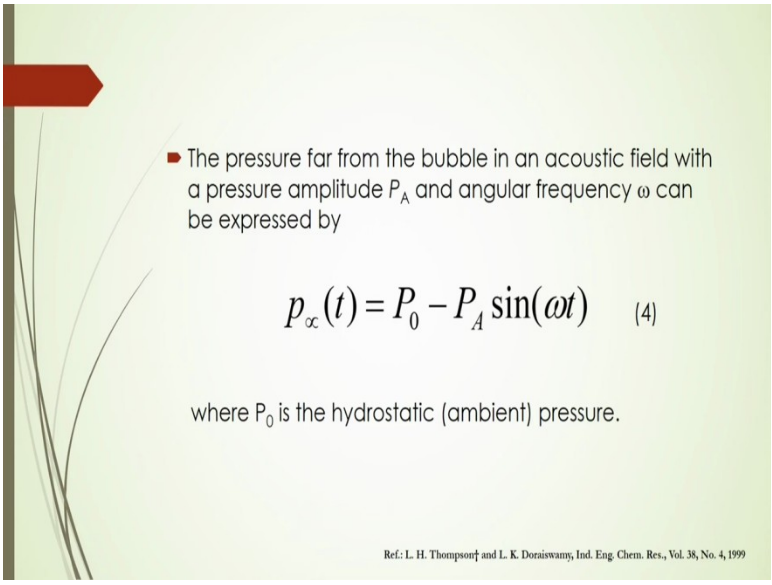

- The pressure far from the bubble in an acoustic field with a pressure amplitude P_A and angular frequency ω can be expressed by

$$p_{\propto}(t) = P_0 - P_A \sin(\omega t) \qquad (4)$$

where P_0 is the hydrostatic (ambient) pressure.

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

The pressure that is far from the bubble in an acoustic field with a pressure of an amplitude of P_A and angular frequency of Omega that can be expressed by this equation number 4,

$$p_{\propto}(t) = P_0 - P_A \sin(\omega t) \qquad (4)$$

where you can get that this P infinity as a function of time that means here pressure how it will be changing with respect to time that is far from the bubble so it is a function of you know that hydrostatic pressure. If you are having more hydrostatic pressure and amplitude is less than in that case this the pressure will be increasing, whereas if for a particular hydrostatic pressure if you are having you know that more pressure amplitude by the acoustic field then in that case this pressure far from the bubble will be less there. So based on this equation number 4 you can easily calculate what should be the pressure far from the bubble.

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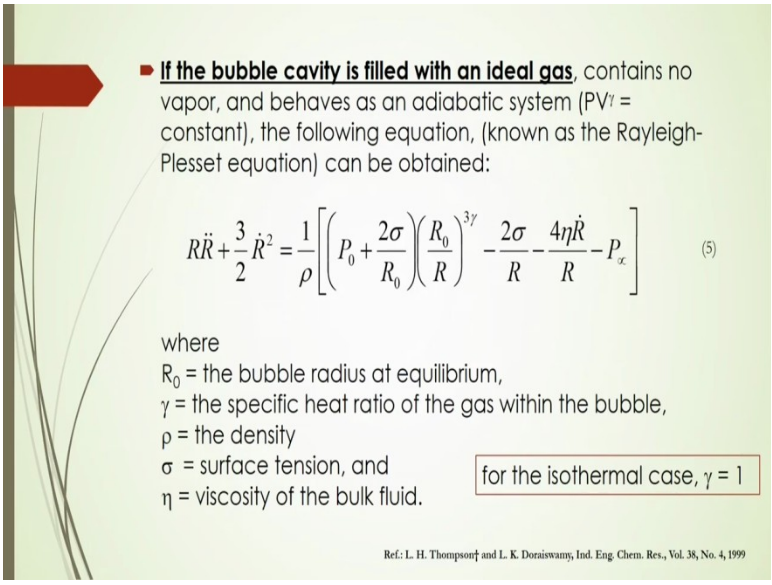

- **If the bubble cavity is filled with an ideal gas**, contains no vapor, and behaves as an adiabatic system (PV^{γ} = constant), the following equation, (known as the Rayleigh-Plesset equation) can be obtained:

$$R\ddot{R}+\frac{3}{2}\dot{R}^2=\frac{1}{\rho}\left[\left(P_0+\frac{2\sigma}{R_0}\right)\left(\frac{R_0}{R}\right)^{3\gamma}-\frac{2\sigma}{R}-\frac{4\eta\dot{R}}{R}-P_\propto\right] \quad (5)$$

where
R_0 = the bubble radius at equilibrium,
γ = the specific heat ratio of the gas within the bubble,
ρ = the density
σ = surface tension, and
η = viscosity of the bulk fluid.

for the isothermal case, γ = 1

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

And after substitution of this you know equation like 3, even you know 2 and 4 in equation number 1 then you can get this final equation 5 like this.

$$R\ddot{R}+\frac{3}{2}\dot{R}^2=\frac{1}{\rho}\left[\left(P_0+\frac{2\sigma}{R_0}\right)\left(\frac{R_0}{R}\right)^{3\gamma}-\frac{2\sigma}{R}-\frac{4\eta\dot{R}}{R}-P_\propto\right] \qquad (5)$$

So in this if the bubble cavity is filled with an ideal gas, in that case it contains no vapour and behaves as an adiabatic system, so in that case P_v to the power Gamma should be is equal to constant to be considered, and in that case the following equation sometimes it is called that Rayleigh Plesset equation that can be obtained, so this equation number 5 is called you know the Rayleigh Plesset equation by which you will be able to calculate what should be the total rate of the bubble or the increase in the size of the bubble with respect to time.

In this case you will see R_0 is one term, where R_0 is bubble radius at equilibrium and Gamma it is represented the specific heat ratio of the gas within the bubble, and ρ is the density, Sigma is the surface tension and Eta is the viscosity of the bulk fluid. So for the case of isothermal condition you will see that Gamma should be is equal to 1, so in that case P_v will be equal to 1, simply you can write, so you can have this simply by equation 5 for that particular cases of isothermal condition.

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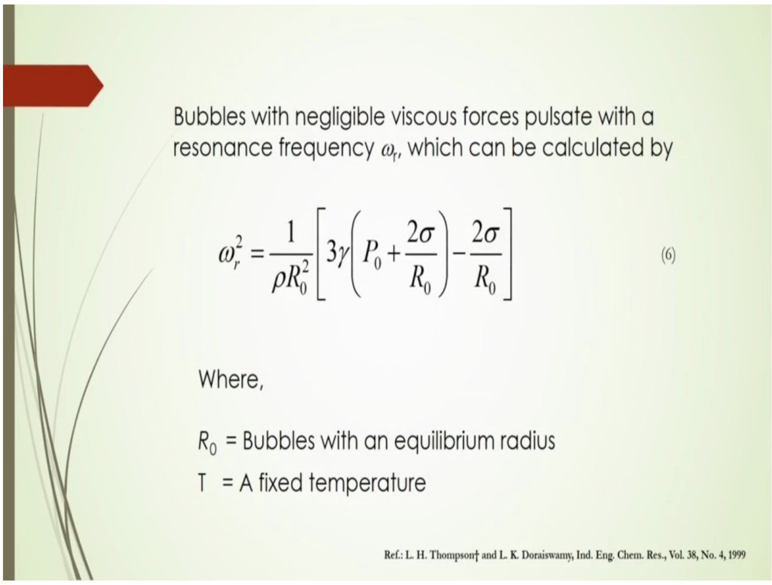

Bubbles with negligible viscous forces pulsate with a resonance frequency ω_r, which can be calculated by

$$\omega_r^2 = \frac{1}{\rho R_0^2}\left[3\gamma\left(P_0 + \frac{2\sigma}{R_0}\right) - \frac{2\sigma}{R_0}\right] \qquad (6)$$

Where,

R_0 = Bubbles with an equilibrium radius

T = A fixed temperature

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

Now bubbles with, if you are considering that there is a negligible viscosity and the viscous force is not actually significant, then you can say that this resonance frequency ω_r can be actually calculated based on that you know that pressure hydrostatic pressure as well as that what is the surface tension there. So based on that variables we are having that ω_r square that means it is called that resonance frequency in the acoustic field that can be calculated by this equation number 6,

$$\omega_r^2 = \frac{1}{\rho R_0^2}\left[3\gamma\left(P_0 + \frac{2\sigma}{R_0}\right) - \frac{2\sigma}{R_0}\right] \qquad (6)$$

where in this case R_0 is the bubble with an equilibrium radius and T as a fixed temperature there.

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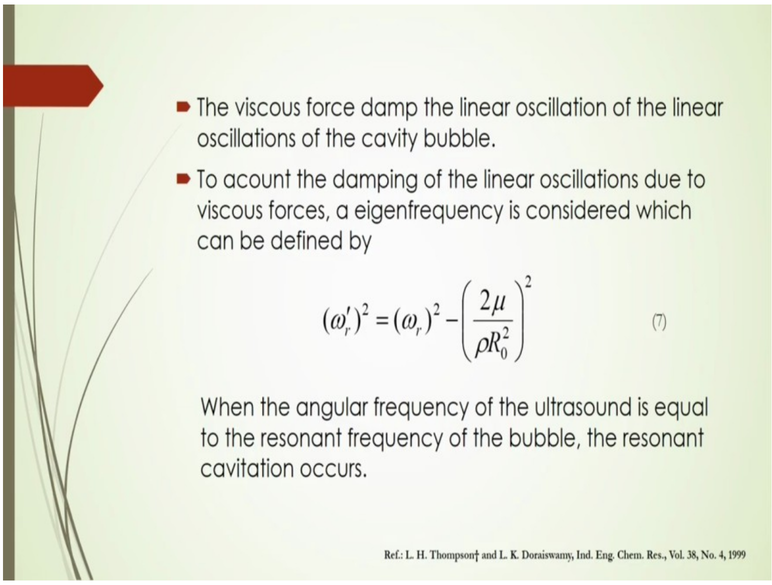

- The viscous force damp the linear oscillation of the linear oscillations of the cavity bubble.
- To acount the damping of the linear oscillations due to viscous forces, a eigenfrequency is considered which can be defined by

$$(\omega_r')^2 = (\omega_r)^2 - \left(\frac{2\mu}{\rho R_0^2}\right)^2 \qquad (7)$$

When the angular frequency of the ultrasound is equal to the resonant frequency of the bubble, the resonant cavitation occurs.

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

And again we can say that, the viscous force if it is damped the linear oscillation of the cavity bubble, then to account the damping of the linear oscillations due to viscous forces you know that eigen frequency to be considered and which can be defined by this $(\omega_r')^2$, here it is given in equation number 7

$$(\omega_r')^2 = (\omega_r)^2 - \left(\frac{2\mu}{\rho R_0^2}\right)^2 \qquad (7)$$

that will be is equal to Omega r square - 2 Mu by Rho R_0 square the whole square. So from this equation number 7 you will be able to calculate what should be the eigen frequency in the acoustic field.

In this case very interesting thing is that it is considered only for damping of the linear oscillation due to viscous forces. Now, when the angular frequency of the ultrasound is equal to the resonant frequency of the bubble, the resonant cavitation will happen there.

