

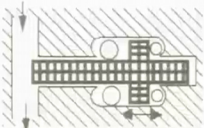
Design Practice - 2
Prof. Shantanu Bhattacharya
Department of Mechanical Engineering
Indian Institute of Technology-Kanpur

Lecture - 21
Electrochemical valves

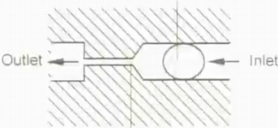
Hello and welcome to this course design practice to module 21 we were discussing about actuators and sensors design and in the last lecture we had extensively covered how pneumatic valves and thermo pneumatic valves can be designed parametrically. We are now going to cover electrochemical valves which are again non-conventional in nature and then depending on hydrolysis of water and formation of a two-phase system there can be a gating, non gating done in a small channel.

(Refer Slide Time: 00:49)

Electrochemical Valves



(a) Outlet



(b) Capillary-force valve

Typical Electrochemical Valves (a) Gate Form (b) Capillary form

Electrochemical valves are actuated using gas bubbles generated by electrolysis of water:

$$2\text{H}_2\text{O} \text{-----} 2\text{H}_2 + \text{O}_2$$

Determine the energy required for generating an electrolysis spherical bubble with an approximate diameter of 28 microns. Compare it to a thermal bubble of the same size. The specific density of hydrogen and oxygen at 1 bar and 25 deg. C are .08988 Kg/m³ and 1.429 kg/ m³, respectively. The surface tension of water is assumed to be constant at .072 N/m. Enthalpy of formation of water is 285.83KJ/ mol. The thermodynamic properties of liquid water at 1 bar are v (25 Deg. C) = 1.0029 X 10⁻³ m³/kg, u (25 deg. C) = 104.88 KJ/Kg and of vapor: v (100 Deg. C) = 1.673 m³/kg, u(100 deg. C) = 2506.5 kJ/Kg.

Specific vol.

I think I had illustrated this example last class in the last slide when we are talking about electrochemically being able to make these bubbles and controlling the rates at which this bubble, bubbles get formulated so that there is a forward or reverse push to this particular gating device you know it gates this micro channel right here. So, the channel has an inlet side somewhere here outlet side in this particular zone and so you can actually control the flow in this manner.

Or alternately you can create again a two phase here the you know with hydrolysis and creating hydrogen oxygen bubbles which can actually block the flow going through this constriction here so that there is again gating or valving. Typically these kind of valves are used very often for

micro flows because obviously you know we are just talking about a gas bubble in the mechanical strength involved in the bubble as the basic force of the valving action in the particular channel.


So, in context of that I had given a design problem here where we talked about determining the energy required for generating electrolysis based spiracle bubble with an approximate diameter of 28 microns ah the reaction that was there the hydrolysis of water reaction is given in this particular equation. So, when we compare it to thermal bubble of the same size obviously there will be differences and that is what we have to compute given some parameters including specific density of hydrogen or oxygen at standard temperature pressure STP.

And also the surface tension of water which is given again at room temperature conditions enthalpy of formation of water which is again given at the standard temperature and pressure conditions. And then some thermodynamic properties of liquid water particularly both at one bar as well as one by 25 degree Celsius as well as one bar 100 degree Celsius and this would be useful for computing the total work done ah you know in order to produce a thermally assisted bubble.

And so basically the comparison lies between what kind of energy would electrolysis process uptake in comparison to a thermal process to formulate such a bubble which we will do this blocking action for the particular micro Channel.

(Refer Slide Time: 03:18)

Assuming a contact angle of zero, the pressure inside the bubble is estimated as



$$\Delta P = \frac{2\sigma}{r}, \quad \sigma = 0.072 \text{ N/m}$$

$$r = \frac{h}{2}, \quad h = 28 \text{ microns}$$

$$\Delta P = \frac{2 \times 0.072 \times 10^{-3}}{14 \times 10^{-6}} = 10^3 \text{ Pa} \approx 1 \text{ bar}$$

Surface energy = $2\pi r \sigma = 2\pi \times 14 \times 10^{-6} \times 0.072 = 6.27 \times 10^{-11} \text{ J}$

All properties being defined at 1 bar

Specific density of the electrolysis gas mixture is

$$\rho_{\text{mixture}} = \frac{\rho_{\text{H}_2} + 2\rho_{\text{O}_2}}{3} = \frac{1.429 + 2 \times 0.00702}{3} = 0.536 \text{ kg/m}^3$$

The amount of water needed to generate the bubble is:

$$m = V_{\text{bubble}} \rho_{\text{mixture}} = \frac{4}{3} \pi (14 \times 10^{-6})^3 \times 0.536$$

$$= 6.127 \times 10^{-17} \text{ kg}$$

So, let us actually start solving this particular problem so here we are assuming a contact angle of almost 0 as you can understand that the bubble is sort of formulated just like cylinder of the same cross-section as the channel in which it is in and with that kind of a contact angle we would like to calculate the the pressure inside the bubble ah at least the difference in pressure between the inside and the outside okay.

