

Material and Energy Balances
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Lecture - 64
Energy Balances: A Review - Part 1

Welcome back for your lecture on energy balances. So we have now come to the end of the energy balances topic. So we have looked at different aspects when we talked about energy balances. We started from very simple systems which actually had only change in temperature as to be observed and then we moved on to systems which were not single phase like in early stages.

So we looked at systems where there was actually a phase change happening and then from there we moved on to systems where we had to account for mixture and solutions and we also looked at reactions and performed extensive calculations for all these types of systems. While we were doing this, we also looked at how we can estimate latent heats, the specific heat capacity and we also looked at how to use psychrometric charts and so on, steam tables.

We actually worked on so many different aspects. So over the past few weeks we have familiarized ourselves with so many aspects and fundamentals related to energy balances. So in the next couple of lectures, I will try to summarize all the concepts which we have learnt and perform problems which actually succinctly provide information about all the concepts and we will try to apply all the principles that we have learnt over the past weeks while we solve this problem.

So these problems will give us a reasonable closure for this topic of energy balances. So let us now start with the overall review for energy balances.

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Terminologies

- Adiabatic system – A system that doesn't exchange heat with the surroundings during a process (perfectly insulated)
- Isothermal system – A system in which temperature doesn't change during a process
- Isobaric system – A system in which pressure doesn't change during a process
- Isochoric system – A system in which volume doesn't change during a process
- State or point function – A variable that depends only on the state of the system and not on how the process occurred
- Path function – A variable that depends on how the process takes place
- Specific property – Intensive property that is obtained by dividing an extensive property by the total amount of the process material

So let us first quickly refresh the terminologies. So I have not put all the terminologies here. I have put some of the crucial ones which are really required for us to perform energy balances. So you can always look up the previous lectures and the lecture notes if you are interested in identifying the other terminologies and trying to catch up on that. So here is a brief summary of important terminologies.

So you have the type of systems which are classified as adiabatic, isothermal, isobaric, or isochoric. An adiabatic system is a system where there is no heat exchange between the system and its surroundings while the process is happening. So this is usually referred to as a perfectly insulated system and in such a system we would actually consider the heat exchange as 0. So the equation, the general energy balance equation which we have been using, the term Q will actually go to 0. So you have an isothermal system.

Here the system does not have any change in temperature while the processes are occurring. So that is why it is called isothermal, the temperature remains a constant. You can also have an isobaric system where pressure remains a constant. So when this pressure does not change throughout the process then it is called as an isobaric system. You can also have an isochoric system. An isochoric system is one where there is no change in volume.

So depending on whether a closed system is isobaric or isochoric you would have to identify the appropriate energy balance equation which you will use. So please refer to the previous lectures to identify why we use internal energy for isochoric systems and enthalpy for isobaric systems while you perform calculations. So you have state or point functions which have been explained. So this is a principle which we have been using for calculating internal energy changes and enthalpy changes.

So because these two parameters are actually state functions, we have been able to build hypothetical paths. So the reason is these are actually dependent only on the state or the point at which it is present. It is not affected by the path taken. So because we do not have to worry about the path taken, we have been building hypothetical paths for calculating internal energy and enthalpy.

So we also have things which are path functions for example where could be a path function. It does not just depend on the position or the point or state. It depends on the path taken for reaching point B from point A. So this would mean such point functions cannot be calculated using hypothetical paths. You would have to use the real path for calculating the value of the path functions.

So we have also been working with specific properties like specific internal energy and specific enthalpy. So specific property is nothing but an intensive property that is obtained by dividing an extensive property by the total amount of the process material. What is an intensive property? It is something which does not depend on the size of the system or the mass of the system. And extensive property will depend on the size and the mass of a system.

So when we convert extensive properties to intensive properties we can actually build tables, steam table would be one example. So when we use the steam table you would see the specific volume, specific internal energy and specific enthalpy listed and this is possible because it is not dependent on the size of the system and it is only given as a specific property.

And we can actually take these values and apply these values while we perform calculations for systems of any size and when we multiply the mass or number of moles of the component to the specific property we will get the total value for these components. So this is really useful while we perform calculations.