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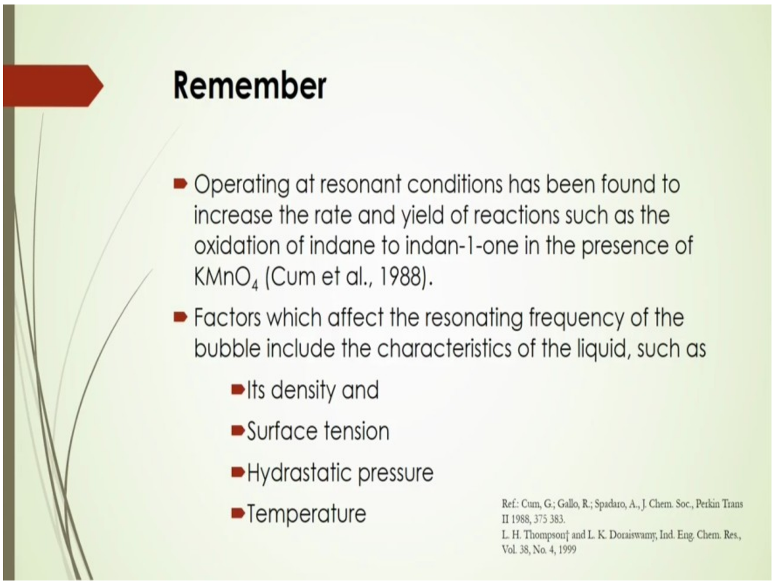

Remember

- Operating at resonant conditions has been found to increase the rate and yield of reactions such as the oxidation of indane to indan-1-one in the presence of $KMnO_4$ (Cum et al., 1988).
- Factors which affect the resonating frequency of the bubble include the characteristics of the liquid, such as
  - Its density and
  - Surface tension
  - Hydrastatic pressure
  - Temperature

Ref.: Cum, G.; Gallo, R.; Spadaro, A., J. Chem. Soc., Perkin Trans II 1988, 375 383.
L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

So in this case you have to remember that the operating at resonant conditions has been found to increase the rate and also yield of reactions such as the oxidation of the Indane to Indane-1 in the presence of potassium permanganate. So it is actually observed by Cum et al in 1988, and according to their observations they concluded that some factors which affects the resonating frequency of the bubble that will include the characteristics of the liquid such as the density and the surface tension and hydrostatic pressure and temperature is there.

So in this case, the resonant conditions that should be actually taken care whenever you are having the more viscous effect there so that to decrease or damping that you know linear oscillation due to that viscous effects, some other frequency like you know eigen frequency to be considered according to this equation number 7.

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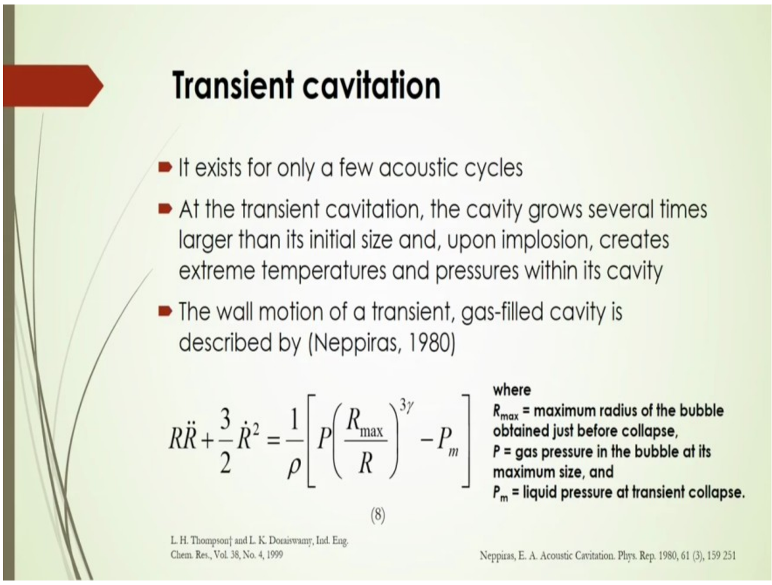

Transient cavitation

- It exists for only a few acoustic cycles
- At the transient cavitation, the cavity grows several times larger than its initial size and, upon implosion, creates extreme temperatures and pressures within its cavity
- The wall motion of a transient, gas-filled cavity is described by (Neppiras, 1980)

$$R\ddot{R}+\frac{3}{2}\dot{R}^2=\frac{1}{\rho}\left[P\left(\frac{R_{\max}}{R}\right)^{3\gamma}-P_m\right] \quad (8)$$

where
R_{max} = maximum radius of the bubble obtained just before collapse,
P = gas pressure in the bubble at its maximum size, and
P_m = liquid pressure at transient collapse.

L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

Neppiras, E. A. Acoustic Cavitation. Phys. Rep. 1980, 61 (3), 159 251

Now, another important phenomenon is called transient cavitation. It generally exists for only a few acoustic cycles, in that case at the transient condition the cavity which will be growing and several times larger than its initial size. And also upon implosion of that bubble that will create extreme temperatures and pressures within you know that its cavity, so that is why at the transient cavitation that you have to see that there will be you know the size will be you know larger than the initial size and also it creates that temperature and pressure within the cavity.

And also during the wall motion of that transient cavity, the gas field cavity is described by this equation of motion that is given in equation number 8 there.

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho}\left[P\left(\frac{R_{\max}}{R}\right)^{3\gamma} - P_m\right] \tag{8}$$

So in this case you will see that it depends on that you know that transient condition this equation wall motion equation actually depends on that what should be the stable size of the bubble or cavity, what is the maximum size of that cavity will be there. So in that case it is a function of Rmax, Rmax means maximum radius of the bubble obtained just before collapse there. And also P is the gas pressure in the bubble at its maximum size, and P m is called the liquid pressure at the transient collapse.

So you will see that there will be, in the liquid if there is acoustic radiation will be happened under you know that certain acoustic cycles, then after formation this bubbles will actually become larger and larger and then you know at different cycles it may be smaller-larger, smaller-larger, since there will be net effect of growth of bubbles and you will see before you know collapse the bubbles will get the stable you know size. So at that stable condition there will be maximum size of the bubbles, and after immediately of that size you will see there will be an explosion of that or you can see it is called implosion of bubbles.

Now, during that implosion there it will create you know extreme temperature and pressure there. So during that transition condition of that you know acoustic cycles of that implosion, so that you know growth rate actually depends on that maximum size of the bubbles and the pressure at which the maximum size of the bubbles or cavities will obtain there before collapse.

And also this is a function of liquid pressure at the transient collapse. Now, and if suppose liquid pressure is decreasing then in that case you will see bubble growth will be more higher in the you know that particular condition and also there you will see the implosion will be you know more and the extreme temperature and pressure that will be you know that more intensity of that temperature and pressure will be there.

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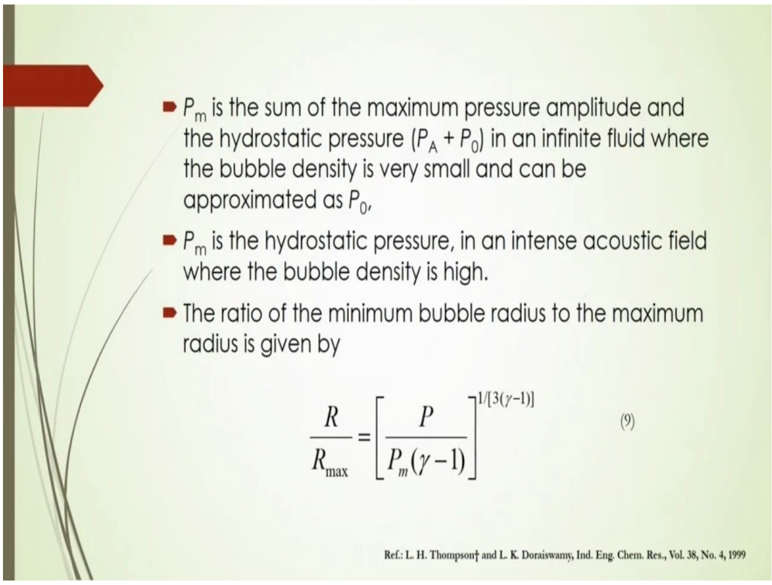

- P_m is the sum of the maximum pressure amplitude and the hydrostatic pressure ($P_A + P_0$) in an infinite fluid where the bubble density is very small and can be approximated as P_0,
- P_m is the hydrostatic pressure, in an intense acoustic field where the bubble density is high.
- The ratio of the minimum bubble radius to the maximum radius is given by

$$\frac{R}{R_{\max}} = \left[\frac{P}{P_m(\gamma - 1)}\right]^{1/[3(\gamma-1)]} \qquad (9)$$

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

Now, in this case how that you know P_m, it is called the liquid pressure at transient collapse can be calculated. This P_m is the sum of the maximum pressure amplitude and the hydrostatic pressure that is if I denote it by P_A as you know that maximum pressure amplitude and P_0 is the hydrostatic pressure, in that case you know that the bubble density if it is very small and can be approximated as that P_0 just by neglecting that P_A there.

So P_m you can directly calculate as P_0 if there is a you know that maximum pressure amplitude will be very small compared to that hydrostatic pressure. And the P_m is actually the hydrostatic pressure in an intense acoustic field where the bubble density will be very high, so that in that case you will see the ratio of the maximum bubble radius to the maximum radius can be actually represented by this equation number 9 there.

$$\frac{R}{R_{\max}} = \left[\frac{P}{P_m(\gamma - 1)}\right]^{1/[3(\gamma-1)]} \qquad (9)$$

So this is R by Rmax that will be is equal to P by Pm into Gamma minus 1 whole to the power 1 by 3 into Gamma minus 1, this is as per equation number 9 you can calculate what should be the you know that maximum bubble radius to the maximum ratio there. So this is actually the basic calculations for the radius at that transient condition.

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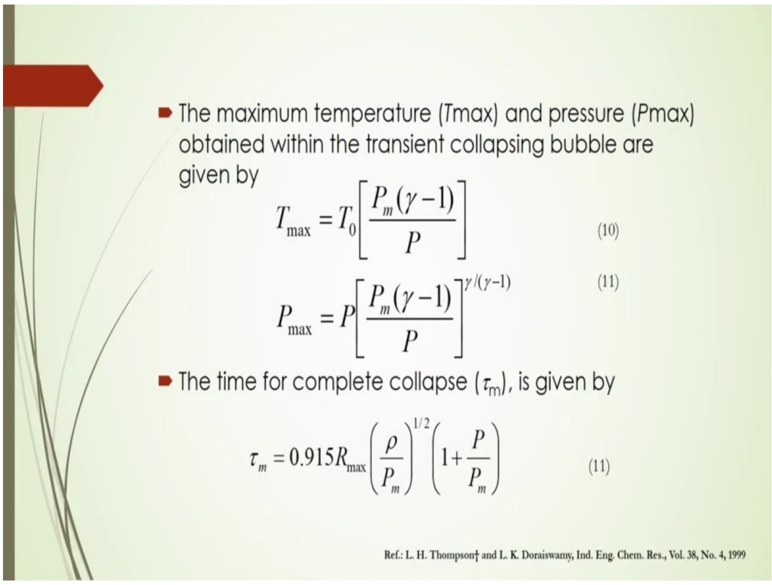

- The maximum temperature (Tmax) and pressure (Pmax) obtained within the transient collapsing bubble are given by

$$T_{\max} = T_0\left[\frac{P_m(\gamma-1)}{P}\right] \qquad (10)$$

$$P_{\max} = P\left[\frac{P_m(\gamma-1)}{P}\right]^{\gamma/(\gamma-1)} \qquad (11)$$

- The time for complete collapse (τ_m), is given by

$$\tau_m = 0.915R_{\max}\left(\frac{\rho}{P_m}\right)^{1/2}\left(1+\frac{P}{P_m}\right) \qquad (11)$$

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

The maximum temperature which is actually formed during that collapse and also pressure during that collapse within the transient collapsing bubble are given by this Tmax will be is equal to what?

$$T_{\max} = T_0\left[\frac{P_m(\gamma-1)}{P}\right] \qquad (10)$$

As per equation number 10 this is actually T0 into Pm into Gamma minus 1 by P and

$$P_{\max} = P\left[\frac{P_m(\gamma-1)}{P}\right]^{\gamma/(\gamma-1)} \qquad (11)$$

Pmax is equal to P into Pm into Gamma minus 1 by P to the power Gamma by Gamma minus 1. So this equation 11 will give you that maximum pressure and the equation 10 will give you the maximum temperature during that you know transient condition of the collapsing of the bubble.

