INDIAN INSTITUTE OF TECHNOLOGY MADRAS

NPTEL
National Programme on Technology Enhanced Learning

Chemical Engineering
Thermodynamics

by

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Lecture 1
Thermodynamics and the Chemical Industry

This is the first lecture of this course on chemical engineering thermodynamics. I thought I would give you an overview of thermodynamics in the chemical industry. The outline of this lecture and I am going to use power point only for this lecture. The outline of the lecture is as follows.

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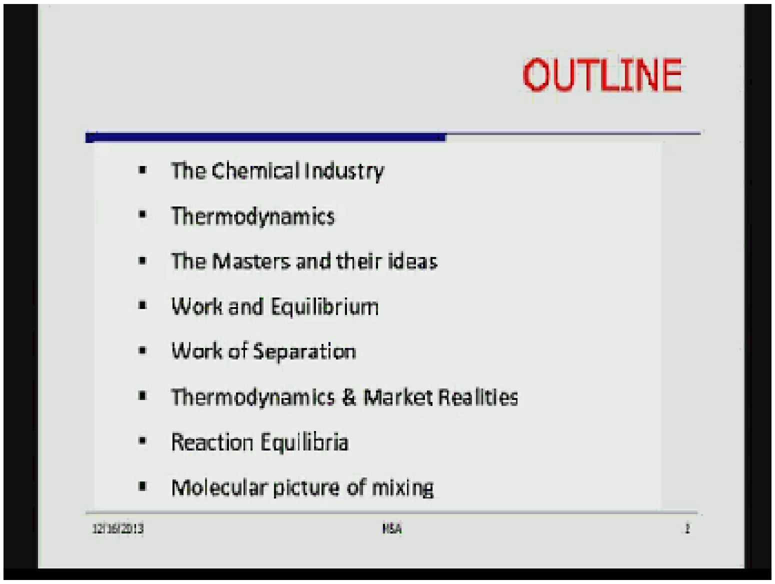

OUTLINE

- The Chemical Industry
- Thermodynamics
- The Masters and their ideas
- Work and Equilibrium
- Work of Separation
- Thermodynamics & Market Realities
- Reaction Equilibria
- Molecular picture of mixing

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I talk about the chemical industry in general and I will tell you a bit about thermodynamics. Then I am going to tell you about the masters and their ideas that is the people who actually developed the subject of thermodynamics. The important aspects of chemical engineering in thermodynamics that we will discuss mainly work and equilibrium. In particular I will talk about work of separation and show you that thermodynamics actually predicts market prices reasonably well and then we will discuss a bit about reaction equilibria and finally I will close with a molecular picture of mixing.

I must say that classical thermodynamics does not depend upon the molecular structure of matter. It is actually independent of that. But the molecular picture helps preview a handle on understanding what the properties mean in molecular terms. So I will start off by telling you something about the chemical industry.

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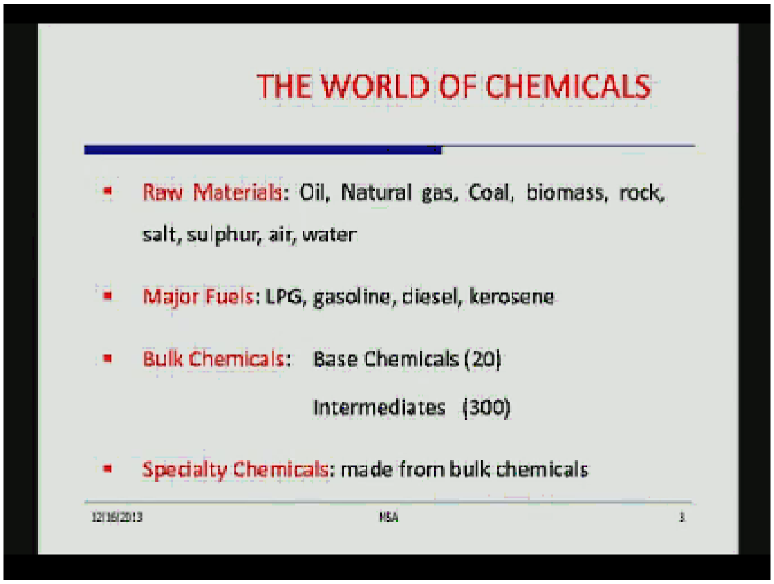

THE WORLD OF CHEMICALS

- Raw Materials: Oil, Natural gas, Coal, biomass, rock, salt, sulphur, air, water
- Major Fuels: LPG, gasoline, diesel, kerosene
- Bulk Chemicals: Base Chemicals (20)
  Intermediates (300)
- Specialty Chemicals: made from bulk chemicals

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The first thing that strikes you about the world of chemicals is you think there are infinite chemicals. But basically there are four groups; they are classified into four groups and the raw materials that we discuss are usually oil, natural gas, coal, biomass, rock salt, sulphur, air and water and the major fuels are LPG, gasoline, diesel, kerosene. The bulk chemicals are divided into base chemicals and intermediates, about 300 intermediates and the specialty chemicals are those that are made from bulk chemicals. These numbers will increase but certainly not infinite, its reasonable numbers that you can handle.

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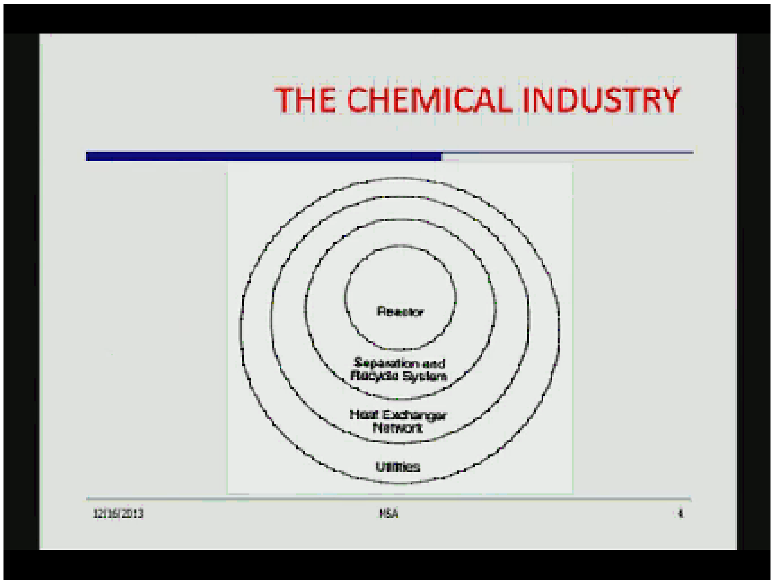

THE CHEMICAL INDUSTRY

The chemical industry basically consists of the following, principle reactor usually at the core, whole lot of separation and recycle systems, heat exchanger networks and utilities is broadly the picture of the chemical industry.

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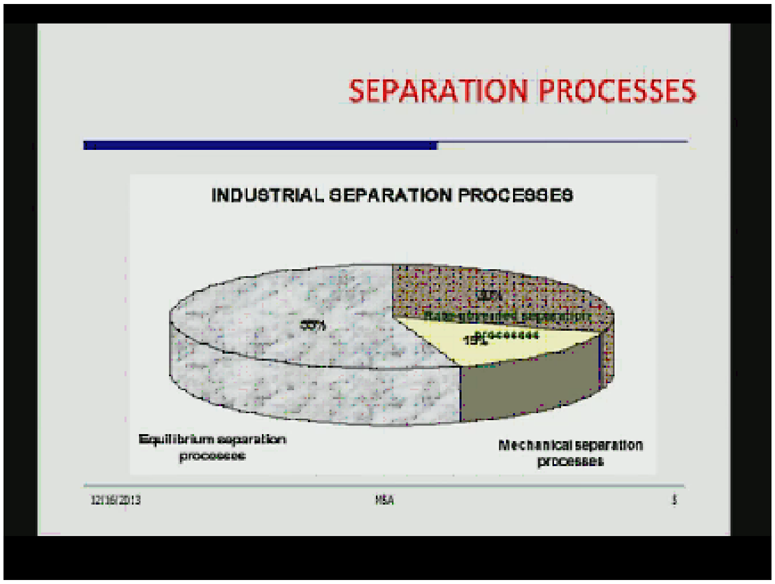

SEPARATION PROCESSES

INDUSTRIAL SEPARATION PROCESSES

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After the reactor there is the separation process and I have to tell you something about separation process. The industrial separation process can be divided as shown in this picture roughly. You have equilibrium separation processes which constitute about 55% of the total and then you have 30% rate govern separation processes, and you have mechanical separation processes in the balance.

The equilibrium separation processes can be designed basically designed on the basis of thermodynamics itself. Thermodynamics deals with the equilibrium and many of these process are work operate so close to equilibrium that you can make quantitative predictions with thermodynamics.

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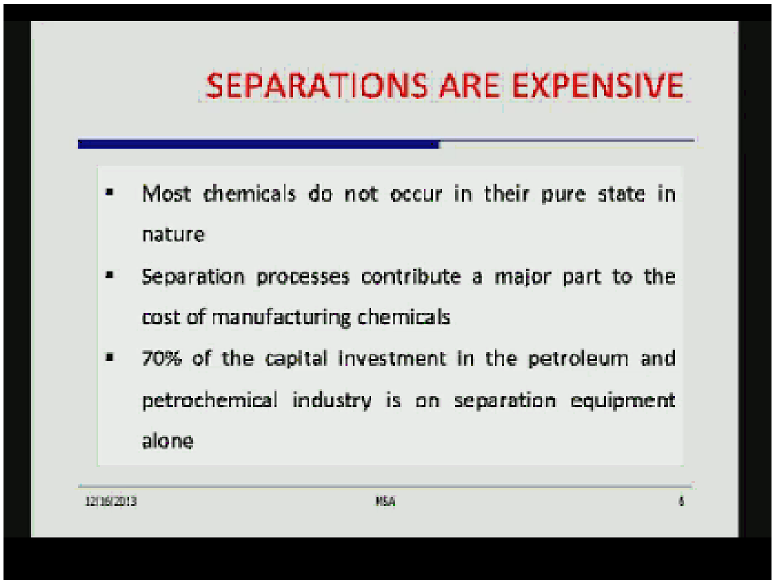

SEPARATIONS ARE EXPENSIVE

- Most chemicals do not occur in their pure state in nature
- Separation processes contribute a major part to the cost of manufacturing chemicals
- 70% of the capital investment in the petroleum and petrochemical industry is on separation equipment alone

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The point is that separations are expensive. Most chemicals do not occur in their pure state in nature, so separation processes contribute a major part and 70% of the capital investment is estimated in the petroleum and the petrochemical industry is on separation equipment alone. Now that is about the chemical industry.