Even when we build the internal energy tables and enthalpy tables while performing energy balances we use specific properties which are the specific enthalpies and specific internal energies because we can then apply the multiply that value using the moles or mass of the individual components and calculate the summation to identify the total enthalpy change for the system.

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Energy transferred between system & surrounding

- Heat

- Energy transfer due to temperature difference between system and surroundings. Heat is positive when it is transferred to the system from the surroundings.
- If the process is adiabatic (perfect insulation) or if the system and its surroundings are at the same temperature, then $Q = 0$

- Work

- Energy transfer due to anything except temperature difference, such as force, torque or voltage. Work is positive when it is done by the system. This convention is arbitrary and some texts follow the opposite.
- If there are no moving parts or electrical currents or radiation, then $W = 0$

When we talk about energy balances, there are different types of energies which we look at while we are balancing them. So we can broadly classify them as two things which is energy which is transferred between the system and the surrounding and the energy which is possessed by the system itself. So we will first look at the energy which is transferred between the system and the surroundings. This would be the heat and work.

So energy which transfers due to temperature differences between the system and the surroundings is called the heat. Heat is considered to be positive when it is transferred to the system from the surroundings and it will be considered negative when we have it the other way

where energy is lost from the system to the surroundings. So this is a convention which we have consistently used throughout this course and this convention can actually be different as well.

In some books it is being used in a different way. So please understand that this convention has been used for our course to be consistent. If the process is adiabatic where you have perfect insulation then there is no exchange of heat between the system and the surroundings. This would mean the term Q would go to 0. So the next form of energy which actually can be transferred between the system and the surroundings is the work term.

So the energy which is transferred due to anything except temperature difference it might be because of force, torque or voltage is called as work and work is treated to be positive when it is done by the system and it is negative when it is done on the system. Again, this convention is arbitrary. Some textbooks tend to follow the opposite. So if there are no moving parts or electrical currents or radiations in a system then work is considered to be 0.

So most of the systems we have been looking at we do not account for electrical work or nuclear work. We are only looking for moving parts and when there is no moving parts we have been assuming work component has been 0.

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Energy possessed by the system

- Kinetic energy
 - Energy due to translational motion of the system as a whole relative to some frame of reference
 - If the system is not accelerating, then $\Delta E_k = 0$
- Potential energy
 - Energy due to the position of the system in a potential field
 - If the system is not falling or rising, then $\Delta E_p = 0$
- Internal energy
 - All energy possessed by the system other than the kinetic and potential energy
 - Depends on the chemical composition, state of aggregation and temperature of the system
 - Independent of pressure for ideal gases and nearly independent of pressure for solids and liquids
 - If T and phase don't change, no reaction occurs and pressure change is less than a few atm, then $\Delta U = 0$

Energy which is possessed by the system can be of 3 different kinds. One is the kinetic energy. The other is the potential energy and the last one is the internal energy. Kinetic energy is the energy which is possessed by the system due to the translational motion of the system as a whole relative to some frame of reference. So if the system is moving, it could be accelerating or decelerating and then you would actually have a change in kinetic energy.

So if the system is moving at all it possesses kinetic energy. So when the system is not accelerating while we perform energy balances we do not worry about the change in kinetic energy so and that term goes to 0. Because we are only interested in change in energies from the initial to final or from inlet to outlet. So we do not worry about whether they have any kinetic energy or not.

We are only worried about whether there is a difference in the kinetic energies of the initial and final or the input and output conditions. So when there is no acceleration or deceleration we consider the change in kinetic energy to be 0. Potential energy is the energy which is possessed by the system in a potential field and this can be treated as 0 when the system is not rising or falling.

So usually when we do not have that kind of a difference in height for the system we tend to say $\Delta E_p = 0$. So we ignore the potential energy term while we perform the energy balance calculations. You also have internal energy. So internal energy is possessed by the system, is the energy which is possessed by the system other than the kinetic and potential energy. It accounts for all the other energies.

So this is defined by the chemical composition, state of aggregation and the temperature of the system. So if you have multiple components each of these would have an internal energy which will contribute towards the total internal energy of the system. So that is why while we were preparing the, while we were trying to calculate the change in internal energy or enthalpy we have been building those internal energy tables or enthalpy tables where individual internal energies are calculated.