So, the pressure inside the bubble is estimated through standard equations for ΔP in this kind of a situation ΔP is twice σ by r σ being the surface tension of the particular liquid water bubble interface. So, the σ is already represented as 0.072 Newton per meter and this is borrowed from the question itself. And in this particular case if we consider h to be the height of the channel.

Let us say this is completely the the span over which the bubble needs to come out so that there is valving of the flow so r in this case becomes $h/2$. We assume the bubble to be centrally located and the bubble center to be the matching with the axial center of the channel. So, in this particular case then ΔP is represented as $2 \cdot \sigma$ which is $72 \cdot 10^{-3}$ divided by the height of the channel in this particular case for the which is equal to the diameter of the bubble is given as 28 microns.

So, in this particular case the ΔP can be $28 \cdot 10^{-6}$ meters times again you have 2 here okay because obviously this whole h is 28 microns for the bubble to occupy the whole channel depth the channel size and this is computed as 10^{-5} Pascal's or approximately 1 bar for the bubble to hold. So, all properties are defined at 1 bar specific density 1 bar pressure.

And the specific density of the the gas mixture which formulates because of the hydrolysis process need to be find out so that we can do something ah to calculate the; already there is a enthalpy of the formation of water given as 285.83 kilo Joule per mole. So, we want to calculate how much energy is needed electrolytic energy is needed for formulation of this particular bubble okay. So, this is the enthalpy of formation.

So, all the property is being defined at one bar in the specific density of the electrolysis gas mixture can be defined as the raw mixture equals the density of oxygen plus twice the density of hydrogen divided by 3. So, this is a sort of an average density assuming the hydrolysis equation

to generate both hydrogen and oxygen gases and this is a sort of a mixture density of both these engage states.

So, we can write this down as 1.429 which is the density of oxygen at the standard temperature pressure conditions. All the units are kg per meter cube okay plus twice the density of the hydrogen which is written down as 0.08988 kg per meter cube divided by 3. So, this comes out to be after calculations 0.536 kg per meter cube. So, that is the average density of the mixture of gases which is post electrophoresis post electrolysis.

And and let us look at that if this is the density of the mixture we have a certain volume depending on what is the radius of the particular diameter we should be able to calculate what is the mass mass of water that is needed to produce that kind of a bubble okay. So, the amount of water that is needed for generating the bubble is $V \rho_{mix}$ V being the volume $\frac{4}{3} \pi r^3$ and the radius being 14 microns 14×10^{-6} whole cube okay $\times 0.536$ which is being calculated as 0.536 kg per meter cube.

And this comes out to 1., 6.127×10^{-15} kgs. So, that is how the M is defined on the total amount of mass of water which gets vaporized. So, having said that we need to now find out what are the number of moles by dividing this with the atomic weight of water which is H_2O or 18 that how many kilo moles of molecules are needed water molecules are needed to generate this gas bubble.

(Refer Slide Time: 10:34)

The mole no. corresponding to the mass of H_2O electrolyzed is

$$n = \frac{6.127 \times 10^{-15} \times 10^3}{18} \rightarrow H_2O \rightarrow 2+16 = 18 \text{ gm}$$

$$= 0.34 \times 10^{-15} \text{ kmol.}$$

The energy required for creating the electrolysis bubble

$$= n (\text{Enthalpy of formation of } H_2O) = 0.34 \times 10^{-15} \times 285.83 = 97.2 \times 10^{-12} \text{ J}$$

The specific vol. of water vapour at STP $1.0029 \times 10^{-3} \text{ m}^3/\text{kg}$
 " " " " $1.673 \text{ m}^3/\text{kg}$

$$m = \frac{V}{\rho} = \frac{\frac{4}{3} \times \pi \times (14 \times 10^{-6})^3 \times 0.536}{1.673} = 6.867 \times 10^{-15} \text{ kg}$$

So, this will give us an idea of what is the specific enthalpy of formation of the bubble. So, the mole number corresponding to the mass of H_2O electrolyzed is 6.127×10^{-15} this

is in kgs. Let us make it in grams okay 10^{-3} / 18 grams H₂O has an atomic weight of 2 + 16, 18 so that is how much is the weight of one mole H₂O, so therefore this number comes out to be 0.34×10^{-15} kilo mole.