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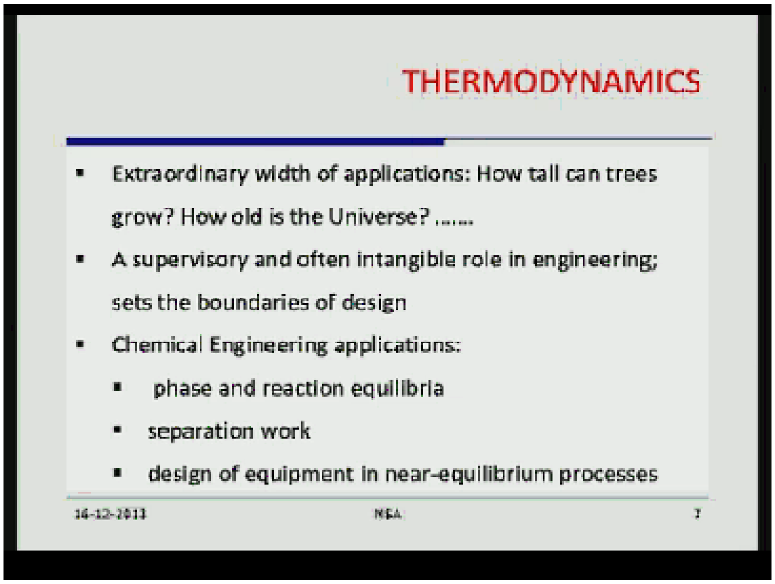

THERMODYNAMICS

- Extraordinary width of applications: How tall can trees grow? How old is the Universe? ……
- A supervisory and often intangible role in engineering; sets the boundaries of design
- Chemical Engineering applications:
  - phase and reaction equilibria
  - separation work
  - design of equipment in near-equilibrium processes

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But thermodynamics, thermodynamics is a subject with extraordinary width of applications. You can ask questions that you may not think as significant but as diverse as how tall can trees grow, how old is the universe and so on. Thermodynamics is a supervisory often intangible role in engineering; it sets the boundaries of design. Fundamentally it will tell you what is the maximum possible thing?

For example what is the maximum work you can extract from a system or what is the minimum work you have to put in, in order to produce a change of state and so on. In chemical engineering, the applications are in phase and reaction equilibria in calculating separation work and in design of equipment in near-equilibrium processes. The 55% separation processes are practically designed on the basis of mass balance, energy balance and this thermodynamics.

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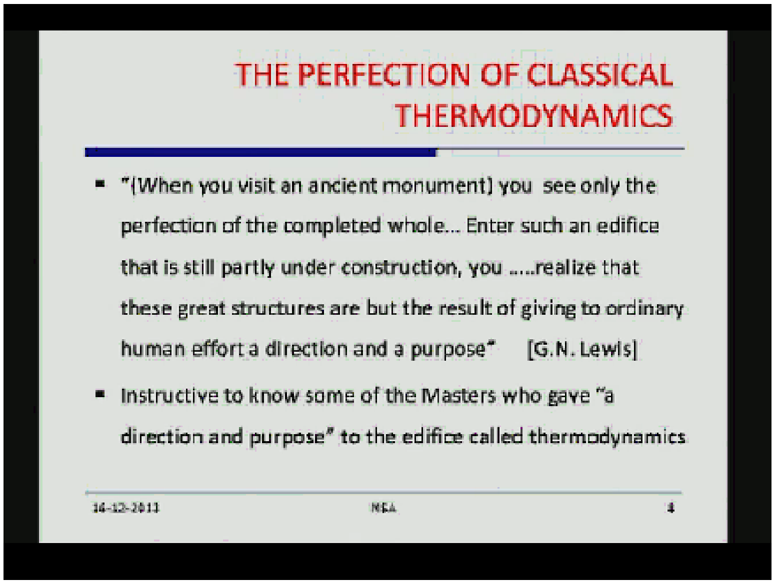

THE PERFECTION OF CLASSICAL THERMODYNAMICS

- "(When you visit an ancient monument) you see only the perfection of the completed whole… Enter such an edifice that is still partly under construction, you …..realize that these great structures are but the result of giving to ordinary human effort a direction and a purpose" [G.N. Lewis]
- Instructive to know some of the Masters who gave "a direction and purpose" to the edifice called thermodynamics

Now the perfection of classical thermodynamics if you, I don not know if you have seen this book by Lewis and Randall on thermodynamics, one of the best books, it is an old book that has been reprinted, I think the revised edition is by Pitcher and Curl but if you look at the preface G. N. Lewis says, when you visit an ancient monument you see only the perfection of the completed whole. Enter such an edifice that is still under construction you realize that these great structures are but the result of giving to ordinary human effort a direction and a purpose.

I think the point that Lewis makes particularly is that thermodynamics is a subject appears so complete and the completion itself gives it a perfection but sometimes a little frustrating for the novice because it seems as if you are drawing conclusions out of nothing. But I think it is nice to go back to the Masters who gave direction and purpose to the edifice called thermodynamics and ask what did they contribute? In some sense it is nice to have a sense of history of the subject. So let me start with few of these people.

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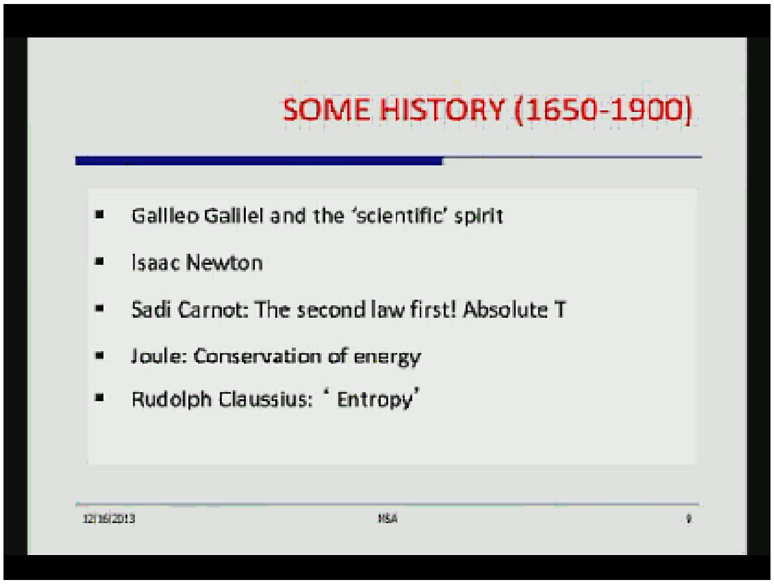

SOME HISTORY (1650-1900)

- Galileo Galilei and the 'scientific' spirit
- Isaac Newton
- Sadi Carnot: The second law first! Absolute T
- Joule: Conservation of energy
- Rudolph Claussius: ' Entropy'

Gallileo Galilel must be recognized as the person who introduced the effect the 'scientific' spirit. He said you not only have to collect data, you have to then use your right brain to arrive at conclusions, far reaching conclusions and then when you hypothesize you have to also verify experimentally because a lot of your imaginations of the right brain is often wrong, because Galileo did not talk about the right brain and the left brain but in our context we can explain what he said in these terms.

Isaac Newton of course was the one who essentially as far as thermodynamics is concerned introduced the concept of work and told you how work is calculated. Sadi Carnot is a case of, rare case of an engineer contributing to fundamental science. The second law actually came before the first law and Sadi Carnot introduced the idea of absolute temperature. Then there was Joule who introduced the conservation of energy in a very rigorous form. I will say a few words about each of these people and Rudoplh Claussius who introduced the word 'Entropy'.

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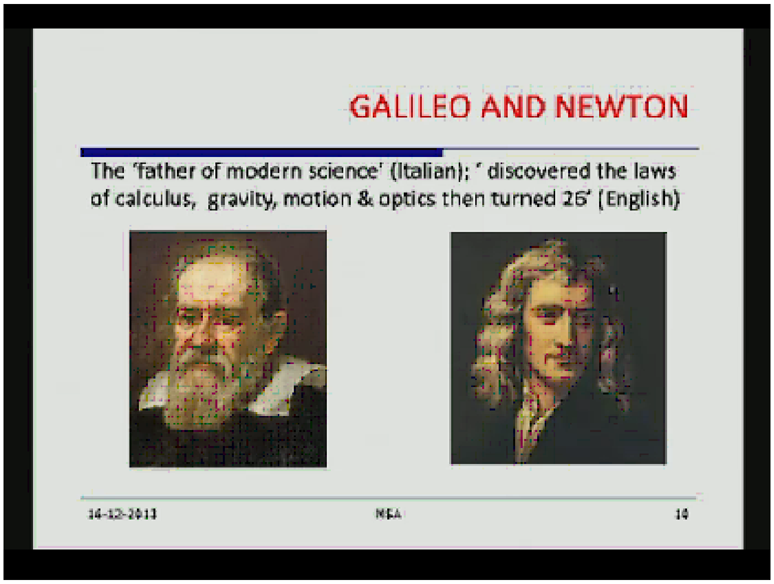

GALILEO AND NEWTON

The 'father of modern science' (Italian); ' discovered the laws of calculus, gravity, motion & optics then turned 26' (English)

So this is, I cannot get a picture of Galileo as a younger person unfortunately but Galileo is the Father of Modern Science in all effectively. Newton discovered the laws as you can see there of calculus, gravity, motion and optics and then turned 26. So this was an Englishmen, his contribution is well known.

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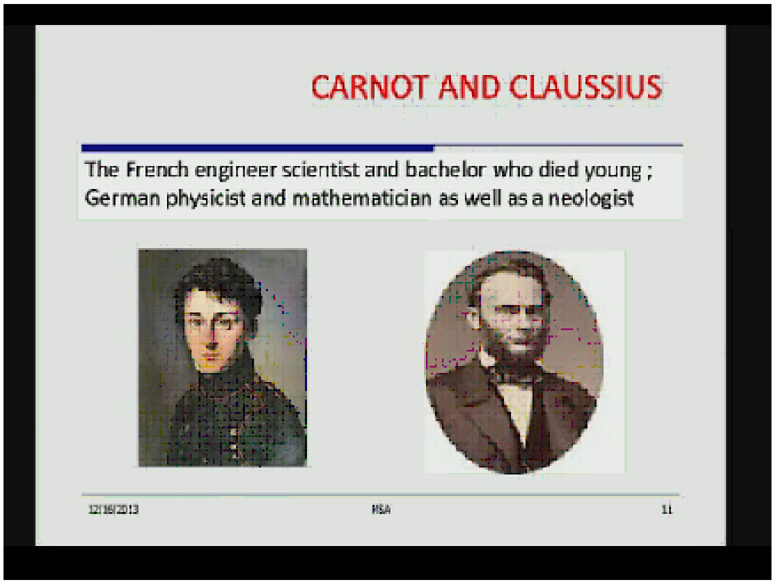

CARNOT AND CLAUSSIUS

The French engineer scientist and bachelor who died young ;
German physicist and mathematician as well as a neologist

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Then Carnot and Claussius, the French engineer scientist, you are moving a couple of centuries after Newton and Galileo. Carnot is the, was a bachelor who died young essentially came up with the second law. The German physicist and mathematician Claussius was also a neologist, he was, had a knack of coining words that remain in use even today, so he introduced the word ‘Entropy’ first.