The time for that complete collapse, you know that one bubble if it is collapsing into finer bubbles, you will see more than one finer bubbles will be creating, in that case how long it will take to get that complete collapse for that, so that can be actually calculated based on this equation that is given in equation number 12

$$\tau_m = 0.915R_{\max}\left(\frac{\rho}{P_m}\right)^{1/2}\left(1+\frac{P}{P_m}\right) \qquad (12)$$

ok, this is equation number 12. So based on this equation number 12 you can calculate what should be the maximum time it can take for the complete collapse there.

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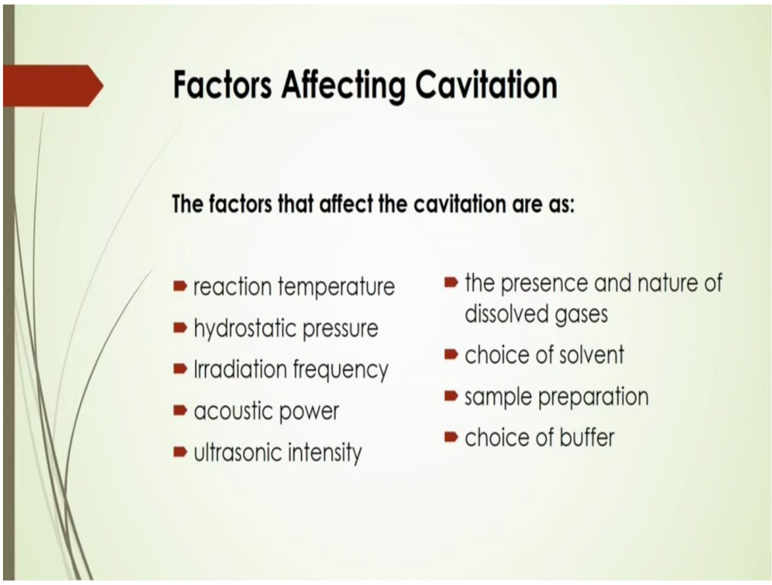

Factors Affecting Cavitation

The factors that affect the cavitation are as:

- reaction temperature
- hydrostatic pressure
- Irradiation frequency
- acoustic power
- ultrasonic intensity
- the presence and nature of dissolved gases
- choice of solvent
- sample preparation
- choice of buffer

Now, let us consider that what are the factors that affect the cavitation? Now there are several factors that affect the cavitation like you know if you are doing reaction, what should be the reaction temperature? If you are doing in a liquid medium then hydrostatic pressure will be one term, and also irradiation frequency also important factor, acoustic power what are the power supplied that is also important factor. Another important which is called ultrasound intensity because you are forming that cavitation because of that ultrasound you know irradiation, so in that case ultrasonic intensity is the factor.

And the presence and nature of dissolved gases, if there is any you know gases are dissolved in the medium or not, now, what types of solvents you are choosing for that you know reaction chemical processes where you are just generating some cavity, and based on that cavity you are doing the you know chemical engineering process. And also how you are preparing the samples that also you know important which affects the cavitation process. And also if there is any buffer that means how you are you know maintaining that pH of the solution that is also important in the cavitation process.

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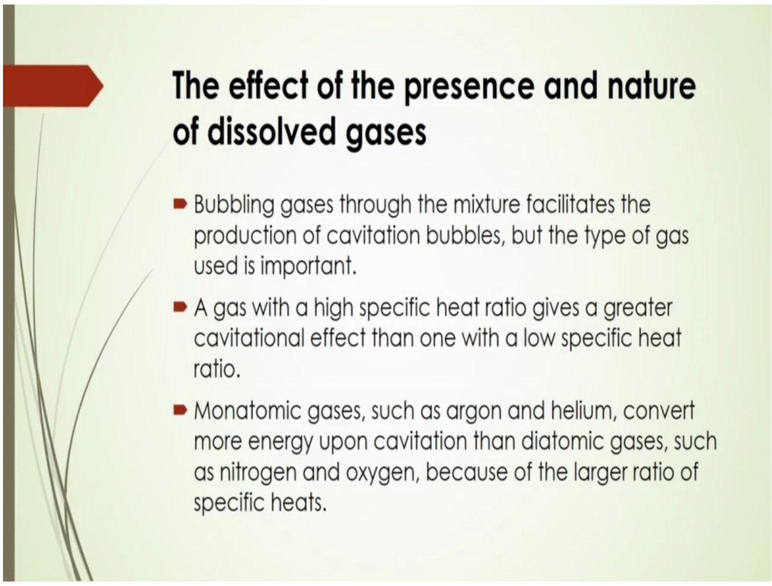

The effect of the presence and nature of dissolved gases

- Bubbling gases through the mixture facilitates the production of cavitation bubbles, but the type of gas used is important.
- A gas with a high specific heat ratio gives a greater cavitational effect than one with a low specific heat ratio.
- Monatomic gases, such as argon and helium, convert more energy upon cavitation than diatomic gases, such as nitrogen and oxygen, because of the larger ratio of specific heats.

Now, if you are considering the effect of the presence and nature of dissolved gases, in that case bubbling gases through the mixture that will facilitates the production of cavitation bubbles, and also a gas with a high specific heat ratio in that case it will give you a greater cavitational effects then one with a low specific heat ratio. And also what type of gas actually you are using like you know that whether it is mono atomic, or diatomic or triatomic so that Gamma value is important there for the mono atomic, diatomic and triatomic gases, this Gamma value will be changing that is what we have discussed in previous slides.

So in that case monatomic gases if you are considering such as argon gas and helium gas, it you know that converts more energy upon cavitation then you know diatomic gases such as nitrogen and oxygen because in that case you know larger ratio of the specifics will be there so that is why you will see that there will be effect of that presence and nature of the dissolved gases for the cavitation.

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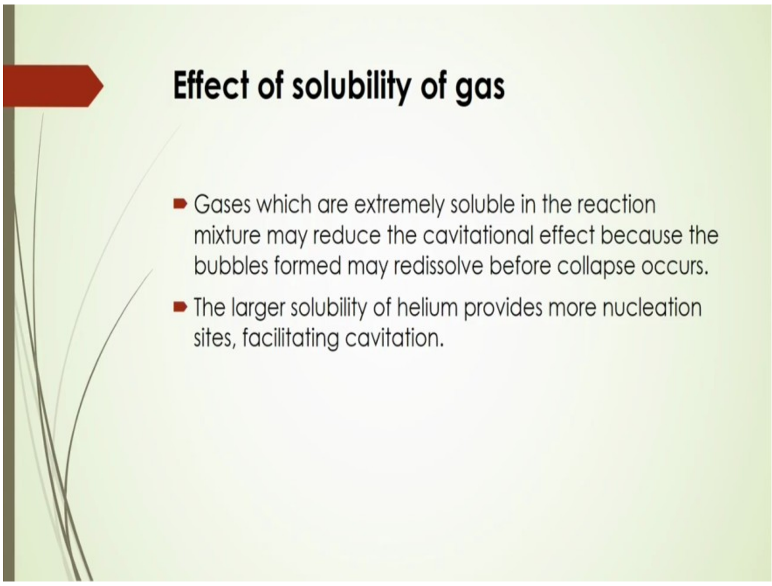

Effect of solubility of gas

- Gases which are extremely soluble in the reaction mixture may reduce the cavitational effect because the bubbles formed may redissolve before collapse occurs.
- The larger solubility of helium provides more nucleation sites, facilitating cavitation.

And also solubility of the gases is also one important factor. In that case gases which are extremely soluble in the reaction mixture may actually reduce the cavitational effect because the bubbles formed may you know re-dissolve before collapsing occurs. And the largest availability of helium that will provide more nucleation sites, which will facilitate the cavitation.

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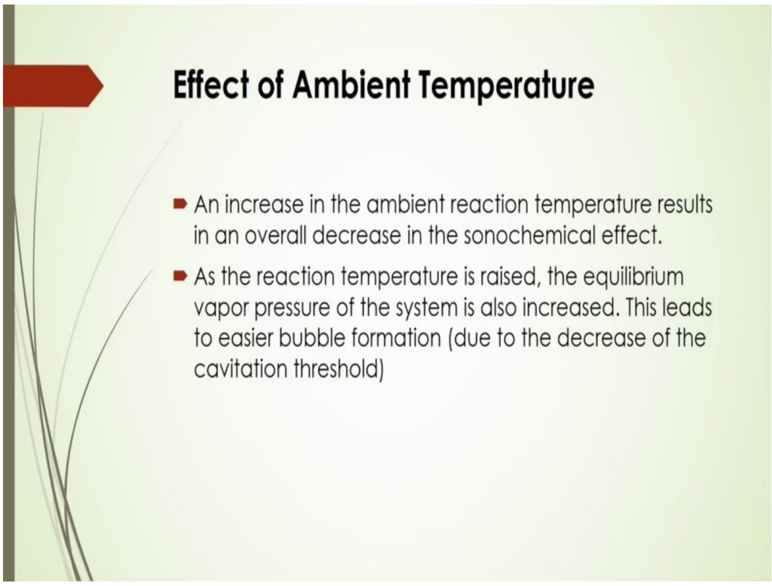

Effect of Ambient Temperature

- An increase in the ambient reaction temperature results in an overall decrease in the sonochemical effect.
- As the reaction temperature is raised, the equilibrium vapor pressure of the system is also increased. This leads to easier bubble formation (due to the decrease of the cavitation threshold)

Now, if there is any ambient temperature that will effect on cavitation or not if you increase the ambient reaction temperature that may you know result in an overall decrease in the sonochemical effect there. So as the reaction temperature increased, you will see the equilibrium vapour pressure of the system will increase. And because of this increase of you know the vapour pressure of the system, it will lead to you know is your bubble formation due to the decrease of the you know cavitational threshold there. So that is why the ambient temperature is important factor where you can have the overall that effect on the sonochemical effect because of that, just increasing the ambient reaction temperature that may decrease the sonochemical effect. So you have to consider the optimum temperature where it is required not to decrease the sonochemical effect.

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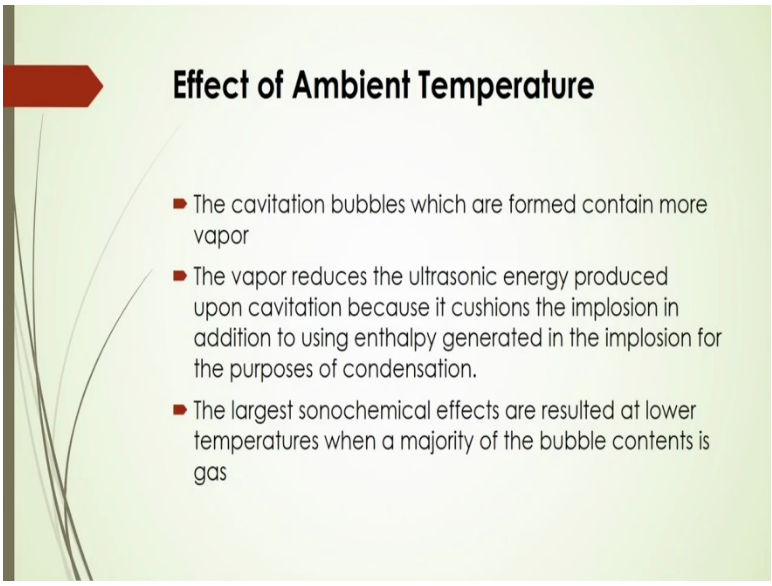

Effect of Ambient Temperature

- The cavitation bubbles which are formed contain more vapor
- The vapor reduces the ultrasonic energy produced upon cavitation because it cushions the implosion in addition to using enthalpy generated in the implosion for the purposes of condensation.
- The largest sonochemical effects are resulted at lower temperatures when a majority of the bubble contents is gas

Now, if suppose these cavitational bubbles which are formed contains more vapour, in that case the vapour will reduce the ultrasonic energy that is produced upon cavitation because in this case you know that the cushions the implosion in you know addition to using enthalpy generated in the implosion for the purposes of condensation there. So the largest sonochemical effects are resulted at that condition at low temperature when a majority of the bubble contents will be gas. So these are the different ambient temperature effects of you know that cavitation process.