And the summation gives you the total internal energy of the inlet or the outlet conditions. So obviously state of aggregation of the phase can also have direct correlation to the internal energy. So if the phase change happens then you are going to have change in internal energy. Similarly if temperature change happens there is going to be change in internal energy. So this is considered to be independent of pressure for ideal gases and it is nearly independent of pressure for solids and liquids.

So if the temperature and phase does not change and no reaction occurs and pressure changes are usually less, then you can assume $\Delta U = 0$ so while you are performing energy balance calculations.

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Energy Balance Equations

- Based on the law of conservation of energy
- Energy balance equation for a closed system

$$\Delta U + \Delta E_k + \Delta E_p = Q - W$$

- Energy balance equation for an open system

$$\Delta \dot{H} + \Delta \dot{E}_K + \Delta \dot{E}_P = \dot{Q} - \dot{W}_s$$

- Mechanical energy balance equation

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + \hat{F} = \frac{-\dot{W}_s}{\dot{m}}$$

So when we write energy balance calculation, when you perform energy balance calculations we have to write appropriate balance equations. So we have to identify balance equations which are based on the law of conservation of energy. Law of conservation of energy states that energy can neither be created nor be destroyed. So based on that we have developed different equations for closed systems, open systems.

And we also have a mechanical energy balance equation where like the thermodynamic effects are smaller whereas the mechanical energies are more significant. So when you have the energy balance equation for a closed system you use the internal energy $\Delta U + \Delta E_k + \Delta E_p =$

$Q - W$. So this is also the first law of thermodynamics for the closed system. For an open system the energy balance equation is $\dot{H} + \dot{E}_k + \dot{E}_p = \dot{Q} - \dot{W}$.

So here for an open system you are using enthalpy. So I hope you remember why we use enthalpy for an open system. Please think about it. The reason is we account for flow work. So the work component in the equation for the closed system W actually can have two components, one can be the shaft work and the other can be the flow work and the flow work is the $P dv$ kind of work and this is incorporated along with the internal energy to get the value for, to convert it into enthalpy.

So when to account for flow work in an open system because an open system always is going to have components flowing in and out of the system. To account for this flow work we are actually using enthalpy instead of internal energy for an open system. Mechanical energy balance equation is $\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z + F_{\text{cap}} = -\dot{W}_s / \dot{m}$. So this derivation for this equation we have already discussed. Please go and look up the old lectures.

You will be able to find the derivation. So this equation can actually be further simplified when F_{cap} which is the friction factor goes to 0 and there is no shaft work. So the equation will become $\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g \Delta z = 0$. So this simplified equation is called as the Bernoulli's equation.

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Energy Balance Objectives

- Pressure, temperature, phase, and composition can change during a process
- Internal energy and enthalpy changes can be calculated when one of the factors is changing with the other factors remaining constants
- If more than one of the factors is changing, build hypothetical paths
- Internal energy and enthalpy changes for mixing of two liquids or dissolving of a gas or a solid in a liquid at constant T and P can be obtained from tables

So while we perform energy balance calculations what are the objectives and procedures? So the objective is we need to understand that pressure, temperature, phase, and composition of a system can change during a process. There could be heat supply which changes the temperature. There could be a constant volume process where there is pressure change or you could have phase change because of components evaporating or condensing or melting and so on.

You could also have change in composition which could be due to different kinds of processes for example reactions can change the composition and so on. You can also have downstream operations like purification process such as distillation, crystallization, all those things you can change the composition of the feed which is coming in to the system. So for such scenario you have to actually calculate the internal energy and enthalpy changes when one of the factors are changing. You can actually do that. You can calculate when only one of them is changing.

If all of them, if more than one is changing then you cannot directly calculate it. So what you do is you would be building hypothetical paths. So what are hypothetical paths? As I already just mentioned, internal energy and enthalpy are point or state functions. So it does not matter what path we take as long as the initial and final conditions are the same. So the real process could be something but we can always build a hypothetical path where for each step only one of the components is changing, one of the factors is changing.

Either temperature changes or pressure changes or phase changes and each step you can calculate the enthalpy. So either using correlations or formulae or using tables and you find the summation of this. It will give you the total change in enthalpy for the actual process which you are looking at. So you can also have internal energy and enthalpy changes when there are two components mixing. So if the components are ideal gases or similar liquids you can ignore this.