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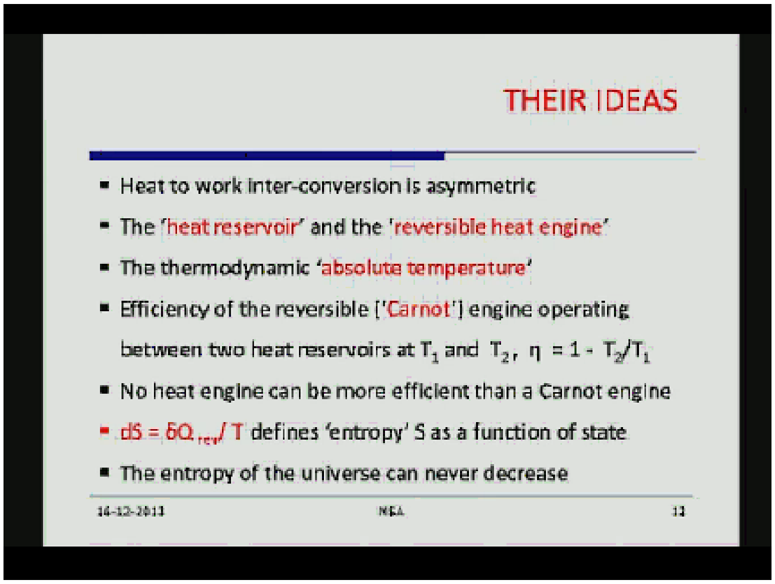

THEIR IDEAS

- Heat to work inter-conversion is asymmetric
- The 'heat reservoir' and the 'reversible heat engine'
- The thermodynamic 'absolute temperature'
- Efficiency of the reversible ['Carnot'] engine operating between two heat reservoirs at T_1 and T_2, $\eta = 1 - T_2/T_1$
- No heat engine can be more efficient than a Carnot engine
- $dS = \delta Q_{rev} / T$ defines 'entropy' S as a function of state
- The entropy of the universe can never decrease

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Let me talk a little bit about their ideas. The heat to work conversion, essentially Carnot pointed out as asymmetric and he introduced the concept of a heat reservoir. Reservoir that was so large that little addition of heat and it will take me a little heat away from it does not change its thermodynamic state and he introduced the concept of a reversible heat engine.

He realized that in order to produce work you have to have a cyclic operation otherwise the amount of work produced will be insignificant and he introduced the concept of a heat engine that would work both ways. The thermodynamic concept of absolute temperature came from Carnot again who also talked about the efficiency of the reversible, now called Carnot engine, operating between two heat reservoirs at T1 and T2 and said that the efficiency must be 1-T2/T1.

He said no heat engine can be more efficient than the Carnot engine. The entropy definition was actually given by Claussius although it was Carnot who pointed out that delta Q/t, while delta Q was a function of power, delta q/t defined a quantity that was a change in a property and he used this to define entropy as a function of state. The conclusion was that the entropy of the universe which is the only isolated system we really know can never decrease.

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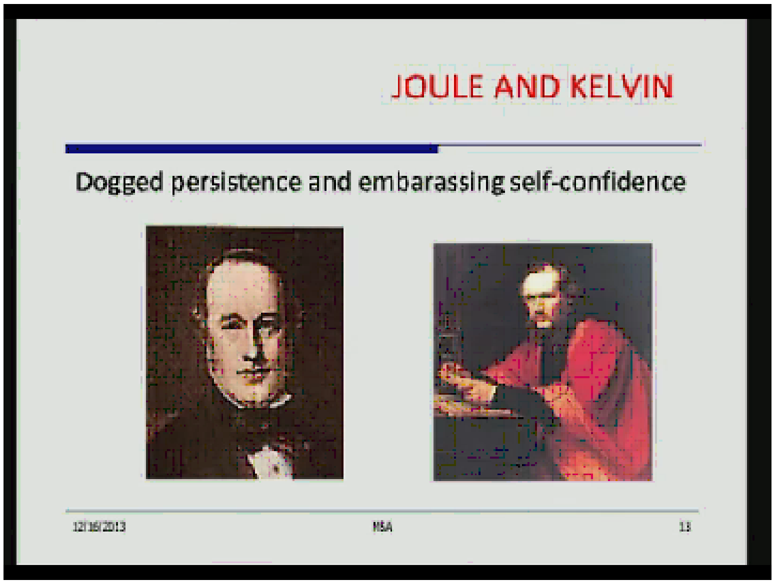

JOULE AND KELVIN

Dogged persistence and embarassing self-confidence

So Joule and Kelvin, these are pictures of Joule and Kelvin. Joule was characterized by dogged persistence and I will say a few words about what he did and then talk about Lord Kelvin.

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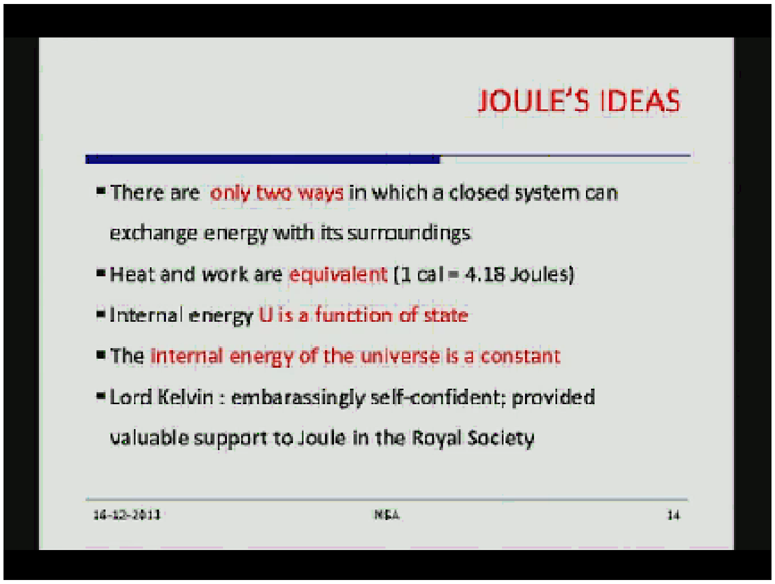

JOULE'S IDEAS

- There are only two ways in which a closed system can exchange energy with its surroundings
- Heat and work are equivalent (1 cal = 4.18 Joules)
- Internal energy U is a function of state
- The internal energy of the universe is a constant
- Lord Kelvin : embarassingly self-confident; provided valuable support to Joule in the Royal Society

But what Joule said it was, even before Joule it was known that there were two ways of exchanging energy with the system and between the system and the surroundings and it was Joule who essentially asserted that there are only two ways as far as the closed system is concerned.

The interaction, energy interaction was either an exchange of heat or exchange of work and he did several experiments to show that this was true. He is supposed to have told the Royal Society again and again demonstrated this in front of the Royal Society till the members of the Royal Society were absolutely convinced. They did not want anymore persuasion but Joule insisted on doing it in several ways. But he essentially showed that heat and work are equivalent and the internal energy is a function of state.

The internal energy of the universe is a constant. Of course internal energy defined as the difference between heat and work. It will give you a more precise definition of the equivalent, and he pointed out that the internal energy of an isolated system is a constant. Lord Kelvin was one of the greatest supporters of Joule. Lord Kelvin came from the aristocracy whereas Joule was an ordinary citizen and this support it is very valuable but Lord Kelvin known to be very embarrassingly self confident.

In a story that he wrote the Tribe Passing, he sent one of the attendants asking him to go look up the results of the Tribe Pass and said find out who is second and he supposed that attendant seems to have come back and said, Lord you are second. So he was actually very confident that he was going to be the first ranker, somebody else had to be second. But he provided lot of support to Joule in the Royal Society in those days.

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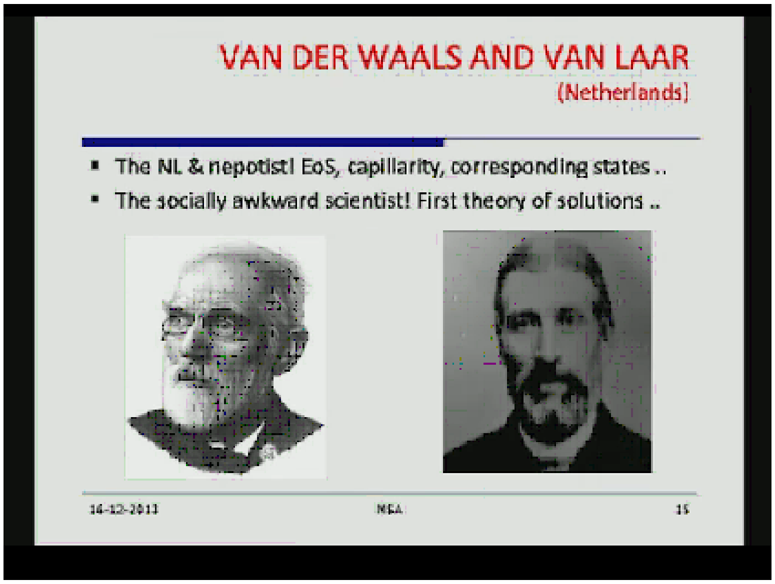

VAN DER WAALS AND VAN LAAR

(Netherlands)

- The NL & nepotist! EoS, capillarity, corresponding states ..
- The socially awkward scientist! First theory of solutions ..

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Then a little later this Van Der Waals and Van Laar, Van Der Waals again from Netherlands, both of them, and Van Der Waals is a Nobel Laureate, one of the first in the area of thermodynamics and also a nepotisti apparently got his son to succeed him. He was the first one to produce an equation of state that is even now used as one of the best equations in conceptual terms. It has no conflict in any fundamental way with thermodynamics, the laws of thermodynamics.

He talked about coppice capillarity and he also introduced the idea of corresponding states. Van Laar was a student, he was socially awkward but he was a great scientist and he is the first one to produce a classical thermodynamic theory of solutions and still one of the best.