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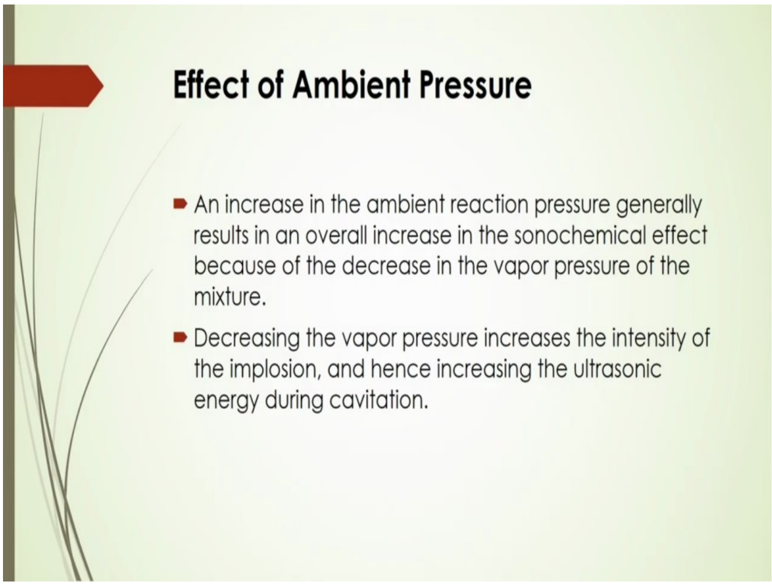

Effect of Ambient Pressure

- An increase in the ambient reaction pressure generally results in an overall increase in the sonochemical effect because of the decrease in the vapor pressure of the mixture.
- Decreasing the vapor pressure increases the intensity of the implosion, and hence increasing the ultrasonic energy during cavitation.

And also very interesting is that if you increase the ambient reaction pressure instead of you know temperature, it may you know result in an overall increase in the sonochemical affect because in this case the vapour pressure will decrease in the mixture and decreasing that vapour pressure that may increase the intensity of the implosion and also hence the increasing the ultrasonic energy during the cavitation there.

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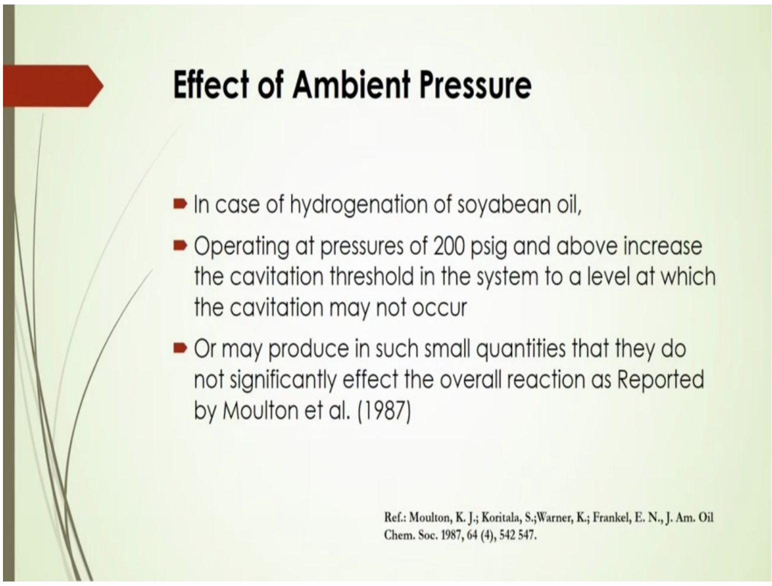

Effect of Ambient Pressure

- In case of hydrogenation of soyabean oil,
- Operating at pressures of 200 psig and above increase the cavitation threshold in the system to a level at which the cavitation may not occur
- Or may produce in such small quantities that they do not significantly effect the overall reaction as Reported by Moulton et al. (1987)

Ref.: Moulton, K. J.; Koritala, S.;Warner, K.; Frankel, E. N., J. Am. Oil Chem. Soc. 1987, 64 (4), 542 547.

And in case of like you know the hydrogenation of soyabean oil as an example, in that case the operating pressure of 200 psig and above increase the cavitation threshold in the system to a level at which the cavitation may not occur, this is actually the conclusion of Moulton et al in 1987. They have reported that you know that if you are increasing the operating pressure above the 200 PSI that are produced in such small quantities that they do not significantly affect the overall reaction as reported. So in that case you know that ambient pressure is also important factor which you know controls the overall reaction effect there based on this pressure or cavitational effect.

So as per Moulton et al, they reported that is the operating pressure up to 200 psig and above increases the cavitation threshold in the system at a level at which the that cavitation may not occur there, so it should be actually noted down.

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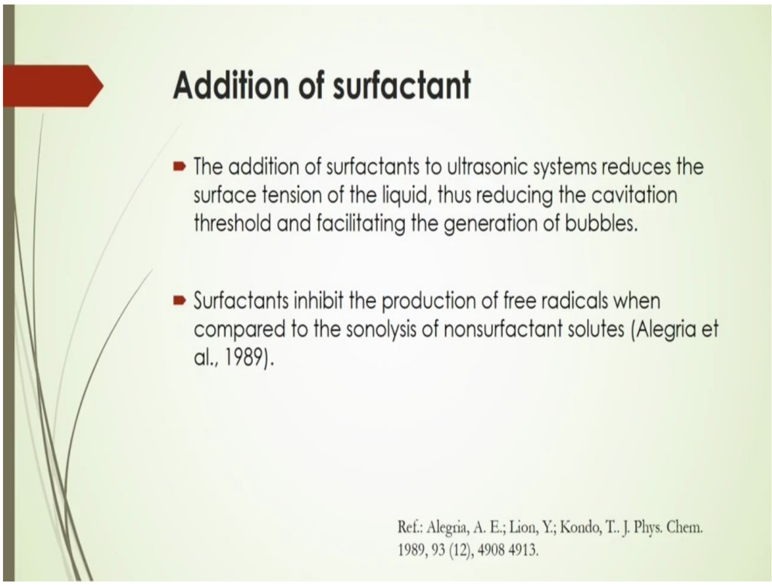

Addition of surfactant

- The addition of surfactants to ultrasonic systems reduces the surface tension of the liquid, thus reducing the cavitation threshold and facilitating the generation of bubbles.
- Surfactants inhibit the production of free radicals when compared to the sonolysis of nonsurfactant solutes (Alegria et al., 1989).

Ref.: Alegria, A. E.; Lion, Y.; Kondo, T.. J. Phys. Chem. 1989, 93 (12), 4908 4913.

Now, other effects like you know that addition of surfactant is there. You will see that addition of surfactants to ultrasound systems reduces the surface tension. Of course that if you at some surfactants there like sodium dodecyl sulfate or C tab or you know that MIBC, these types of surfactants if you are adding there, you see there of course the surface tension will reduce then water.

In that case the cavitation thresholds will reduce and it will facilitate the generation of cavities. And in this case sometimes you will see that if you are using the surfactant that may not be you know that feasible for any reaction system some reaction systems, in that case sometimes the surfactant inhibits the production of free radicals when compared to the sonolysis of that non-surfactant solutes there.

Like if you are using suppose free radicals formation of ozone there in you know that solution in surfactant medium, you will see that ozonation activity will be less that means because there production of the free radicals in that ozone reaction will be less there, so that is why some surfactant sometimes you will see that inhibits the production of free radicals when compared to the sonolysis of nonsurfactant solutes.

So in that case again if you add some surfactants their cavitation will be more that is surface area will be more, but in that case parallely the reduction of the free radical formation, so you have to use optimally what amount of surfactants can be used for. But some that is physical processes where that surfactant may not actually used no effect on that physical operations, in that case the surfactants addition may increase the use know that chemical process intensity or process you know efficiency there based on this cavitation there.

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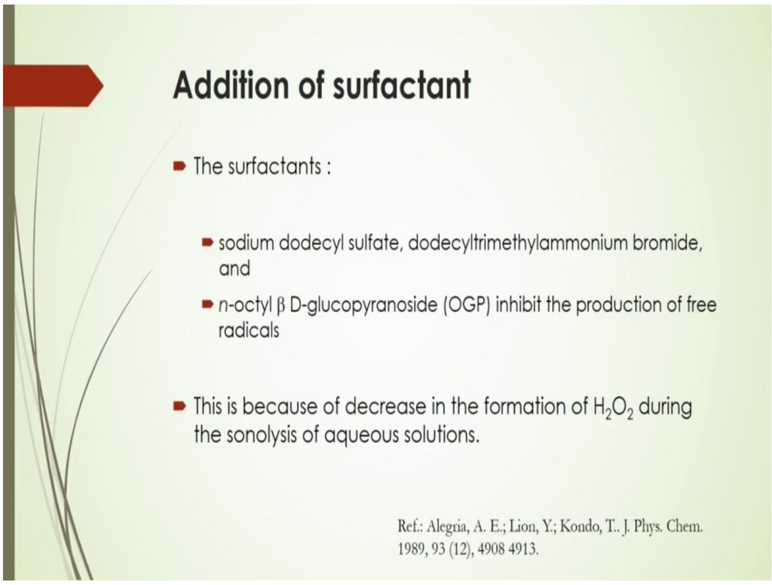

Addition of surfactant

- The surfactants :
  - sodium dodecyl sulfate, dodecyltrimethylammonium bromide, and
  - *n*-octyl β D-glucopyranoside (OGP) inhibit the production of free radicals
- This is because of decrease in the formation of H_2O_2 during the sonolysis of aqueous solutions.

Ref.: Alegria, A. E.; Lion, Y.; Kondo, T.. J. Phys. Chem. 1989, 93 (12), 4908 4913.

And like some surfactants here like we can sodium dodecyl sulfate, dodecyltrimethyl ammonium bromide, and even normal-octyl Beta D-glucopyranoside, in that case inhibits the production of free radicals there. This is because of decrease in the formation of hydrogen per oxide during the sonolysis of aqueous solutions there, so you have to remember that why this you know that decrease in the formation of hydrogen peroxide during the sonolysis of aqueous solution.

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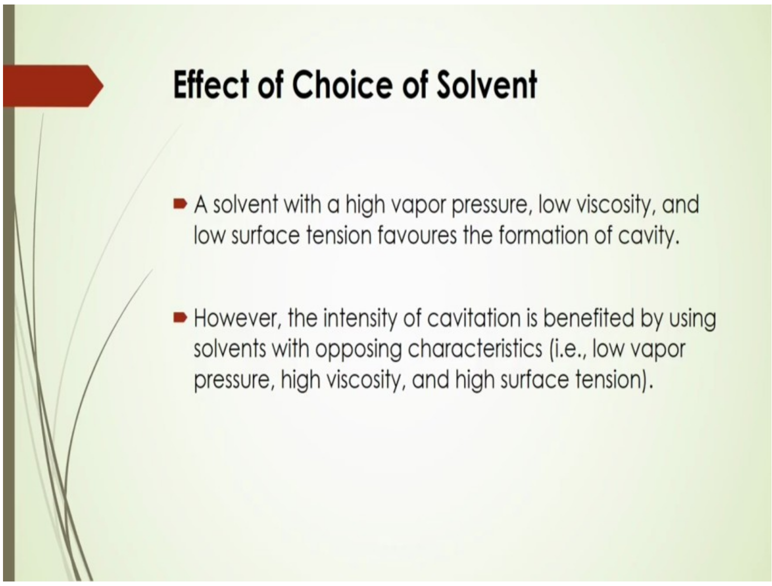

Effect of Choice of Solvent

- A solvent with a high vapor pressure, low viscosity, and low surface tension favoures the formation of cavity.
- However, the intensity of cavitation is benefited by using solvents with opposing characteristics (i.e., low vapor pressure, high viscosity, and high surface tension).