Let us calculate the energy required for making the electrolysis bubble. So, the energy required for creating the electrolysis bubble is the mole number times the enthalpy of formation of water so that is $0.34 \times 10^{-15} \times 285.83$ kilo Joule per kilo mole this is the enthalpy of formation per kilo mole and this comes out to be 97.2×10^{-12} joules. So, so much amount of energy is needed for electrolytically formulating the bubble in the particular channel.

Now let us look at the thermal generation or thermal aspect and what is the kind of energy needed for the thermal aspect and then we will try to calculate some efficiencies particularly the electrochemical bubble formation efficiency and the thermal bubble formation efficiency. So, let us suppose at the standard temperature pressure transition the specific volume of water vapor is reported as 1.0029×10^{-3} meter cube per kg.

The specific volume of water this is at STP standard temperature pressure condition at 100 degrees Celsius and one bar pressure is reported here as 1.673 meter cube per kg and these are from the stated questions earlier stated question earlier. So, we want to calculate in the size of the bubble and the volume of the bubble which is calculated before assuming the radius to be about 14 microns.

What is going to be the total amount of mass of water assuming thermally actuated mechanism where bubble gets formulated and assuming a specific volume at the boiling point of water that is under a degree Celsius to be 1.673 meter cube per kg so, obviously this is going to be different than what the mass was of the electrolytic bubble. So, let us see what is that difference so here the mass becomes equal to the volume by the specific volume.

And the volume here of the bubble again is the same $\frac{4}{3} \pi r^3$ and the specific volume in this case is 1.673 so this comes out to be $= 6.867 \times 10^{-15}$ kgs. Well so this is somewhat different then what this value this other value was 6.127×10^{-15} and that is because the mechanism of bubble formation is completely different. So, you can say that in the state in the gaseous state the energy storage is little bit higher than what happened in the electrochemical case.

And because of such a difference there will be definitely a difference in the overall efficiency when we consider the expansion process and the bubble formation process. So, with this kind of a mass of the thermal bubbles okay let us ignore all the other heat losses and let us compute what is the energy required for making such a thermal bubble.

(Refer Slide Time: 15:19)

Ignoring the heat losses, the energy required for making a thermal bubble

$$\Delta U_{\text{thermal}} = m(u_2 - u_1) = 6.817 \times 10^{-15} (2506.5 - 104.88) \times 10^3 = 1.14 \times 10^{-8} \text{ J}$$

$u_2(100^\circ\text{C}) = 2506.5 \text{ kJ/kg}$, $u_1(25^\circ\text{C}) = 104.88 \text{ kJ/kg}$

In both cases the expansion work done by the bubble is

$$W = \int_0^{\frac{2r}{\rho}} p \, dv = \int_0^{\frac{2r}{\rho}} 4r^2 \, dr = 2 \times 72 \times 10^{-3} \times 4 \times 2.14 \times 10^{-10} = 1.772 \times 10^{-10} \text{ J}$$

The maximum efficiency of the electrolytic bubble is $\eta = \frac{W}{W + \Delta U_{\text{thermal}}} = \frac{1.772 \times 10^{-10}}{1.772 \times 10^{-10} + 1.14 \times 10^{-8}} = 0.015$

So, ignoring the heat losses the energy required for making a thermal bubble is $\Delta U_{\text{thermal}}$ which is equal to the mass M times of the internal internal energy at 100 degrees Celsius minus the internal energy at 25 degrees Celsius. So, obviously the internal energies are different at both the temperatures and you are going from the room temperature STP to one bar hundred degree Celsius for the thermal bubble to be formulated. So, there is obviously going to be a difference in the internal energy because heat is being added to the system to formulate the gas state. And so if we consider the mass that we calculated in the earlier equation through the specific volume term that is 6.867×10^{-15} kg times you know if I looked at u_1, u_2 at 100 degrees Celsius has been given in the question as 2506.5 kilo Joule per kg I am sorry kilo joule per kg.