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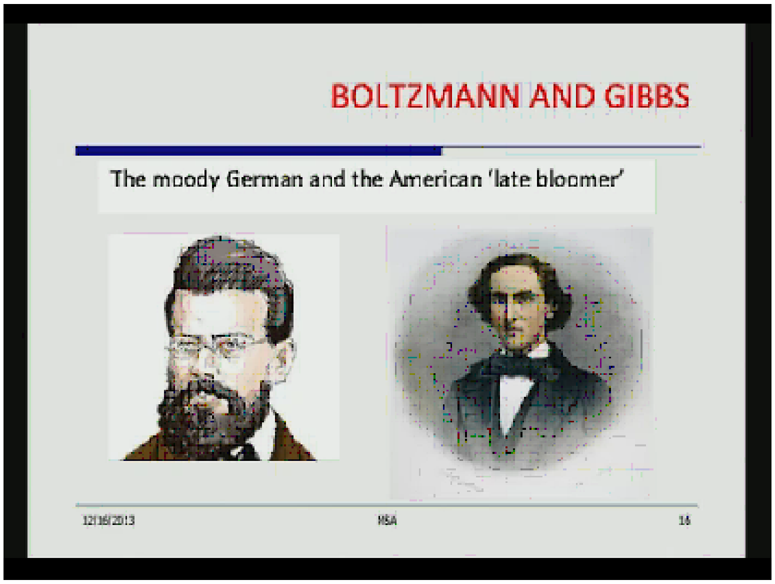

BOLTZMANN AND GIBBS

The moody German and the American 'late bloomer'

Then there was Boltzmann and Gibbs, Boltzmann was a moody German, he actually finally committed suicide but his ideas were far ahead of his time and he introduced kinetic theory essentially.

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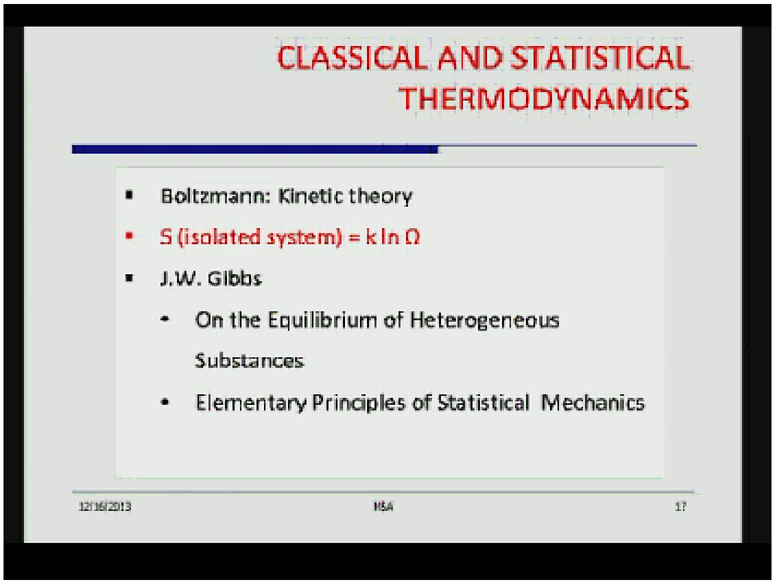

CLASSICAL AND STATISTICAL THERMODYNAMICS

- Boltzmann: Kinetic theory
- S (isolated system) = k ln Ω
- J.W. Gibbs
  - On the Equilibrium of Heterogeneous Substances
  - Elementary Principles of Statistical Mechanics

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And then there was Gibbs, Boltzmann, on the tomb of Boltzmann this formula of S for an isolated system is given S=k log omega where the omega is the number of microscopic states in which the microscopic system can exist. Gibbs was one of the most remarkable people, the best of the early expositors. He also developed the statistical mechanical principles. He was a remarkable man. He was in Yale for many years without any payment and subsequently he was finally recognized, before he died he was finally recognized as one of the great scientists.

And his book on Elementary Principles of Statistical Mechanics still reads beautifully and after about 150 pages that he had written all of this work was done in isolation, all by himself. He finally calculates the specific heat of Argon and he makes a comment that the specific heat that we predict does not agree with experiment, therefore we must consider our methods as tentative.

Actually couple of years later, the specific heat is actually re-measured and it was found that Gibbs' prediction was right and the old experimental data was wrong. So he is an absolutely remarkable person and lot of results, a lot of things you can do. Classical thermodynamics in many ways is a very complete subject and a lot of things you think you can derive on your own you will find in a footnote to Gibbs' notes. It can be shown that in the results recorded there.
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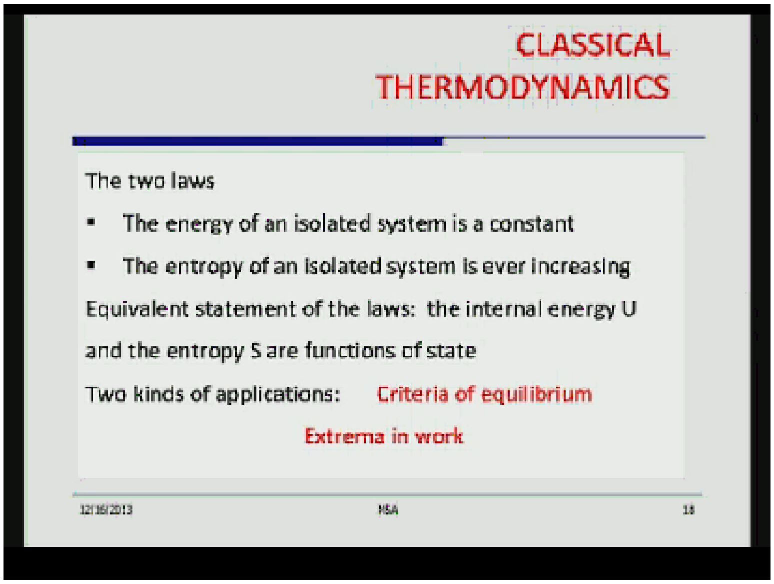

CLASSICAL THERMODYNAMICS

The two laws

- The energy of an isolated system is a constant
- The entropy of an isolated system is ever increasing

Equivalent statement of the laws: the internal energy U and the entropy S are functions of state

Two kinds of applications: Criteria of equilibrium

Extrema in work

So basically let me just say that classical thermodynamics essentially two laws, it says the energy of an isolated system is a constant and the entropy of an isolated system is ever increasing. The equivalent statement of the laws as far as we are concerned is that the internal energy U and the entropy S are functions of state. You know other functions of state like pressure, temperature, composition, volume and so on but these two were introduced because of the two laws of thermodynamics.

Once these are introduced the rest of it is practically calculus, you can derive all the results in thermodynamics through calculus. Essentially chemical engineers are interested in two kinds of applications. One is criteria of equilibrium and the other is extrema in work.

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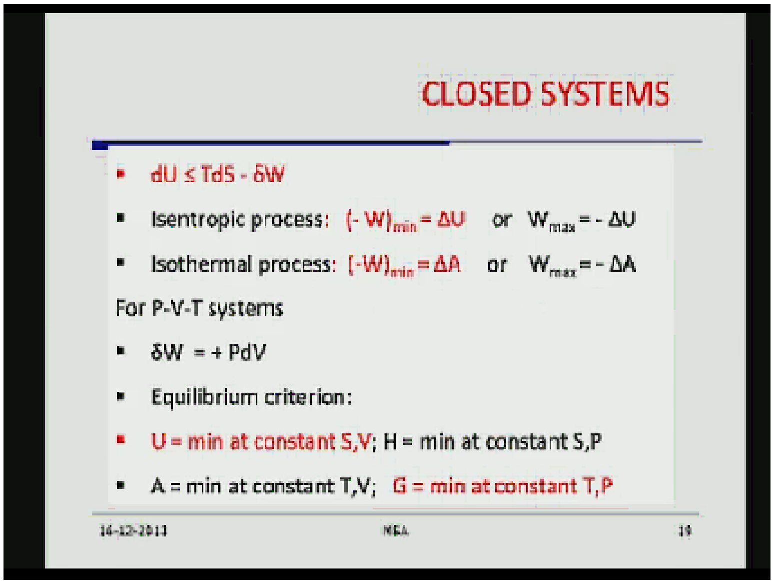

CLOSED SYSTEMS

- $dU \leq TdS - \delta W$
- Isentropic process: $(-W)_{min} = \Delta U$ or $W_{max} = -\Delta U$
- Isothermal process: $(-W)_{min} = \Delta A$ or $W_{max} = -\Delta A$

For P-V-T systems

- $\delta W = + PdV$
- Equilibrium criterion:
- U = min at constant S,V; H = min at constant S,P
- A = min at constant T,V; G = min at constant T,P

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Let me talk a little bit about closed systems, the combined form of the two laws and we will see these in some more detail as the course unfolds but I am trying to give you an overview here. Essentially we are going to draw the conclusion that the change in the internal energy is less than or equal to tds – delta w. The convention used here for work is that for work and heat the conventions are, heat is positive if it is added to the system, work is positive if it is work done by the system.

In modern conventions it is actually the other way round. So in terms of delta w and delta w the science in this presentation, in most of the course would actually be the opposite of what is presented in most books, today's books. But it is a trivial difference because finally in terms of actually measurable quantities the equations will be the same. So in isentropic processes you can show that the maximum work you can get when a system changes from one state to another is actually equal to minus the change in internal energy and –W which is the work done on the system.

The minimum work you have to do to produce a change of state is equal to delta e. In isothermal processes we will show that this is actually equal to a free energy change delta a. For PVT systems delta w is PDV and the equilibrium criterion becomes simply u = min at constant s and v, because you can rearrange that first equation, you put delta w = PdV so you get dU < or = 0 and S and V are constant, which means U has to be a minimum at equilibrium. But this a constraint of constant S and V, so if you subtract of minus TS from both sides you get the result that A should be a minimum at constant T and V, when net constant S and P, similarly H should be a minimum and G will be a minimum at constant theory.

It is clear that because temperature and pressure, temperature and volume are the pairs of variables that can be held constant through, easily you can monitor these values. So A being a minimum and G being a minimum are the important equations.