Also another effect it is called the effect of choice of solvent there, if you are adding some solvents with a high vapour pressure and also with low viscosity and low surface tension that will favor the formation of cavity. However, in this case you have to remember that the intensity of the cavitation is benefited by using solvents with opposing characteristics like low vapour pressure, high viscosity and high surface tension, so in this case it is noted that you have to use some solvent which will be low vapour pressure, high viscosity, high surface tension though there will be a less effect of formation of cavity there.

So, you have to produce that cavity in such a way that the optimum condition of the vapour pressure solvent and low viscous solvent or low surface tension solvents to be used where cavitation will be more, but parallely you have to also see the optimal value of the beneficiation of the intensity of the cavitation bit with you know the opposite characteristics like low vapour pressure, high viscosity and high surface tension there.

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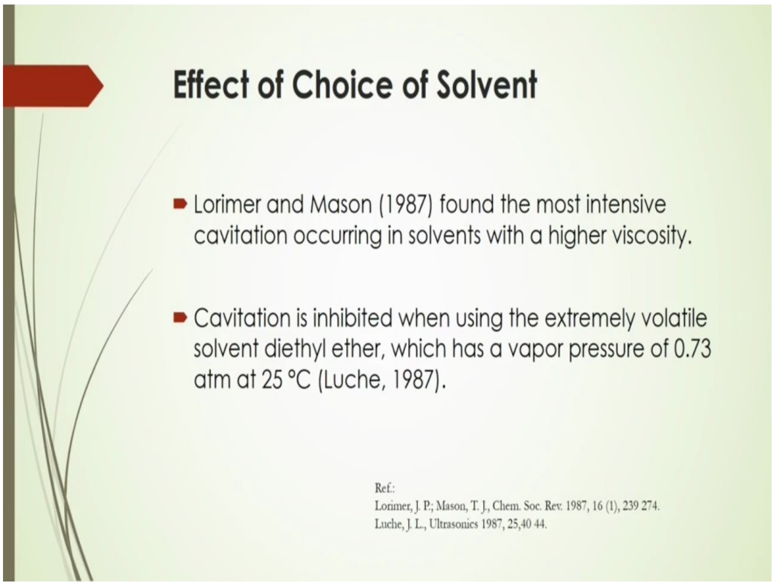

Effect of Choice of Solvent

- Lorimer and Mason (1987) found the most intensive cavitation occurring in solvents with a higher viscosity.
- Cavitation is inhibited when using the extremely volatile solvent diethyl ether, which has a vapor pressure of 0.73 atm at 25 °C (Luche, 1987).

Ref.:
Lorimer, J. P.; Mason, T. J., Chem. Soc. Rev. 1987, 16 (1), 239 274.
Luche, J. L., Ultrasonics 1987, 25,40 44.

In this regard it is very important to point out that Lormier and Mason’s work their experimental work, according to their observations they actually noted or they actually reported that the most intensive cavitation is occurred in solvents with higher viscosity and also cavitation will be inhibited when using the extremely volatile diethyl ether which has the vapour pressure of you know 0.73 atmosphere at 25 degree centigrade so this is also actually reported by Luche in 1987.

So, there are 2 observations here according to these researchers, what in this case that most intensive cavitation that may occur in solvents with higher viscosity, whereas Luche they actually observed that the cavitation is inhibited when using the extremely volatile solvent diethyl ether which has a vapour pressure of this at 25 degrees centigrade. So during the choice of solvents you have to remember these points of observations that are obtained by experiment by these investigators.

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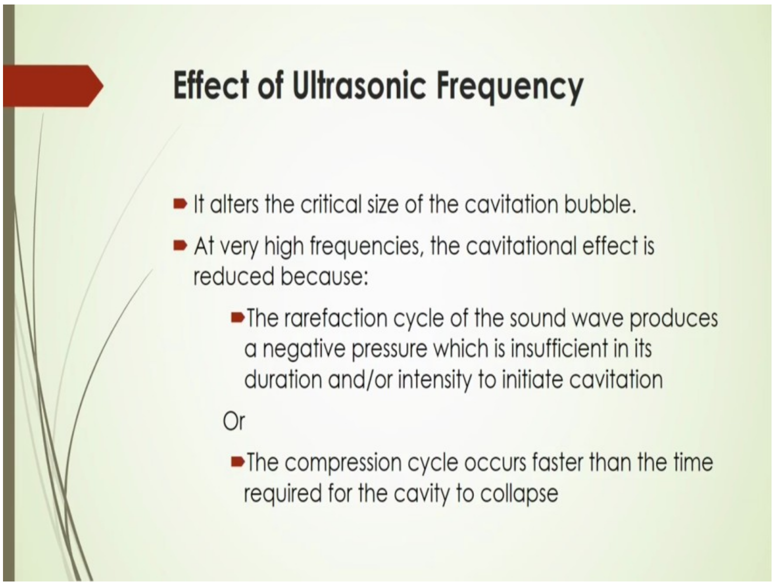

Effect of Ultrasonic Frequency

- It alters the critical size of the cavitation bubble.
- At very high frequencies, the cavitational effect is reduced because:
  - The rarefaction cycle of the sound wave produces a negative pressure which is insufficient in its duration and/or intensity to initiate cavitation

  Or

  - The compression cycle occurs faster than the time required for the cavity to collapse

Now effects of ultrasonic frequency, now in this regards the point to be remember here because the frequency of that you know ultrasonic cavity formation that depends mostly on that ultrasonic frequency, this frequency actually changes the critical size of the cavitation bubble and also you will see that at high frequency the cavitation effect may be you know that reduced because of you know the rare fraction cycle of the sound waves that produces a negative pressure.

And in that case negative pressure if it is sufficient in its duration and intensity of the initiate cavitation in that case high frequency, though high frequency will be there, the cavitational effect will be reduced. Or the compression cycle occurs faster than the time required for the cavity to collapse so because of this there at high frequency the cavitation effects will be reduced there.

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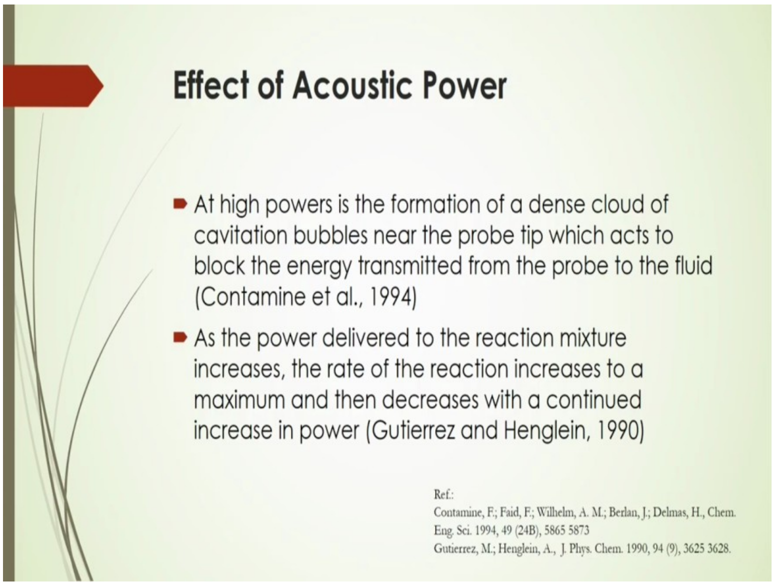

Effect of Acoustic Power

- At high powers is the formation of a dense cloud of cavitation bubbles near the probe tip which acts to block the energy transmitted from the probe to the fluid (Contamine et al., 1994)
- As the power delivered to the reaction mixture increases, the rate of the reaction increases to a maximum and then decreases with a continued increase in power (Gutierrez and Henglein, 1990)

Ref.:
Contamine, F.; Faid, F.; Wilhelm, A. M.; Berlan, J.; Delmas, H., Chem. Eng. Sci. 1994, 49 (24B), 5865 5873
Gutierrez, M.; Henglein, A., J. Phys. Chem. 1990, 94 (9), 3625 3628.

And another important point it is called acoustic power, if you are supplying high powers in the formation of dense cloud of cavitation bubbles in the you know that near about the probe tip which may acts to block the energy transformation from the probe to the fluid element, so in that case the formation of cavity may hinder at these high-powers there. So as the power delivered to the reaction mixture increases the rate of reaction increases to a maximum and then decreases with a continued increase in power.

So because here that you know that dense cloud of the cavitation bubbles near the probe tip, so these are actually observations based on the experimental works done by you know Contamine et al 1994, they have done tremendous work on cavitational work or cavitational process just by varying that acoustic power, how it will be changing.

Also you know Gutierrez and Henglein in 1990; they have also observed some you know that power effect on the cavitational effect there in the reaction mixture. So they have also stated that the rate of reaction increases to a maximum and then decreases with a continued increase in the power. So these are very nice work they have done on this cavitational system.

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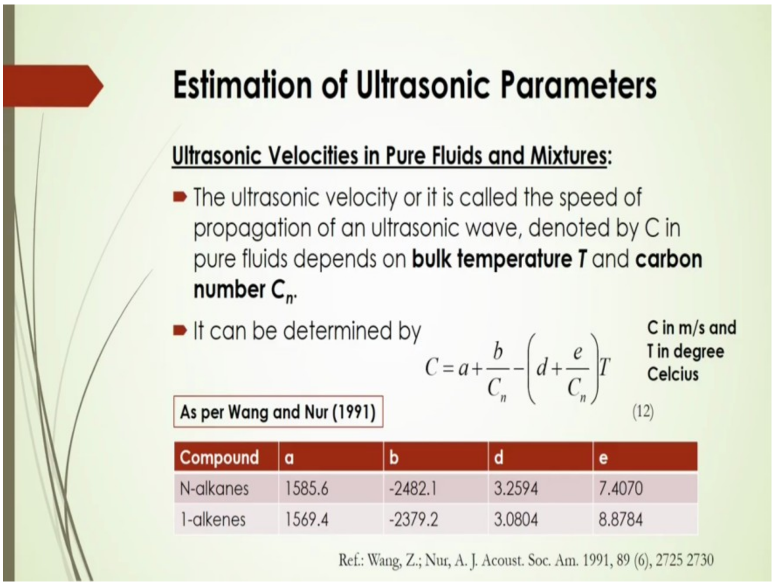

Estimation of Ultrasonic Parameters

Ultrasonic Velocities in Pure Fluids and Mixtures:

- The ultrasonic velocity or it is called the speed of propagation of an ultrasonic wave, denoted by C in pure fluids depends on **bulk temperature *T*** and **carbon number C_n.**
- It can be determined by

$$C = a + \frac{b}{C_n} - \left(d + \frac{e}{C_n}\right)T \tag{12}$$

C in m/s and T in degree Celcius

As per Wang and Nur (1991)

Compound	a	b	d	e
N-alkanes	1585.6	-2482.1	3.2594	7.4070
1-alkenes	1569.4	-2379.2	3.0804	8.8784

Ref.: Wang, Z.; Nur, A. J. Acoust. Soc. Am. 1991, 89 (6), 2725 2730

Now according to Wang's and Nur's observations in their experimental works and they have analysed that there will be an effect of ultrasonic velocities in pure or liquids and mixtures on the cavitation process, and they have estimated that ultrasonic parameters during their experimentation. And they actually also suggested correlation based on their experimental observations, and it is shown in equation number 12

$$C = a + \frac{b}{C_n} - \left(d + \frac{e}{C_n}\right)T \qquad (12)$$

here that they actually concluded that ultrasonic velocity, it is sometimes called speed of propagation of ultrasonic wave that is denoted by C here, this C in pure liquids that depends on you know bulk temperature and also carbon number is there.