However, for dissimilar liquids or when you have a gas or a solid dissolving in a liquid at a constant temperature and pressure you would have to account for enthalpy of mixing and solutions. This can be obtained from tables.

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Energy Balance Procedures

- First step for any energy balance problem is to complete the required material balances
- Write open/closed system energy balance equation and simplify it by eliminating terms that are zero or negligible
- Choose a reference state – phase, T and P – for each species involved in the process
 - If data will be looked up tables, then choose the reference used to generate the table
 - If not, use inlet or outlet state as the reference
 - For reactive processes, use the state for which the heat of reaction is known (heat of reaction method) or use the elemental species in their native form (heat of formation method)

So now that we have a clarity on the objectives for energy balances what are the procedures? What do we have to do for performing energy balance calculations? So the first step for any energy balance problem is to complete the required material balances. I have been repeatedly saying this. In some cases the material balances might not be required. It might be directly available to you. But in many cases you might actually have to perform material balances.

So we have looked at many examples where we had to perform material balances before you went ahead to do the energy balance calculations. So always remember that first step for any energy balance problem is to confirm the material balances. You complete the material balances.

You would have to have all the flow rates or the masses or the moles of the components which you need for the further calculations in the energy balances.

So you can also write, so once you have the material balances completed, you would have to identify what type of a system and write the correct general balance equation. So you would have to identify whether it is an open or a close system and you would have to write the correct equation. Then you would simplify this equation by eliminating the terms which go to 0 and terms which are actually negligible.

So as we already discussed, if there are no moving parts we would eliminate work and if you do not have any acceleration or deceleration you will eliminate kinetic energy and if there is no change in height or position, then potential energy changes can be ignored. So if you have an adiabatic system where it is perfectly insulated and there is no exchange of heat then Q can go to 0 too. So taking all this into consideration, we will simplify the equation to get something which is the final equation that needs to be solved.

So once you have this equation, you have to calculate individual terms. So one of the terms which you might have to calculate would be the enthalpy term or an internal energy term. For calculating the total change in enthalpy you would first have to identify a reference state. So as you all know, absolute value for internal energy and enthalpy cannot be calculated. It is always a difference between the current state and the reference state.

So for taking that into account, we have to identify our reference state and from there we have to perform the calculations. So the reference state would have to be defined as the phase temperature and pressure for all the component which are present in the system. So it could be different chemical components that are present and we would have to perform, we would have to identify correct reference states for that.

So if you want to look up the enthalpy values or internal energy values from a table then use the reference which is used in the table. So if you are using steam tables then you would use water liquid at triple point as the reference state because that is what is used in the steam tables which

we have access to from Felder Rousseau. So if you have, if you do not plan to use the table, if you have to make calculations, then you can either use the inlet or the outlet condition as the reference state so that you can actually eliminate some of the calculations.

So when you have reactive processes you have to identify which technique you want to use and based on the method you are choosing to use you would have to choose an appropriate reference state. So if you are using the heat of reaction method, then you would have to identify the compounds and elements which are taking part in the reaction and the state in which they are participating in the reaction as the reference states.

And you would have to use the elemental species in the native form as the reference state for heat of formation method. So depending on the technique you are going to use, you will have to identify the appropriate reference states.

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Energy Balance Procedures

- Construct specific internal energy or specific enthalpy tables
- Calculate all the values in the table based on the reference state chosen
- Calculate change in internal energy or enthalpy as the difference between the total internal energies or enthalpies of final & initial or outlet & inlet conditions
- Calculate any non-zero term in the energy balance equation
- Complete the required calculations

Once you have the reference states you would have to construct the specific internal energy or the specific enthalpy tables. You would have to calculate all the values which are there in the table. So which would include all the flow rates or masses or moles and also the internal energies or enthalpies using the reference state as the point of reference you would have to calculate these values.

So what you would have is the reference state as the first point and it reaches the condition, whether it is the inlet condition or the outlet condition. So you can build hypothetical parts which are required to calculate this value for internal energy or enthalpy. So then you would have to calculate the change in internal energy or enthalpy as the difference between the total internal energies or enthalpies of the final and initial or outlet and inlet conditions.