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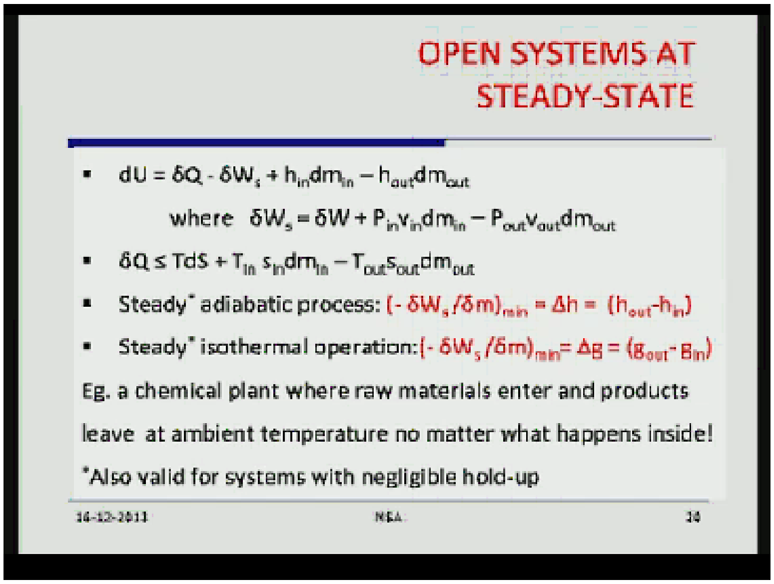

OPEN SYSTEMS AT STEADY-STATE

- $dU = \delta Q - \delta W_s + h_{in} dm_{in} - h_{out} dm_{out}$

  where $\delta W_s = \delta W + P_{in} v_{in} dm_{in} - P_{out} v_{out} dm_{out}$
- $\delta Q \leq TdS + T_{in} s_{in} dm_{in} - T_{out} s_{out} dm_{out}$
- Steady* adiabatic process: $(-\delta W_s/\delta m)_{min} = \Delta h = (h_{out} - h_{in})$
- Steady* isothermal operation: $(-\delta W_s/\delta m)_{min} = \Delta g = (g_{out} - g_{in})$

Eg. a chemical plant where raw materials enter and products leave at ambient temperature no matter what happens inside!

*Also valid for systems with negligible hold-up

If you look at open systems you have to subtract off flow work so you define, redefine shaft work or useful work as delta w + what I have written there and if you put that in you can ask what is the minimum work you have to do in a flow process, in a steady adiabatic process and you get the result that – delta ws by delta m = delta h. Similarly in steady isothermal operation it is equal to delta g.

Now this is also valid for systems with negligible hold up and a chemical plant for example, if you take a whole plant where raw materials enter and the products leave at ambient temperature and pressure, no matter what happens inside the plant you can calculate simply the delta g between the product angle, products and the raw materials and this is the minimum work you have to do because the actual work will be much more. But it is remarkable that thermodynamics is able to make such predictions while not paying attention to the details. So let me show you an example.

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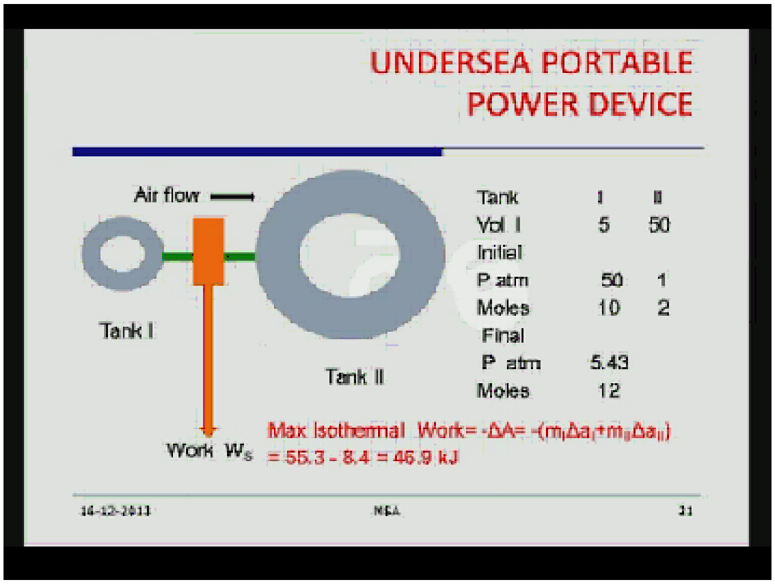

UNDERSEA PORTABLE POWER DEVICE

Tank	I	II
Vol l	5	50
Initial		
P atm	50	1
Moles	10	2
Final		
P atm	5.43	
Moles	12	

Max Isothermal Work= $-\Delta A= -(m_I \Delta a_I + m_{II} \Delta a_{II})$

$= 55.3 - 8.4 = 46.9$ kJ

Here is an example of an undersea portable device and I have a tank 1 and tank 2, this can be used for example for working on the hull of ships and this is a portable device just carried on the back of a diver, and you can ask how much work can this do? What you have is air in tank 1 at very high pressure which expands into tank 2 because you are talking of pressures under the sea and the pressure can be quite high even at ten meters can be quite high.

So what you do is always have an evacuated tank which is much larger into which the air expands and in doing so it does work WS when asked what is the amount of work done? So I have given you some example, tank 1 you start at 50 atmospheres and tank 2 is at 1 atmosphere at T=0 and you allow the air from tank 1 to go into tank 2.

The volume of tank 1 is 5 liters and tank 2 is 50 liters and you can ask when it comes to equilibrium what will be the final pressure, you can show that the pressure as 5.43, the operation is isothermal because the whole thing occurs underwater at a particular depth and the temperature is constant effectively. So what you can do is calculate therefore maximum work, maximum work according to thermodynamics is delta a and you are talking of M1, the mass of air in tank I.

Having a change delta A1 that is a specific free energy 'a' and M2 delta A2 that is the gas in tank 2 and this second part is compressed, the first part expands so you have a network tone of 46.9kgJ. So if you are looking at, what we are really looking at is mixtures in chemical engineering thermodynamics and you have to start with the basic laws for DG for example, because Gibbs free energy is the most important variable because typically chemists deal with closed systems and they use ‘a’ as a very important variable and chemical engineers deal mostly with flow systems so we are looking at ‘g’ as the most important variable.

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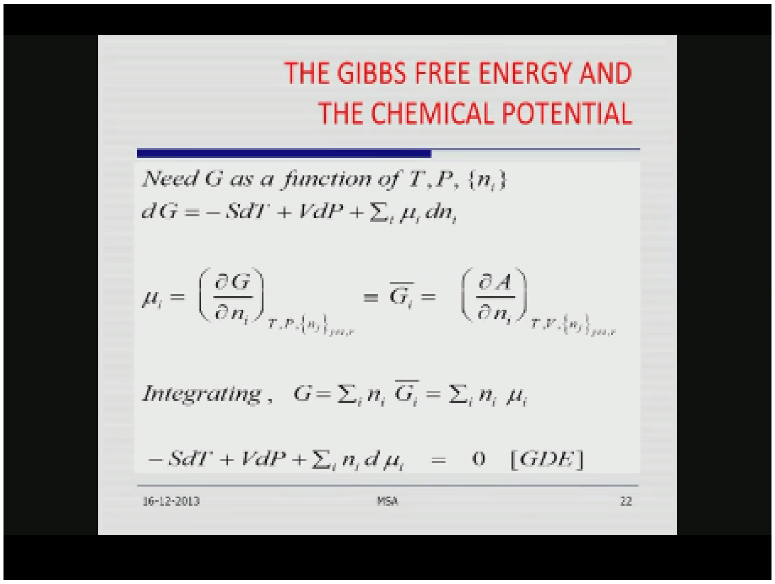

THE GIBBS FREE ENERGY AND THE CHEMICAL POTENTIAL

Need G as a function of $T, P, \{n_i\}$

$$dG = -SdT + VdP + \Sigma_i \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,\{n_j\}_{j\neq i}} \equiv \overline{G_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,\{n_j\}_{j\neq i}}$$

Integrating , $G = \Sigma_i n_i \overline{G_i} = \Sigma_i n_i \mu_i$

$$-SdT + VdP + \Sigma_i n_i d\mu_i = 0 \quad [GDE]$$

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The Gibbs energy dG is simply – Sdt + VdP + $^{\varepsilon\ d}$μ, you are looking at the natural function of temperature and pressure and mole numbers and the change in ‘g’ with respect to ni at constant tp etcetera, and other mole numbers is a variable that will appear again and again, its called partial molar property gi/, it is given a name chemical potential μ, μ has other definitions but basically you can take the first equation dG = – Sdt + VdP + $^{\varepsilon\ d}$μ, sum over μ and i, and because if you are looking at the process that constant t and p and because μ is an intensive variable if you look at changing g from a system with n moles to k times n moles you actually get this result by integrating the first equation, you get g = sum over ni μ i.

This is true of any partial molar property so in particular for the Gibbs free energy the chemical potential is the partial molar property and g is simply = sum over μ and you can write this by differentiating this again and comparing with the first equation you get what is called the Gibbs duhem equation, – Sdt + VdP + $^{\varepsilon\ d}$μi.

So Gibbs pointed out that chemical potential is actually the natural variable for discussing thermodynamic theory not composition but like the composition variables the mole fractions for example, out of n only n-1 are independent because there is a constraint that sum over xi is – 1 or sum over dxi = 0. An equivalent equation can be derived for the chemical potential and that is this equation here.

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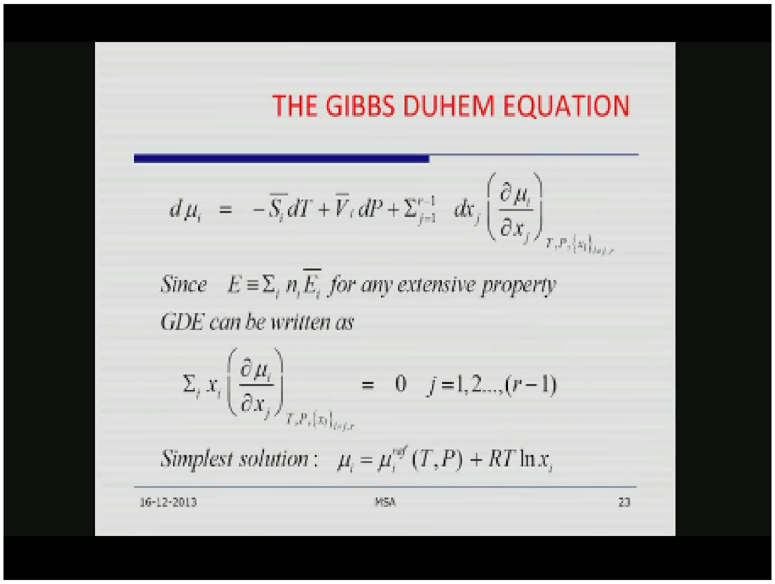

THE GIBBS DUHEM EQUATION

$$d\mu_i = -\overline{S}_i dT + \overline{V}_i dP + \Sigma_{j=1}^{r-1} \; dx_j \left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P,\{x_l\}_{l\neq j,r}}$$

Since $E \equiv \Sigma_i n_i \overline{E}_i$ *for any extensive property*

GDE can be written as

$$\Sigma_i x_i \left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P,\{x_l\}_{l\neq j,r}} = 0 \quad j = 1, 2 \ldots, (r-1)$$

Simplest solution : $\mu_i = \mu_i^{ref}(T,P) + RT \ln x_i$

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Because chemical potential is given by this equation from calculus and you can use the Gibbs Duhem equation, re-express the Gibbs Duhem equation by substituting this for duhem ui and you get a simple result that sum over i of xi dome ui of of dome xa, the sum over all i = 0 for every j = 1 to r-1. So you have a total of r-1 equation for r chemical potential in any given phase.