So it can be determined by this correlation 12, in this case you will see some parameters like a, b, d, e is there, so this a, b, d, e actually these values these parametric values they have obtained based on their experimental work and they got these values shown in the tables here for this compound of normal alkanes and also one alkanes there. So based on their observations we can have this equation to calculate the you know that ultrasonic velocity for a certain you know that liquid medium where this carbon number is known to you and also temperature is known to you.

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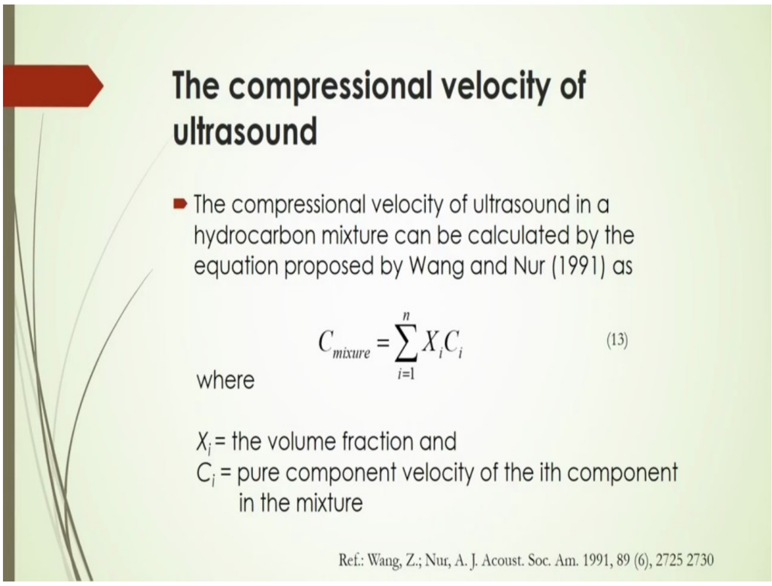

The compressional velocity of ultrasound

- The compressional velocity of ultrasound in a hydrocarbon mixture can be calculated by the equation proposed by Wang and Nur (1991) as

$$C_{mixure} = \sum_{i=1}^{n} X_i C_i \qquad (13)$$

where

X_i = the volume fraction and
C_i = pure component velocity of the ith component in the mixture

Ref.: Wang, Z.; Nur, A. J. Acoust. Soc. Am. 1991, 89 (6), 2725 2730

Now, in this case the compression velocity of the ultrasound also to be you know calculated or also to be predicted based on that you know cavitational process. Now, in this case compressional velocity of the ultrasound in a hydrocarbon mixture can be calculated by the equation that is proposed by that Wang and Nur in 1991. So they have suggested that this C mixture will be is equal to $\sum_{i=1}^{n} X_i C_i$ where X_i is called volume fraction of the mixture and C_i is called pure component velocity of the ith component in the mixture. So by this equation number 13

$$C_{mixure} = \sum_{i=1}^{n} X_i C_i \qquad (13)$$

you will be able to calculate what should be the compressional velocity of the ultrasound in the mixture.

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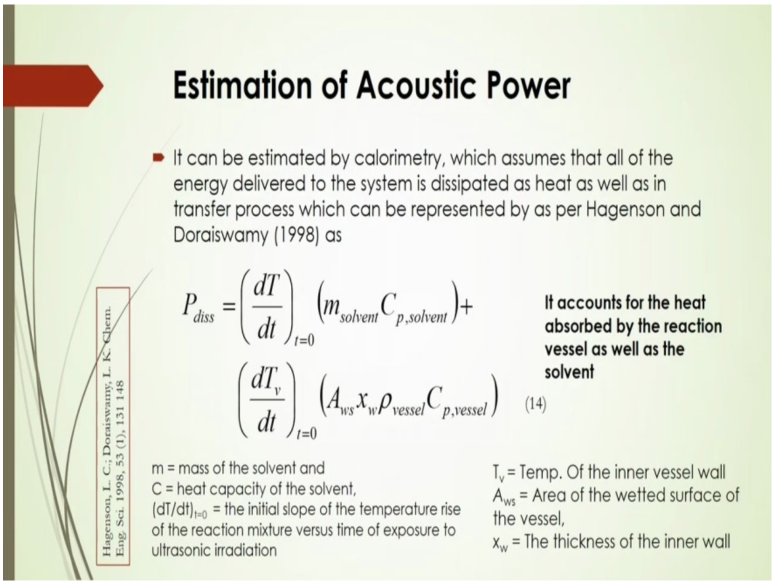

Estimation of Acoustic Power

- It can be estimated by calorimetry, which assumes that all of the energy delivered to the system is dissipated as heat as well as in transfer process which can be represented by as per Hagenson and Doraiswamy (1998) as

$$P_{diss} = \left(\frac{dT}{dt}\right)_{t=0} \left(m_{solvent} C_{p,solvent}\right) + \left(\frac{dT_v}{dt}\right)_{t=0} \left(A_{ws} x_w \rho_{vessel} C_{p,vessel}\right) \quad (14)$$

It accounts for the heat absorbed by the reaction vessel as well as the solvent

m = mass of the solvent and
C = heat capacity of the solvent,
$(dT/dt)_{t=0}$ = the initial slope of the temperature rise of the reaction mixture versus time of exposure to ultrasonic irradiation

T_v = Temp. Of the inner vessel wall
A_{ws} = Area of the wetted surface of the vessel,
x_w = The thickness of the inner wall

Hagenson, L. C.; Doraiswamy, L. K. Chem. Eng. Sci. 1998, 53 (1), 131 148

Now, how to estimate that acoustic power that we told that if you increase the acoustic power, initially the reaction intensity may be increased, but after a certain you know power by increase that may be you know decrease now, how to estimate that acoustic power this is actually helpful for the formation of the bubble. Now it can be estimated by you know calorimetry which assumes that all of the energy that will be delivered to the system and it will be dissipated as heat as well as in transfer process which can be represented by as per you know that Hagenson and Doraiswamy in 1998. So they have given nice actually equation to interpret that acoustic power there.

$$P_{diss} = \left(\frac{dT}{dt}\right)_{t=0} \left(m_{solvent} C_{p,solvent}\right) + \left(\frac{dT_v}{dt}\right)_{t=0} \left(A_{ws} x_w \rho_{vessel} C_{p,vessel}\right) \quad (14)$$

So the power dissipation can be calculated as dT by dt at time is equal to 0 that $m_{solvent}$ into $C_{p,solvent}$ + dT_v by dt into $A_{ws}x_w$ ρ_{vessel} and $C_{p,vessel}$ that is you do as per equation number 14 you know as per their suggestions you can you know calculate the power dissipation for the acoustic you know cavitation. In this case m is called the mass of the solvent and C_P is the heat capacity of the solvent and also dT by dt this is the initial slope of the temperature rise of the reaction mixture and also you can say that this can be obtained whatever this profile is coming for the temperature with respect to time from that profile you will be able to calculate what should be the slope and based on which we will calculate that acoustic power.

And in this case T_v is called the temperature of the linear vessel wall and A_{ws} is the area of the weighted surface of the vessel and x_w is the thickness of the inner wall. So if you know that the temperature variation with respect to time of the reaction mixture as well as the temperature variation with respect to time of that inner vessel wall then you will be able to calculate what will be the acoustic power that is required for the formation of the cavity in the system. Generally it accounts for the heat absorbed by the reaction vessel as well as the solvent there as an acoustic power.

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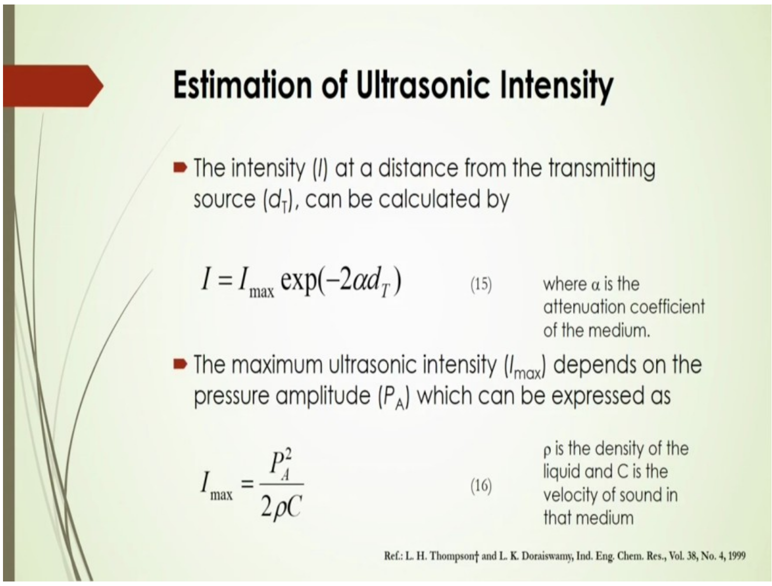

Estimation of Ultrasonic Intensity

- The intensity (I) at a distance from the transmitting source (d_T), can be calculated by

$$I = I_{\max} \exp(-2\alpha d_T) \qquad (15)$$

where α is the attenuation coefficient of the medium.

- The maximum ultrasonic intensity (I_{max}) depends on the pressure amplitude (P_A) which can be expressed as

$$I_{\max} = \frac{P_A^2}{2\rho C} \qquad (16)$$

ρ is the density of the liquid and C is the velocity of sound in that medium

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

Now, how to estimate the ultrasonic intensity? The intensity I at distance from the transmitting sources dT can be calculated by this equation number 15 here.

$$I = I_{\max} \exp(-2\alpha d_T) \qquad (15)$$

So this will be is equal to I that can be calculated as a function of you know I_{max} and also this transmitting source, so based on this equation number 15 you will be able to calculate the ultrasonic intensity.

Also in this case you have to calculate what will be the maximum ultrasonic intensity to be actually there during that you know that cavitation process, so that maximum ultrasonic intensity that actually depends on the pressure amplitude and based on this equation number you know 16,

$$I_{\max} = \frac{P_A^2}{2\rho C} \qquad (16)$$

By equation number 16 you will be able to calculate this maximum intensity as a function of pressure amplitude as well as the density and also the velocity of the sound. So here I_{max} will be is equal to P_A square by 2 into ρC, here ρ is the density of the liquid and C is called sound velocity in the medium.

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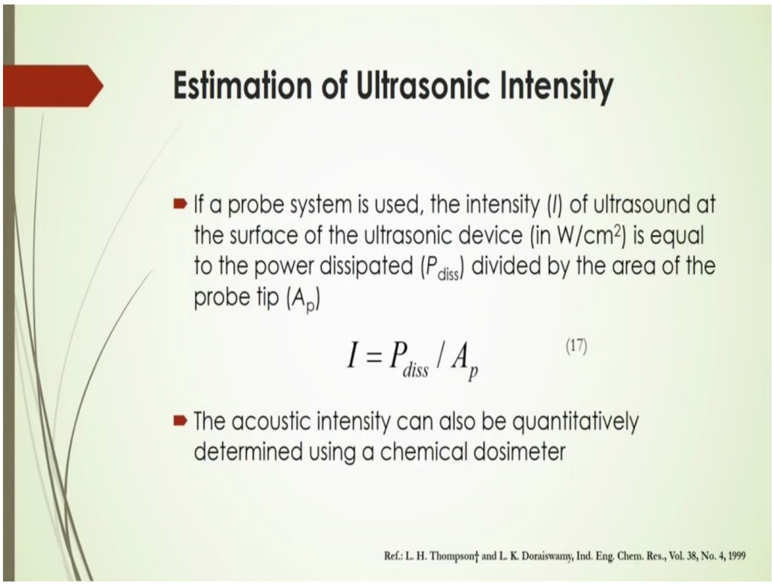

Estimation of Ultrasonic Intensity

- If a probe system is used, the intensity (I) of ultrasound at the surface of the ultrasonic device (in W/cm^2) is equal to the power dissipated (P_{diss}) divided by the area of the probe tip (A_p)

$$I = P_{diss} / A_p \tag{17}$$

- The acoustic intensity can also be quantitatively determined using a chemical dosimeter

Ref.: L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999

And if the probe system is used, in that case the intensity of the ultrasound at the surface of the ultrasonic device that can be calculated in watt per centimeter square in terms of you know that power dissipation, so it can be calculated by equation number 17 which can be expressed as

$$I = P_{diss} / A_p \qquad (17)$$

So A_p is actually the area of the probe tip there, so if you know the power dissipation from the equation number 14, and if you know the area of the probe team then you will be able to calculate what should be the intensity of the ultrasound at the source of the ultrasonic device.