And u_1 add agree self has been given as 104.88 kilo joule per kg so I am going to just outlay these two numbers here $2506.55 - 104.88$ and I am left with 1.64×10^{-8} joules this of course is the number in kilo Joule so we will just multiply it with 1000 to convert the equivalent in Joule number. So, this is what the thermal energy of the bubble would be when it gets formulated from one bar standard room temperature 100 degree Celsius 1 bar pressure.

So, in both cases obviously an expansion work has been done because even if it is a boiling phenomena and generation of a vapour state the bubble has to nucleate at some point and slowly

expand to come to that 28 micron size. In the similar manner in electrolysis as well it has to nucleate at some center around the electrode probably where the electrons are being pumped in and grow in size eventually against the ΔP pressure.

So, some amount of work is needed to overcome that pressure and maintain the two-phase condition so that the bubble can expand in size. So, let us look at that work done in this particular case and so if I looked at in both the cases that is the thermal and the electrolytic case the expansion work done by the bubble. So, it can be written as again you know the integral $P dv$ where P is really the pressure difference across which the bubble is expanding.

And you know that that pressure difference ΔP is already represented as a function of the bubble radius. So, more is the radius lesser would be the ΔP and vice versa and it is also dependent on the surface tension. So, in this particular problem if we assume the bubble to nucleate as a spherical bubble and formulate generally a zero contact angle over all occupancy within the channel the spherical volume being $\frac{4}{3} \pi r^3$ the dv in that particular case would be $4 \pi r^2 dr$ okay.

So, you want to just compute the W here by representing 2σ by our $4 \pi r^2 dr$ integral and r is obviously expanding from 0 to 14 microns, 14 microns is the final radius where the contact angle is almost zero. So, we are assuming that the contact angle is 0 as the bubble expands. And probably it may come from a flat electrode spanned over a certain length you know which would generate this bubble from the electrode surface onwards.

So, in this particular case if we wanted to substitute all the values we have the surface tension as 72×10^{-3} Newton per meter and obviously the r goes away here and we are left with a 4π expression coming out of the integral times the value of the integral between 0 and 14 10^{-6} meters this is a square by 2. So, when we calculate this value right here and multiply the overall number that comes out here for the total amount of work done is 1.772×10^{-10} joules.

So, that is what the expansion work is when we talk about electrochemical or even thermal bubble. So, a thermal bubble is also to generate from a sort of a flat surface so that we can assume the bubble to have zero contact angle okay. Just as we are generating the electrochemical bubble and so let us now have a difference in comparison between the different efficiencies that

is one of the electrochemical process and one of the thermal process and try to realize what all are those differences.

So, the maximum efficiency of the electrolysis bubble in this particular case can be written down as let us say we call it Eta electric electrolytic so this is the work of work of expansion and divided by the total amount of work of expansion plus the change in the electrochemical state of water the in electrometric generated because of the change in electrochemical state of water which is because of the enthalpy of the reaction.

And when we calculate this number it comes out to be 1.772×10^{-10} divided by $1.722 \times 10^{-10} + \Delta u_{\text{electrochemical}}$ which we calculated earlier in this particular expression and we found this to be 97.2×10^{-12} joules so we put this value back here 97.2×10^{-12} joules and similarly if I wanted to calculate the thermal the maximum thermal efficiency.

(Refer Slide Time: 22:50)

The maximum thermal efficiency of the thermal bubble

$$\eta_{\text{Thermal max}} = \frac{w}{w + \Delta u_{\text{Thermal}}} = \frac{1.77 \times 10^{-10}}{1.77 \times 10^{-10} + 1.64 \times 10^{-8}} = 0.51\%$$

$\eta_{\text{Electrochemistry}} \gg \eta_{\text{Thermal expansion}}$

Let us look at that number and the maximum thermal efficiency of the thermal bubble so we have $\eta_{\text{Thermal max}}$ is $w / w + \Delta u_{\text{Thermal}}$ again in this case the work of expansion being same the only difference which would happen is what amount of thermal energy is being generated and that value has again been recorded here as 1.64×10^{-8} joule so 1.64×10^{-8} joule 11 and if you compare these efficiency values so the efficiency for the thermal case is computed as 0.51% and that for the electrochemical case or electrolytic case is 64.59% .