Therefore there is one degree of freedom, now you can therefore guess the composition depends on the chemical potential of one species then all the others are determined by the Gibbs Duhem equation. The simplest of these solutions is called µ = µ rt and xi and if its valued all the way for the whole range of compositions then nxi = 1 µ reference becomes the chemical potential of your i.

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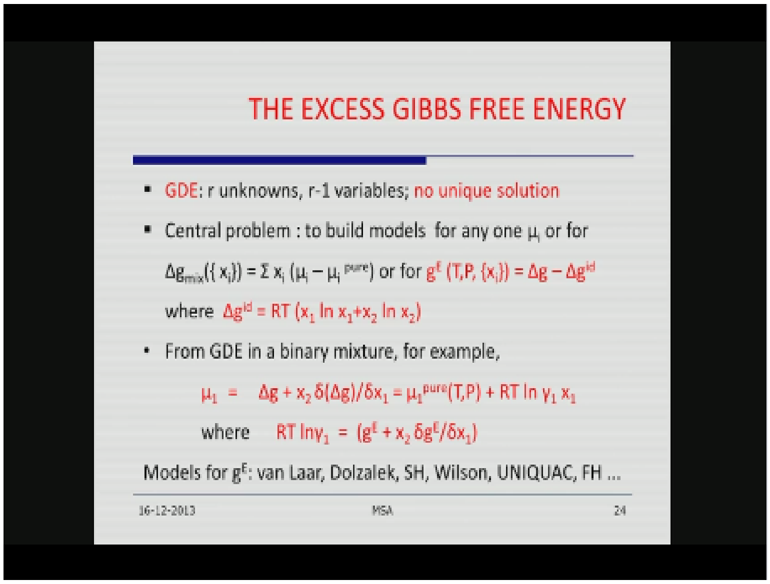

THE EXCESS GIBBS FREE ENERGY

- GDE: r unknowns, r-1 variables; no unique solution
- Central problem : to build models for any one μ_i or for $\Delta g_{mix}(\{x_i\}) = \Sigma x_i (\mu_i - \mu_i^{pure})$ or for $g^E(T,P,\{x_i\}) = \Delta g - \Delta g^{id}$ where $\Delta g^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2)$
- From GDE in a binary mixture, for example,

$$\mu_1 = \Delta g + x_2 \delta(\Delta g)/\delta x_1 = \mu_1^{pure}(T,P) + RT \ln \gamma_1 x_1$$

where $RT \ln\gamma_1 = (g^E + x_2 \delta g^E/\delta x_1)$

Models for g^E: van Laar, Dolzalek, SH, Wilson, UNIQUAC, FH …

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So as I said the Gibbs Duhem equation has r unknowns and r-1 variables and r-1 equation, sorry, so it has no unique solution. The central problem then is to build models for any one chemical potential, instead of doing it for one chemical potential you try and do it for delta g mix because delta g mix is simply the free energy change due to mixing of components so after mixing become the, the Gibbs ebergy is xi µi sum over all i and before mixing it was all pure substances so it is xi µi pure, and delta g – delta g ideal is called gxs, so if you can make a guess for gxs then you can calculate the chemical potentials and in given gxs for example in a binary the chemical potential µi is simply delta g + x 2 times partial of delta g with respect to X1.

And this is formally written as µi pure + rt log gamma xi where gamma represents a non idearity and delta log gamma 1 is gxs + x2 delta of gxs by delta x1. So this way all you have do is to guess what gxs is or delta g of mixing is. There are various models for this because you have complete freedom, only thing is the module that you proposed has to give results that agree with experiment for large number of systems then its stays in the literature otherwise its forgotten. So the modules for example one large module are like these classical thermodynamic modules, the others are all molecular modules, you have various modules like the Wilson, UNIQUAC, scratch ideal and so on.

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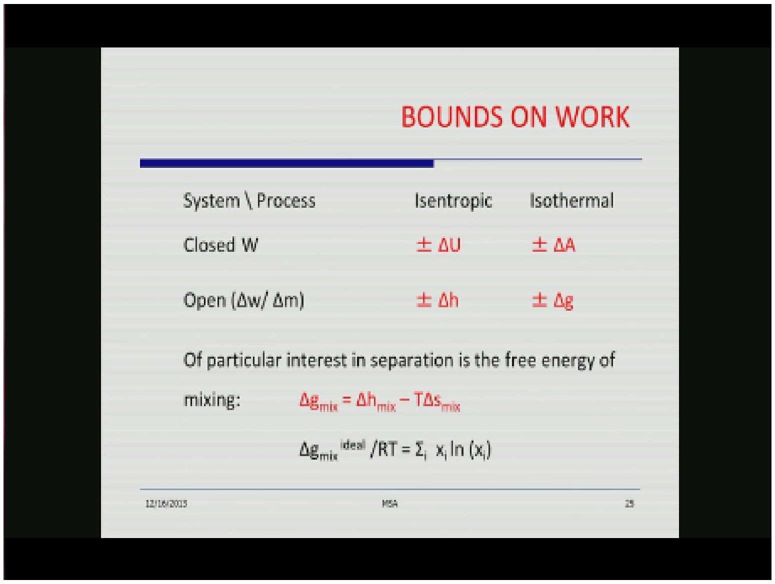

BOUNDS ON WORK

System \ Process	Isentropic	Isothermal
Closed W	$\pm \Delta U$	$\pm \Delta A$
Open ($\Delta w / \Delta m$)	$\pm \Delta h$	$\pm \Delta g$

Of particular interest in separation is the free energy of mixing: $\Delta g_{mix} = \Delta h_{mix} - T\Delta s_{mix}$

$$\Delta g_{mix}^{ideal} / RT = \Sigma_i \; x_i \ln (x_i)$$

So basically what you are looking at is bounds for work, you have to calculate the change in the thermodynamic properties either U or A or the specific enthalpy or the specific Gibbs free energy. Particular interest in separation process in the free energy of mixing as I pointed out already, delta g mix is delta h mix – t delta s mix, all of the modules normally calculate, try and calculate H, delta h or delta s and then set the other, have a default option for the other. For example you can say delta h is 0 and I will calculate the entropy of mixing or you can say delta s mix is the same as the delta s ideal mixture and calculate that module delta h. Delta h ideal, delta g ideal is simply rt times xi log xi.

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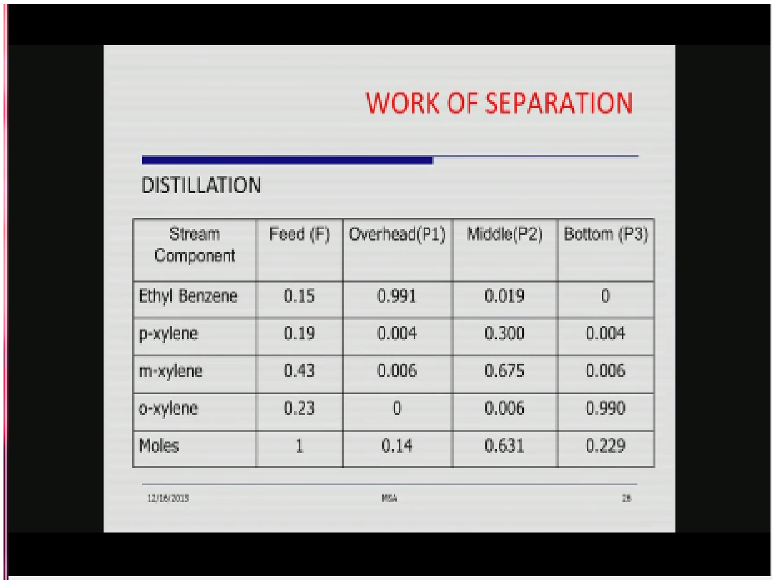

WORK OF SEPARATION

DISTILLATION

Stream Component	Feed (F)	Overhead(P1)	Middle(P2)	Bottom (P3)
Ethyl Benzene	0.15	0.991	0.019	0
p-xylene	0.19	0.004	0.300	0.004
m-xylene	0.43	0.006	0.675	0.006
o-xylene	0.23	0	0.006	0.990
Moles	1	0.14	0.631	0.229

Just to give you an illustration take work of separation for example, you have let us say a distillation column and mutual separating ethyl benzene from the three xylene's are mitra and ortho and I have a certain feed, I have a certain overhead composition in the distillation called, and I have a middle composition and a bottom composition. The question is how much work is required for this?

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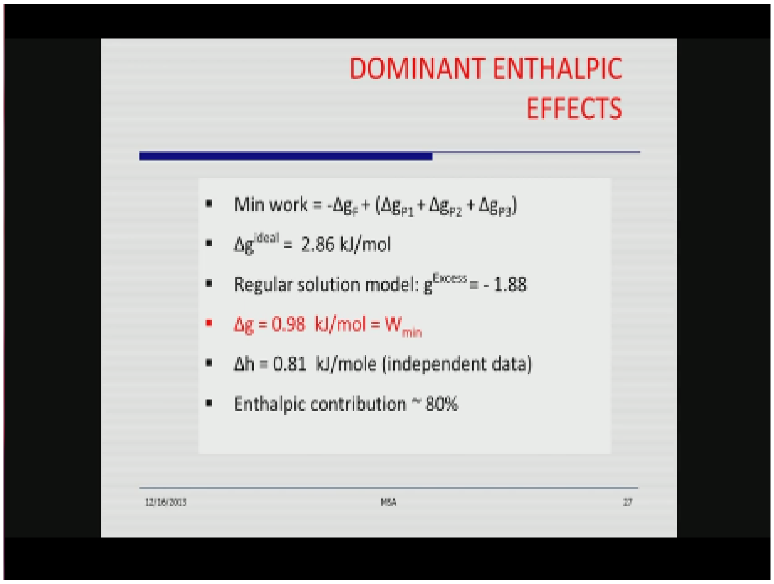

DOMINANT ENTHALPIC EFFECTS

- Min work = $-\Delta g_F + (\Delta g_{P1} + \Delta g_{P2} + \Delta g_{P3})$
- Δg^{ideal} = 2.86 kJ/mol
- Regular solution model: g^{Excess} = - 1.88
- Δg = 0.98 kJ/mol = W_{min}
- Δh = 0.81 kJ/mole (independent data)
- Enthalpic contribution ~ 80%

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Now the minimum work that you have to put into the system is simply g of the products – g of the feed and in this case there are three product streams so delta g of p1 + delta g of p2 + delta g of p – delta g of. You can write it in terms of delta g for each stream because the pure component free energies will cancel in any case.