The acoustic intensity can also be quantitatively determined using you know chemical dosimeter. So dosimeter you know you can use to calculate the acoustic intensity directly based on this principle.

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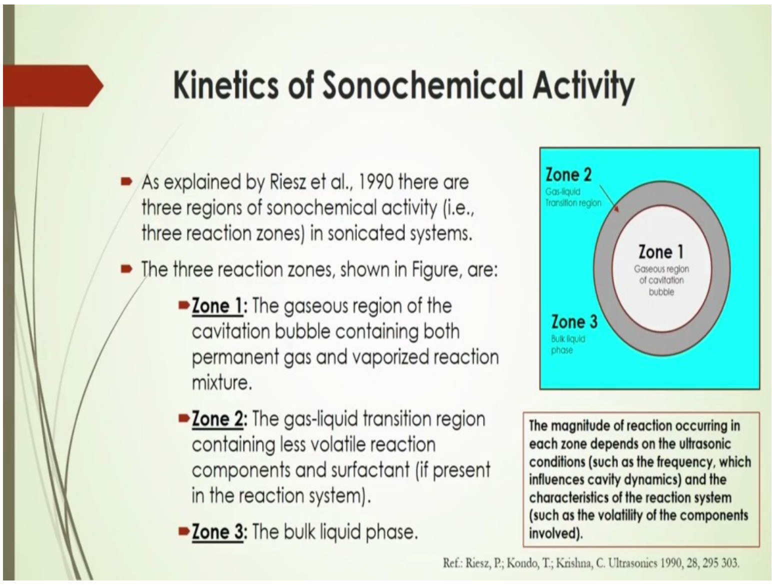

Kinetics of Sonochemical Activity

- As explained by Riesz et al., 1990 there are three regions of sonochemical activity (i.e., three reaction zones) in sonicated systems.
- The three reaction zones, shown in Figure, are:
  - **Zone 1**: The gaseous region of the cavitation bubble containing both permanent gas and vaporized reaction mixture.
  - **Zone 2**: The gas-liquid transition region containing less volatile reaction components and surfactant (if present in the reaction system).
  - **Zone 3**: The bulk liquid phase.

The magnitude of reaction occurring in each zone depends on the ultrasonic conditions (such as the frequency, which influences cavity dynamics) and the characteristics of the reaction system (such as the volatility of the components involved).

Ref.: Riesz, P.; Kondo, T.; Krishna, C. Ultrasonics 1990, 28, 295 303.

Now, Kinetics of sonochemical activity is very important here how actually this Kinetic is actually effected by during the cavitation process. You know in this case the work of you know Riesz et al in 1990 is very important because that case they have actually done tremendous work on you know that reaction Kinetics in the sonochemical environment, so they explained that there are three regions of sonochemical activity like you know that it is called three reaction zones in the sonicated system.

The three reaction zones are actually identified as zone 1 where the gaseous region of the cavitation bubbles that will contain both permanent gas and vaporised reaction mixture, and in zone 2 here as shown in figure here, the gas-liquid transition region where this region contains less volatile reaction components and surfactant if there is any present of the surfactant in the reaction system or not.

And in the zone the bulk liquid phase will be there considered, so in this case according to their observation they actually stated that the reaction zone can be divided into three parts like zone 1, zone 2 and zone 3. In this case the magnitude of the reaction that is occurred in each zone that will depend on the ultrasonic conditions such as the frequency which influences activity dynamics, and also you can say that the characteristics of the reaction systems such as whether the compounds you are using that will be volatile or not so that is also important there.

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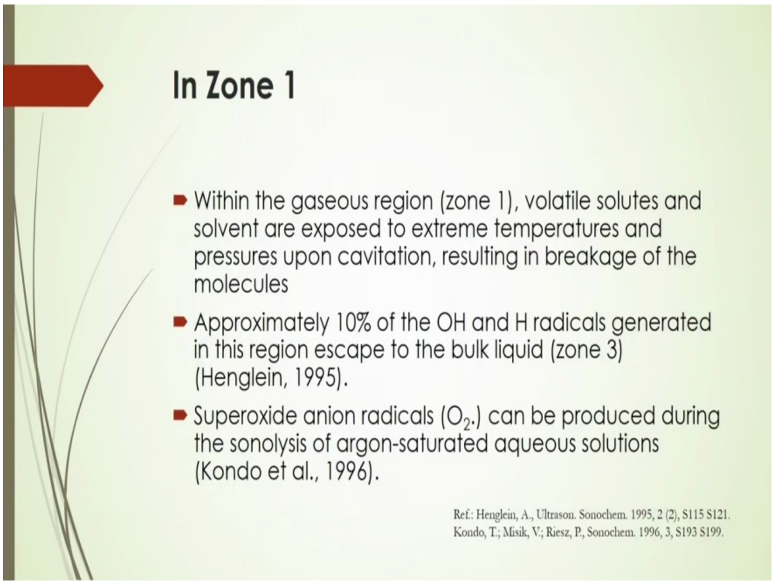

In Zone 1

- Within the gaseous region (zone 1), volatile solutes and solvent are exposed to extreme temperatures and pressures upon cavitation, resulting in breakage of the molecules
- Approximately 10% of the OH and H radicals generated in this region escape to the bulk liquid (zone 3) (Henglein, 1995).
- Superoxide anion radicals ($O_2.$) can be produced during the sonolysis of argon-saturated aqueous solutions (Kondo et al., 1996).

Ref.: Henglein, A., Ultrason. Sonochem. 1995, 2 (2), S115 S121.
Kondo, T.; Misik, V.; Riesz, P., Sonochem. 1996, 3, S193 S199.

Now, in the zone 1 then the gaseous region can say volatile solutes and solvents are exposed to extreme temperatures and pressures upon cavitation which will result in breakage of the molecules. And in this case approximately 10 percent of the OH and hydrogen radicals that will be generated in the region that may escape to the bulk liquid in the zone 3. And also super oxide, anion radicals can be produced during the sonolysis of the you know argon saturated aqueous solutions as observed by Kondo et al. (1996).

So this Kondo et al also, they have observed you know that how this super oxide and anion radicals is produced during that sonolysis of Mono atomic gas saturated aqueous solutions there.

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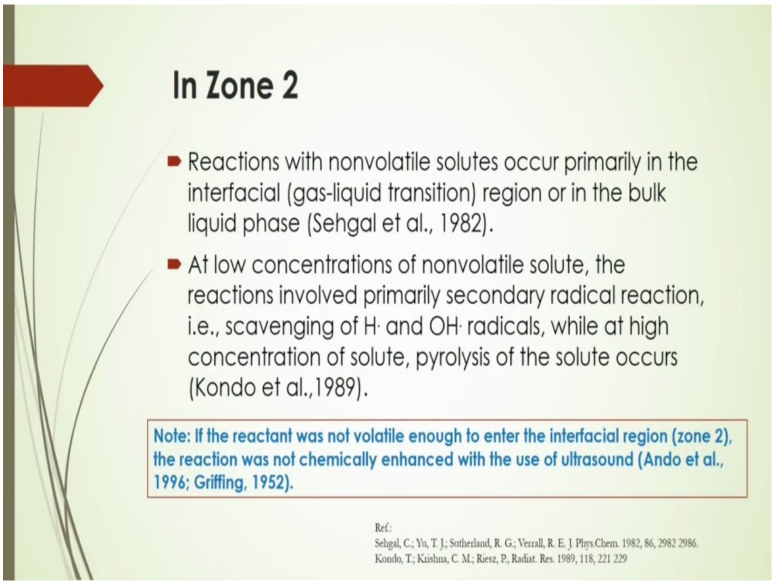

In Zone 2

- Reactions with nonvolatile solutes occur primarily in the interfacial (gas-liquid transition) region or in the bulk liquid phase (Sehgal et al., 1982).
- At low concentrations of nonvolatile solute, the reactions involved primarily secondary radical reaction, i.e., scavenging of H· and OH· radicals, while at high concentration of solute, pyrolysis of the solute occurs (Kondo et al.,1989).

Note: If the reactant was not volatile enough to enter the interfacial region (zone 2), the reaction was not chemically enhanced with the use of ultrasound (Ando et al., 1996; Griffing, 1952).

Ref.:
Sehgal, C.; Yu, T. J.; Sutherland, R. G.; Verrall, R. E. J. Phys.Chem. 1982, 86, 2982 2986.
Kondo, T.; Krishna, C. M.; Riesz, P., Radiat. Res. 1989, 118, 221 229

In the reaction zone 2, the reactions with nonvolatile solutes occurs primarily in the interfacial gas-liquid transition phase and also in that case you know that bulk liquid phase may be here to be considered where that interfacial phenomenon will be you know primarily involved there for the reactions of nonvolatile solutes. At low concentrations of nonvolatile solutes, the reactions involved primarily secondary radical you know reaction like you know that scavenging of hydrogen radicals, waste radical you know that while at high concentration of solutes that pyrolysis of the solute occurs as per the observations of Kondo et al. (1989).

So in this case again the Sehgal et al.'s observation and Kondo et al.'s observations are you know that very important you know observations where you can you know say that how that cavitational effect can actually change the reaction conditions at different solutes and also at different concentrations of the nonvolatile solutes there.

So, if the reactant is not volatile enough to enter the interfacial region in zone 2, in that case the reaction may not be the chemically enhanced with the use of ultrasound there as per you know that observation of Ando et al. (1996). So in the reaction zone we can say that there will be effect of you know solutes and also its concentration is important for the involving of the secondary radical reaction in the cavitation process.

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In Zone 3

- Bulk liquid-phase (zone 3) reactions involve radicals which escape the implosion.

In zone 3, the bulk liquid phase it is called in that case reaction is involves radicals escape the implosion during that cavitation process.