So obviously electrochemical efficiency is more in the compare with thermal efficiency you can say Eta electrochemical it is quite high in comparison to the thermal efficiency. So, one can think of this actuation scheme electrochemical actuation scheme to be better than simply a thermal scheme of formulation of a an ah actuation mechanism which would create a gate to move forward or backward. And one of the reasons why electrochemical may be showing better efficiency is that if we compare the internal energies in the case of formulation of a bubble thermally and electro chemically they were very different in nature and so that kind of gets expressed into the final efficiency equation.

So, we will now try to go ahead and do some other kind of schemes for doing actuation.
(Refer Slide Time: 24:59)

Capillary Force Valves

Electro capillary effect:

- It is also known as electro-wetting effect, and it changes the surface tension between two immiscible, conductive liquids or between a solid surface and a liquid by varying their potential difference.
- As we already know there is the formation of an electrostatic double layer between any two surfaces. This may be a surface and a fluid or a fluid and another fluid.
- By changing the electrostatic potential between the double layer, the surface tension σ between the 2 liquids become:

$$\sigma = \sigma_0 - (C/2)(V - V_0)^2$$

where C is the capacitance per unit area of the double layer, V is the applied potential across the liquid interface.

There is for example this capillary force valves which are again actuated through something called electrostatic double layer based actuation mechanism. It is also otherwise known as electro capillary effect or electro wetting effect and it changes the surface tension between two immiscible conductive liquids or between solid surface in a liquid by varying their potential difference.

So, the surface tension equation that is provided because of a change in and the overall dual-layer aspect the electrostatic dual layer aspect is given by $\sigma = \sigma_0 - C / 2 V - V_0$ whole square C is the capacitance per unit area of this particular spherical bubble so the recap the cylindrical bubble and particularly the capacitance of the double layer of charges we can assume these ends to be lengthwise miniscule in comparison to the overall length of the bubble.

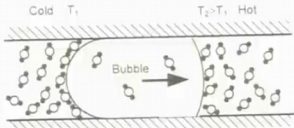
V is the applied potential across the liquid interface so basically the difference in potential between you know the both the electrodes the positive and the negative electrodes is V , σ_0 probably was the initial surface tension and the σ is the final surface tension when V potential is applied over and above V_0 . So, as the potential is increased between both surfaces of the bubble that is surface 1 and surface 2 obviously there is going to be a difference in the surface tension and because of the difference in surface tension there would be migration.

So, that generally the bubble moves towards the lower surface tension. So, this is a way to sort of guide a bubble and actuate again valving through in micro channels in micro flows through just creating a potential difference.

(Refer Slide Time: 27:07)

Thermo-capillary effect

- Thermo-capillary effect is caused by the temperature dependence of the surface tension.
- The surface tension reflects the surface energy. At higher temperature, the molecules of the liquid move faster and their attractive force becomes smaller.
- The smaller attractive force causes lower viscosity and lower surface tension.
- At the right side, the temperature is higher, so the surface tension is lower.
- That causes a pressure gradient across the bubble, which leads to bubble movement from left to right.



The diagram illustrates the thermo-capillary effect in a microchannel. A bubble is shown moving from left to right. The left side of the channel is labeled 'Cold T_1 ' and the right side is labeled ' $T_2 > T_1$ Hot'. The bubble is larger on the right side, indicating a pressure gradient that drives its movement towards the higher temperature region. The channel walls are shown as hatched lines.

There is also a thermo capillary effect which can be used sometimes to do actuation it is caused by temperature dependence just as you saw the charge dependence and change in surface tension. There can be a temperature difference across the profile of a bubble and you know that as temperature increases the surface tension decreases okay. So, it reflects a sort of the difference in the surface energy so at higher temperatures the molecules of the liquid would move faster their attractive force becomes smaller and vice-versa.

And because of such a difference in the surface tension again there would be movement from the cold zone to the hot zone and generally the bubble would try to move towards the hot zone because the surface tension is lower. And this pressure gradient would be good for actuate again a bubble in place so that there can be obstruction of flow in a suitably designed actuator. So,

when we talk about such micro valves there are many such actuation schemes which are available.

You saw that there is a thermo capillary effect there is a electrostatic you know capillary wetting effect there is also thermo pneumatic effect or numeric effect and then electrochemical effect and these all are different ways of performing actuation for with suitable designs can be initiated to do this basic phenomena valving. So, I think I have gone through some of the very critical aspects of micro valuing.

I like to close on this particular module and the next module probably will take up another section of where actuators are highly needed which is micro flow causing devices or micro pumps so I am going to end this module now thank you very much.