So delta g ideal in this case turns out to be 2.86 kj/mol, if you use a regular solution module, learn all these modules later in the course you can show that it gives you an excess free energy of -1.88, so net delta g is 0.98 which is the minimum work that you have to do, it should be –w within parenthesis then minimum because its work done on the system. Now delta h is .81, so you can, the Enthalpic contribution is approximately 80%.

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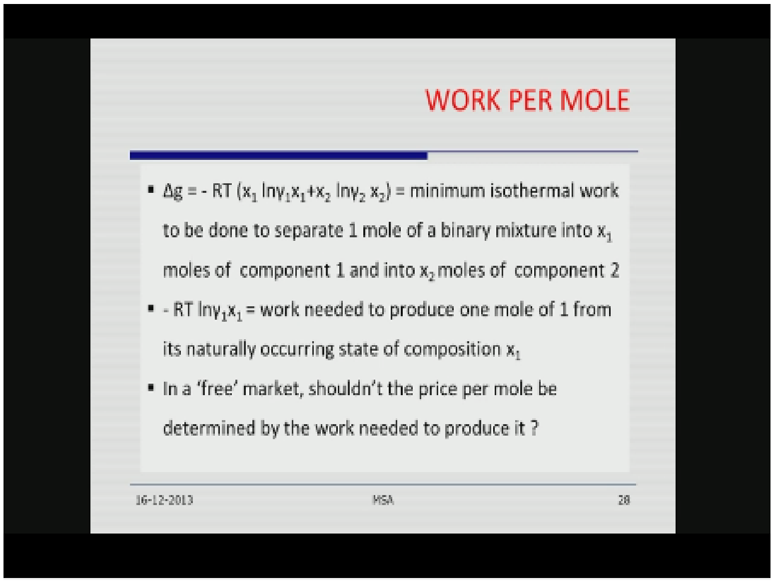

WORK PER MOLE

- $\Delta g = -RT(x_1 \ln\gamma_1 x_1 + x_2 \ln\gamma_2 x_2)$ = minimum isothermal work to be done to separate 1 mole of a binary mixture into x_1 moles of component 1 and into x_2 moles of component 2
- $-RT \ln\gamma_1 x_1$ = work needed to produce one mole of 1 from its naturally occurring state of composition x_1
- In a 'free' market, shouldn't the price per mole be determined by the work needed to produce it ?

This particular case that we discuss is an example of a dominant enthalpic effect. Now if you look at work per mole - RT times (x1Lny1x1+x2Lny2x2) represents delta G, its minimum isothermal work to be done to separate 1 mole of a binary mixture into x1 moles of component 1 and x2 moles of component 2. Of this -RT LNy1x1 is the work needed to produce 1 mole of the substance from its naturally occurring state of composition X1. Now in a free market the price you would expect, the price per mole be determined by the work needed to produce it and I will give you an example of a product.

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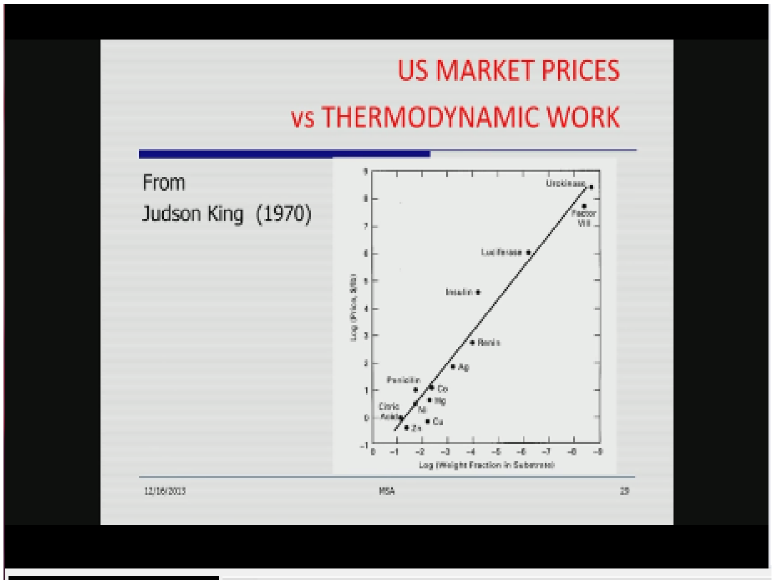

US MARKET PRICES
vs THERMODYNAMIC WORK

From
Judson King (1970)

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This is from Judson King, the classic book of 1970 and he plots log of the price in Dollars per Pound against log of the weight fraction. It should be mole fraction times the activity co efficient, but as a crude approximation you can use the weight fraction and if you make a plot you get a remarkable straight line. The two data are from completely different sources, one is the market price and the other is the log of the weight fraction as it occurs in nature and this approximately calculates the work required.

So you can see that the thermodynamic work required correlates very well with the price, the slope also depends, the slope of this will depend on several factors including the economic factors, the wages and so on. Now you look at, it is a free market so everything falls in place.

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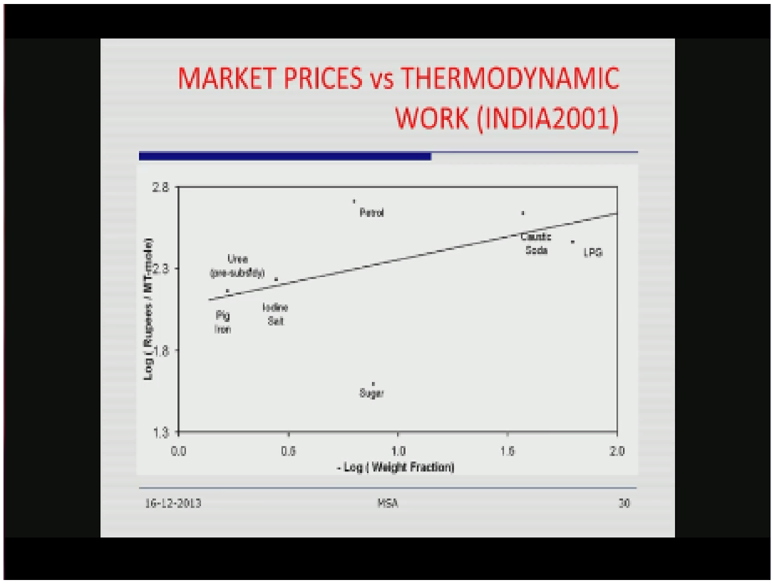

MARKET PRICES vs THERMODYNAMIC WORK (INDIA2001)

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Look at some data for India that we plotted, this is 2001 data, it is old data bit it still gives you a flavor, You can see that petrol is much higher, it is artificial because you have an excise duty on petrol and you can see that pre, urea pre subsidy is right bang on the line, the actually price of urea is much lower in order to get the vote of the farmers.

To make it available for the farmers the government makes it available at much lower prices. Sugar again is a political decision, to subsidize sugar so you get sugar at much lower price than the work warrants.

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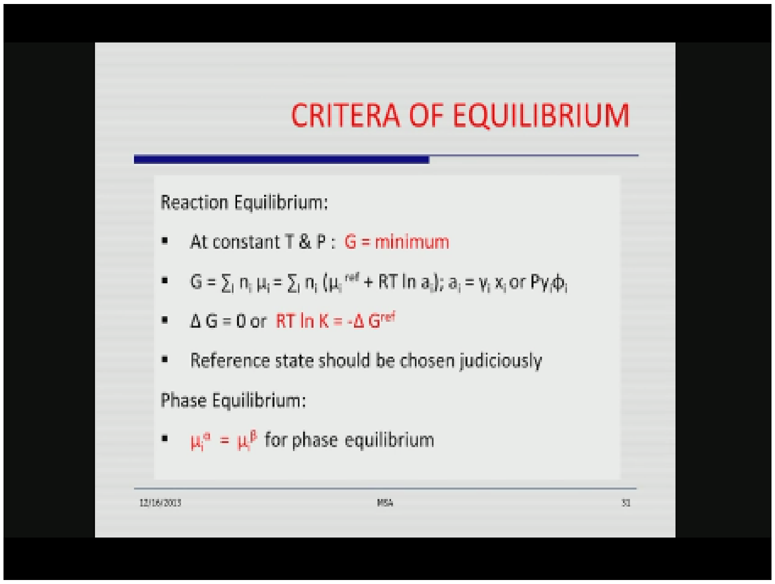

CRITERA OF EQUILIBRIUM

Reaction Equilibrium:

- At constant T & P : G = minimum
- $G = \sum_i n_i \mu_i = \sum_i n_i (\mu_i^{ref} + RT \ln a_i); a_i = \gamma_i x_i$ or $P y_i \phi_i$
- $\Delta G = 0$ or $RT \ln K = -\Delta G^{ref}$
- Reference state should be chosen judiciously

Phase Equilibrium:

- $\mu_i^{\alpha} = \mu_i^{\beta}$ for phase equilibrium

So criteria of equilibrium, I want to say a few words about the other aspects of thermodynamics, at constant t and p thermodynamics will tell you that g should be a minimum and g as in μi, you can write it as activity coefficients and it is either the activity corruptions and if it is a liquid mixture it is = pyi times vi, if it is a gaseous mixture, there are different ways of expressing the non idealitary and by asking that delta g = 0 for equilibrium you actually come to the conclusion.

That RTL and k, k's equilibrium constant is = -delta g reference. The reference state should be chosen judiciously and finally for phase equilibrium you can show that the chemical potentials in 2 phase of the same substance should be equal, at equilibrium.

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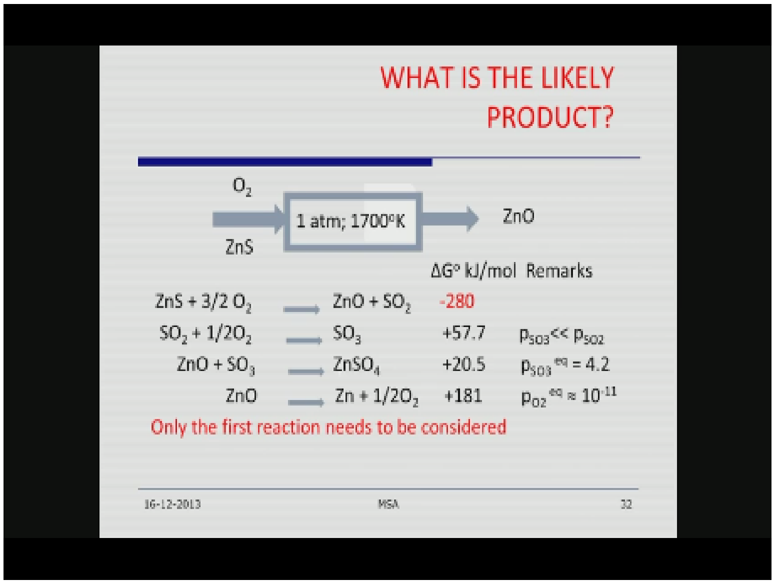

WHAT IS THE LIKELY PRODUCT?