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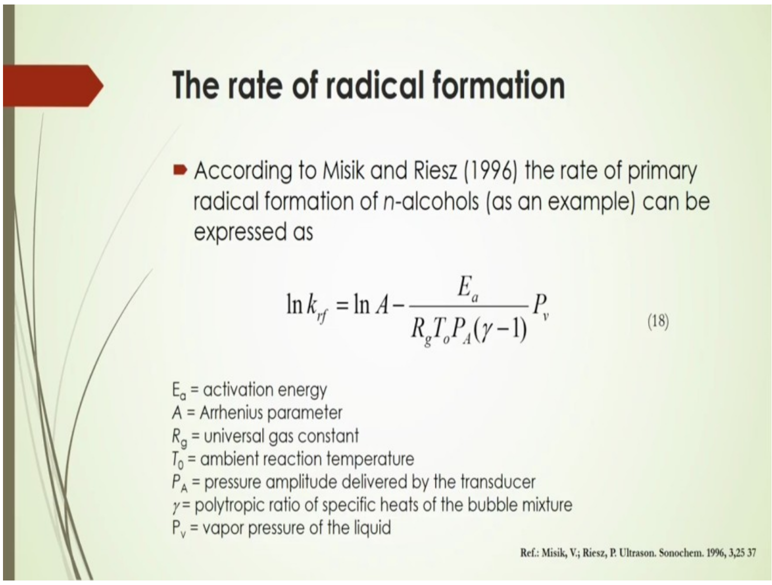

The rate of radical formation

- According to Misik and Riesz (1996) the rate of primary radical formation of *n*-alcohols (as an example) can be expressed as

$$\ln k_{rf} = \ln A - \frac{E_a}{R_g T_o P_A(\gamma - 1)} P_v \qquad (18)$$

E_a = activation energy
A = Arrhenius parameter
R_g = universal gas constant
T_0 = ambient reaction temperature
P_A = pressure amplitude delivered by the transducer
γ= polytropic ratio of specific heats of the bubble mixture
P_v = vapor pressure of the liquid

Ref.: Misik, V.; Riesz, P. Ultrason. Sonochem. 1996, 3,25 37

Now, how actually this radical is formed and what is the rate of that radical formation? Now in this case the work that is done by Misik and Riesz in 1996, according to their observation the rate of primary radical formation of you know normal alcohols as an example that can be expressed as, the rate of you know this primary radical formation can be expressed by this equation number 18 here.

$$\ln k_{rf} = \ln A - \frac{E_a}{R_g T_o P_A(\gamma - 1)} P_v \qquad (18)$$

This is the function of pressure amplitude delivered by the transducer there, and also what would be the vapour pressure also it is very important.

So this rate of radical formation can be calculated by this equation number 18 as $\ln k_{rf}$ is given here, where in this case E_a is called activation energy, A is called Arhenius parameter and you know R_g is called universal gas constant, T_0 is the ambient reaction temperature and P_A is the pressure amplitude that is delivered by the transducer, Gamma is the polytropic ratio of specific heats of the bubble mixture and P_V is the vapour pressure of the liquid.

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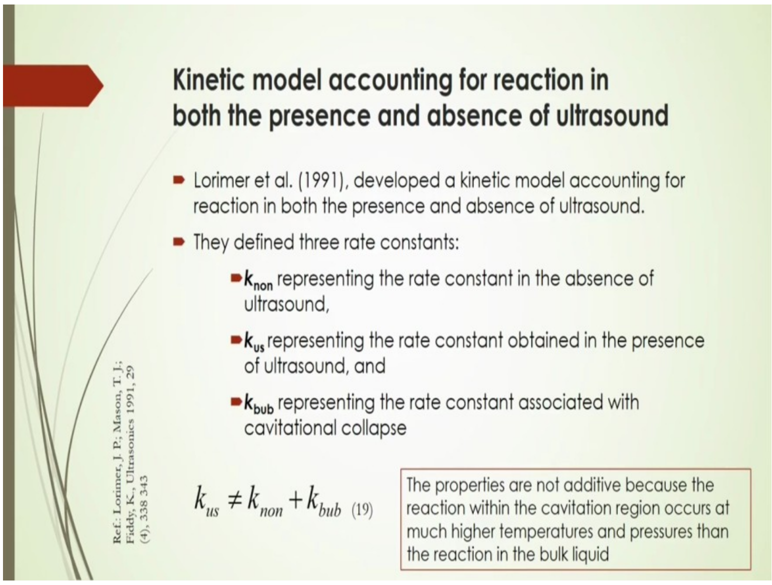

Kinetic model accounting for reaction in both the presence and absence of ultrasound

- Lorimer et al. (1991), developed a kinetic model accounting for reaction in both the presence and absence of ultrasound.
- They defined three rate constants:
  - k_{non} representing the rate constant in the absence of ultrasound,
  - k_{us} representing the rate constant obtained in the presence of ultrasound, and
  - k_{bub} representing the rate constant associated with cavitational collapse

$$k_{us} \neq k_{non} + k_{bub} \quad (19)$$

The properties are not additive because the reaction within the cavitation region occurs at much higher temperatures and pressures than the reaction in the bulk liquid

Ref: Lorimer, J. P.; Mason, T. J.; Fiddy, K., Ultrasonics 1991, 29 (4), 338 343

Now, you see that Lorimer et al. (1991) developed this Kinetic model accounting for reaction of both presence and absence of ultrasound. According to their observation, they defined three rate constants; here it is called K_{non} representing the rate constant in the absence of ultrasound, where K_{us} represents the rate constant opted in the presence of ultrasound and also K_{bub} which is represented as the rate constant associated with cavitational collapse.

And according to their observation that they told that the K_{us} that may not be equal to the summation of K_{non} and K_{bub} there.

$$k_{us} \neq k_{non} + k_{bub} \qquad (19)$$

In this case the properties are not additive because the reaction within the cavitation region that occurs at a much higher temperature and pressure than the reaction in the bulk liquid.

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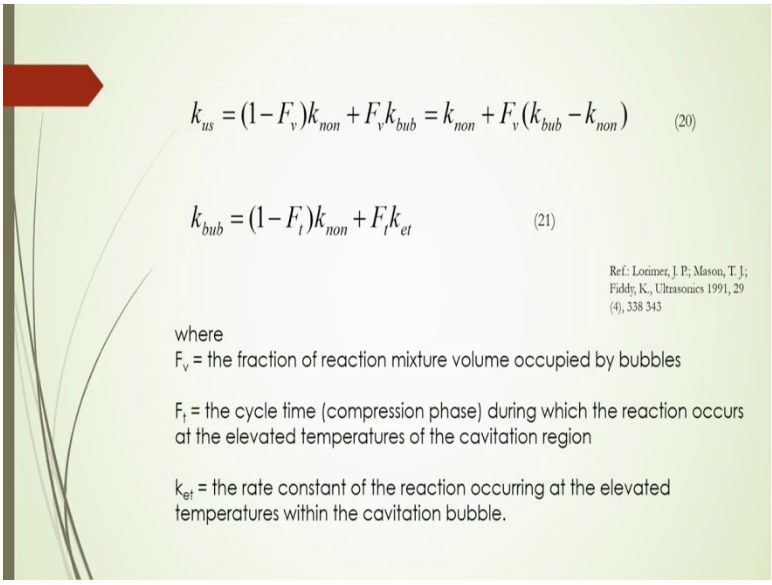

$$k_{us} = (1-F_v)k_{non} + F_v k_{bub} = k_{non} + F_v(k_{bub} - k_{non}) \qquad (20)$$

$$k_{bub} = (1-F_t)k_{non} + F_t k_{et} \qquad (21)$$

Ref.: Lorimer, J. P.; Mason, T. J.; Fiddy, K., Ultrasonics 1991, 29 (4), 338 343

where
F_v = the fraction of reaction mixture volume occupied by bubbles

F_t = the cycle time (compression phase) during which the reaction occurs at the elevated temperatures of the cavitation region

k_{et} = the rate constant of the reaction occurring at the elevated temperatures within the cavitation bubble.

And as per equation number 20

$$k_{us} = (1-F_v)k_{non} + F_v k_{bub} = k_{non} + F_v(k_{bub} - k_{non}) \qquad (20)$$

you can calculate the K_{us} and equation number 21 we will give you the conclusion of this K_{bubble}.

$$k_{bub} = (1-F_t)k_{non} + F_t k_{et} \qquad (21)$$

So in this case also some factors like you know the F_v, F_v is the fraction of reaction mixture volume that is occupied by bubbles and F_t is the cycle time, K_{et} is called the rate constant of the reaction that occurs at the evolve temperature within that cavitation bubbles.

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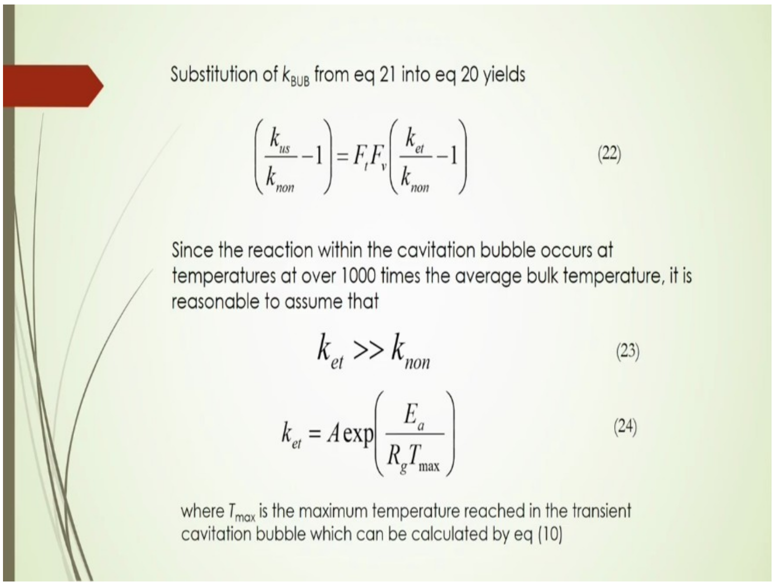

Substitution of k_{BUB} from eq 21 into eq 20 yields

$$\left(\frac{k_{us}}{k_{non}} - 1\right) = F_t F_v \left(\frac{k_{et}}{k_{non}} - 1\right) \qquad (22)$$

Since the reaction within the cavitation bubble occurs at temperatures at over 1000 times the average bulk temperature, it is reasonable to assume that

$$k_{et} >> k_{non} \qquad (23)$$

$$k_{et} = A\exp\left(\frac{E_a}{R_g T_{max}}\right) \qquad (24)$$

where T_{max} is the maximum temperature reached in the transient cavitation bubble which can be calculated by eq (10)

And equation 22 will give you the yields after substitution of K_{bub} from the equation 21 into equation 20.

$$\left(\frac{k_{us}}{k_{non}}-1\right)=F_tF_v\left(\frac{k_{et}}{k_{non}}-1\right) \qquad (22)$$

And at the condition of Equation 23 like

$$k_{et} >> k_{non} \qquad (23)$$

where the reaction within the cavitation bubbles occurs at temperature at over 1000 times the average bulk temperature, it is reasonable to assume that this K_{et} will be greater than greater than is equal to K_{non}. So in that case this K_{et} can be calculated from equation number here 24

$$k_{et}=A\exp\left(\frac{E_a}{R_gT_{\max}}\right) \qquad (24)$$

where T_{max} in this case is the maximum temperature that will reach in the transient cavitation bubbles which can be calculated by equation number 10 there it is given.

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Further reading……

- David Reay, Colin Ramshaw, and Adam Harvey, Process Intensification: Engineering for effgiciency, sustainability and flexibility, IchemE, 2nd edition, 2013, Elsevier.
- L. H. Thompson† and L. K. Doraiswamy, Ind. Eng. Chem. Res., Vol. 38, No. 4, 1999
- Kamelia Boodhoo and Adam Harvey. Process Intensification for Green Chemistry Engineering Solutions for Sustainable Chemical Processing, Edited by Kamelia Boodhoo and Adam Harvey , School of Chemical Engineering & Advanced Materials Newcastle University, UK. Willey, 2013
- Juan Gabriel Segovia-Hernández, Adrián Bonilla-Petriciolet Editors, Process Intensication in Chemical Engineering Design Optimization and Control, Springer, 2016.
- S. K. Majumder, Hydrodynamics and Transport Processes of Inverse Bubbly Flow, 1st ed. Elsevier, Amsterdam (2016)

So, in this lecture we have actually given the you know idea of how actually the different parameters will affect that cavitation process and how that acoustic parameters can be calculated, and also how it will be effect on the you know that cavitation process in the Chemical Engineering Processes. So I would suggest to read more about this you know that effect of different operating parameters on the cavitation process from these references, so it will be more helpful to you.

So in this module we have discussed the different aspects of cavitation process, how it is actually formed and also what are the different configurations of the cavitation reactor and also what are the different effects of different variables on that cavitational process. So this modules also that is also will give you the more compact information about the cavitation process, thank you.