O_2

ZnS

1 atm; 1700°K

ZnO

			ΔG° kJ/mol	Remarks
$ZnS + 3/2\ O_2$	$\longrightarrow$	$ZnO + SO_2$	-280	
$SO_2 + 1/2O_2$	$\longrightarrow$	SO_3	+57.7	$p_{SO3} << p_{SO2}$
$ZnO + SO_3$	$\longrightarrow$	$ZnSO_4$	+20.5	$p_{SO3}^{eq} = 4.2$
ZnO	$\longrightarrow$	$Zn + 1/2O_2$	+181	$p_{O2}^{eq} \approx 10^{-11}$

Only the first reaction needs to be considered

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And let us, for example let us take a very simple example, almost all the over's appear as sulphides and oxides, in the case of zinc it is zinc sulphide, you roast it in oxygen, what do you expect to get? You can show that you expect essentially zinc oxide, the possible reactions are listed there, zinc sulfide + oxygen will give you zinc oxide + sulfide oxide and the delta G is 0, the free energy change in standard state is – 280. Look at all the others, sulphur dioxide going to sulphur trioxide, zinc + sulphur trioxide giving you a zinc sulphide and zinc oxide giving you zinc + oxygen.

All of these are positive and you can say only the first reaction needs to be considered, the product will be zinc oxide. So thermodynamics can tell you right away what to expect in terms of product.

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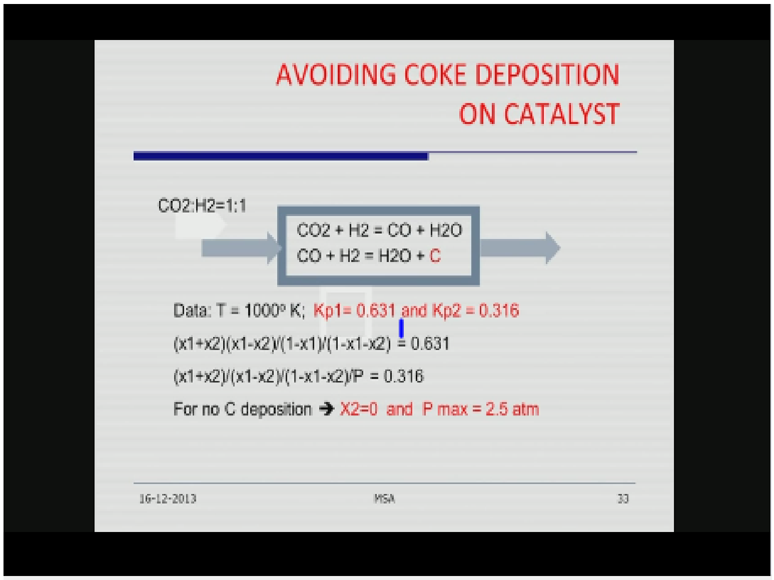

AVOIDING COKE DEPOSITION ON CATALYST

$CO_2:H_2=1:1$

$CO_2 + H_2 = CO + H_2O$

$CO + H_2 = H_2O + C$

Data: T = 1000° K; $Kp_1 = 0.631$ and $Kp_2 = 0.316$

$(x_1+x_2)(x_1-x_2)/(1-x_1)/(1-x_1-x_2) = 0.631$

$(x_1+x_2)/(x_1-x_2)/(1-x_1-x_2)/P = 0.316$

For no C deposition → $X_2=0$ and P max = 2.5 atm

You can of course price quantitively calculate the terms. Then you take a couple of reactions, for example these reactions carbon dioxide + hydrogen gives you carbon monoxide + water, and then CO + hydrogen can give you carbon deposition, now you ask if you do not, this carbon can deposit on the catalyst and choke and make the catalyst ineffective and so you want to know what should be the pressure at which you should operate, or what should be the range of pressures over which you should operate?

This example is that T = 1000 degrees, normally the temperature shows on the base of kinetic considerations, not on the base of thermodynamic considerations, and some data is available, you can do this calculation quite quickly and show that for pressures below 2.5 atmospheres you will have no carbon deposition. These are very powerful conclusions from where we started so let me summarize results, the thermodynamic theory is so beautiful and so complete that it sort of gives you results of the same form in many contexts. If char is a characteristic intensive property at equilibrium.

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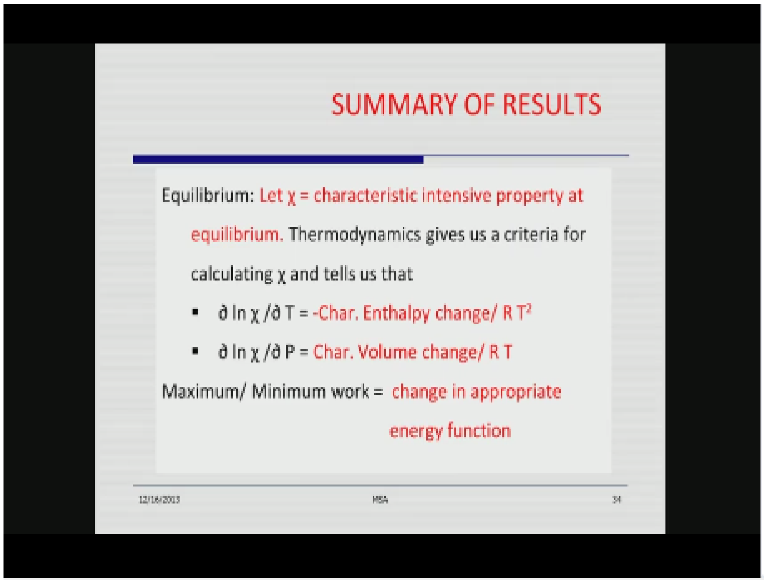

SUMMARY OF RESULTS

Equilibrium: Let χ = characteristic intensive property at equilibrium. Thermodynamics gives us a criteria for calculating χ and tells us that

- $\partial \ln \chi / \partial T$ = -Char. Enthalpy change/ R T^2
- $\partial \ln \chi / \partial P$ = Char. Volume change/ R T

Maximum/ Minimum work = change in appropriate energy function

Right through thermodynamics will tell you how to calculate Ψ from one of the criteria that we already discussed. It will also tell you that the change of log Ψ with respect to T is given by an equation that says - characteristic enthalpy change by RT squared. Similarly in the change of log Ψ with respect to p will give you a characteristic volume change by RT and the maximum minimum work will be change in the appropriate energy function. So these are the summary of results that you get in thermodynamics, they are always of the same form.

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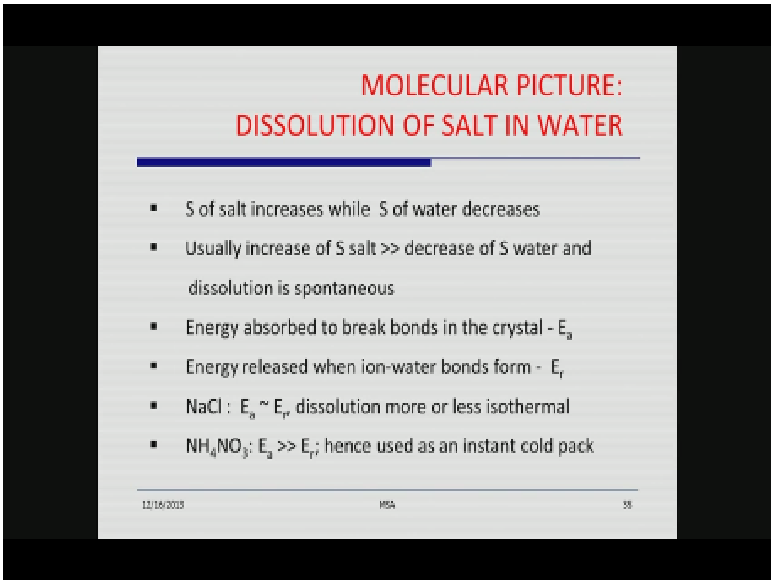

MOLECULAR PICTURE:
DISSOLUTION OF SALT IN WATER

- S of salt increases while S of water decreases
- Usually increase of S salt >> decrease of S water and dissolution is spontaneous
- Energy absorbed to break bonds in the crystal - E_a
- Energy released when ion-water bonds form - E_r
- NaCl : $E_a \sim E_r$, dissolution more or less isothermal
- NH_4NO_3: $E_a >> E_r$; hence used as an instant cold pack

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And let me now pass and give you a molecular picture, for example in the case of one example. As I said classic thermodynamics does not depend upon the molecular structure of matter, if you look at the picture from a molecular structure, however it is quite insightful if you look at dissolution of salt in water and the salt molecules that are added to water the, because of the high dilute constant the ionic forces are much weaker in water and the salt ions can separate.

So effectively the salt has more states in which it can exist and therefore its entropies actually increases. Molecular theory tells you that the entropy depends on the number of possible states in which a system can exist. In this entropies of the salt increases while the entropy water decreases because of the presence of salt molecules. Now the increase of entropy of the salt is much greater normally than the decrease of entropy of water and dissolution is therefore spontaneous, plus resulting entropy chain is a driving force.

The energy absorbed to break the bonds in the crystal, in order to do this at a molecular level you have to break the bonds in the crystal and this energy, we will call this E and energy released when iron water bonds are formed, let us call Er. Now the comparison of Ea and Er will determine whether the dissolution is going to be accompanied by a temperature change. For example in the case of NACL, EA is approximately equal to Er and the dissolution is more or less isothermal. Now if you take ammonium nitrate Ea is so much greater than Er that the resulting decrease in temperature is so significant it is often used as an instant cold pack.

So what molecular theory does for you is give you a mechanistic handle and therefore most of the theories in thermodynamics for calculating property changes come from molecular theory. The classical thermodynamic theories are very few and they say dimension to Van Laar for calculating delta g and they both came up with classical theories.

We will discuss them in the course. So in summary the whole purpose of this course is to help you calculate thermodynamic properties and therefore calculate changes in thermodynamic properties. It is these changes that are going to be very important as far as the chemical industry is concerned and because your prediction of both equilibrium and the maximum work that you can get from a system as well as the minimum work.

That you need to put into your system are both determined by these changes. So I think that is the summary of the course, you can see that there is a relevance with thermodynamics directly to the industry.

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THANK YOU FOR YOUR PATIENCE

That plot that I showed you of specially the agreement between, the co-relation between the price and the marketplace and the mole fraction or the weight fraction of the substance as it occurs in nature is particularly revealing, so this sort of a motivation for studying the subject. You must realize that when the Masters set up the subject it was not at all clear that there were going to be such far reaching applications. It is a remarkable fact that by pursuing the lowest and pushing the frontiers you can get results of great significance for the modern chemical industry as well.

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