So what you do is you multiply the number of moles or mass with the specific internal energy or enthalpy and find the summation of all that for the inlet stream and do the same for the outlet stream. The value for the outlet stream minus the value for the inlet stream would give you the total change in enthalpy for the process. So similarly you can do it for closed systems using internal energy.

So now that you have the ΔH or ΔU value which you have needed for the energy balance calculation you have to again go back to the simplified energy balance which you had. You need to identify which are all the nonzero terms that still remain and you need to calculate them. In some cases you might have kinetic or potential energy calculation which are still remaining.

So kinetic energy you will calculate as $\frac{1}{2}mv^2$ and you will find the difference between the kinetic energy and you can also calculate potential energy as mgh and find the difference in the potential energies. So if there is going to be work given then that factor has to be accounted for. If Q is given to you then you would have to use that and in that case you might be looking to find something else like an outlet temperature.

So then you perform all the required calculations to identify the values for the variables which you are looking for. So this is the overall procedure which we have been following. I have tried to follow this meticulously so that you also get a feel for a simple procedure which can always be applied for any kind of a problem. As you saw the technique which we have used is efficient for solving simple problems and even some of the most complex problems.

So by following this meticulously we would be able to extrapolate the technique from very easy to all the way to the most tough problems.

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Calculating $\Delta\hat{U}$ and $\Delta\hat{H}$

- Only P changes at constant T & phase
 - For solids and liquids, $\Delta\hat{U} \approx 0$ and $\Delta\hat{H} \approx \hat{V}\Delta P$
 - For ideal gases, both $\Delta\hat{U}$ and $\Delta\hat{H}$ are zero
 - For non-ideal gases, use thermodynamic tables or sophisticated correlations
- Only T changes at constant P & phase
 - Sensible heat – used to increase the temperature of a system
 - $\Delta\hat{U} = \int_{T_1}^{T_2} C_V(T)dT$ and $\Delta\hat{H} = \int_{T_1}^{T_2} C_P(T)dT$
 - $C_p \approx C_v$ for solids and liquids, $C_p = C_v + R$ for ideal gases

So while we calculate kinetic energy changes and potential energy changes we already have the equations. How do we calculate change in internal energy and enthalpy? We have been doing this throughout the last few weeks. So just as a refresher, we can only find the change in internal energy and enthalpy when pressure, temperature or phase, only one of the three has to change.

If more than that is changing you would have to build hypothetical paths so when only pressure changes at constant temperature or phase. For solids and liquids, change in internal energy can be approximated to 0 and change in enthalpy can be approximated to $V \text{ cap } \Delta P$. So usually this term is very small for solids and liquid because $V \text{ cap}$ is very small. So this term $V \text{ cap } \Delta P$ is crucial if the change in pressure is very high.

For ideal gases, both $\Delta\hat{U}$ and $\Delta\hat{H}$ are 0 for constant pressure processes. For non-ideal gases like steam you might have to use thermodynamic tables or other sophisticated correlations to get these values. If only temperature is changing at a constant pressure and phase then what you are observing is sensible heat which is the heat which is being supplied to increase the temperature.

So you can actually calculate internal energy changes or enthalpy changes as $\int C_v dT$ or $\int C_p dT$. $\int C_v dT$ would be the change in specific internal energy and $\int C_p dT$

dT will be the change in specific enthalpy. So C_p and C_v for solids and liquid are approximately the same. And $C_p = C_v + R$ for ideal gases. So using these correlations you can calculate C_v because mostly C_p is available to you from tables.

So you can calculate C_v for performing calculations where you need to obtain internal energies instead of enthalpies.

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Calculating $\Delta\hat{U}$ and $\Delta\hat{H}$

- Only phase changes at constant T & P
 - Latent heat is the $\Delta\hat{H}$ for phase change at constant T & P
 - Different from sensible heat
 - Can be obtained from tables or using correlations
 - Assuming ideal gas behaviour, $\Delta\hat{U}_v \approx \Delta\hat{H}_v - RT$
- Mixing or solution at constant T & P
 - Can be ignored for ideal mixtures (a good approximation of gases and similar liquids) and very dilute solutions
 - For non-ideal mixtures, values need to be obtained from tables
- Reaction at constant T & P
 - Can be calculated using heat of formation or heat of combustion by applying Hess's law

When only phase changes at a constant temperature and pressure, what you are looking at is the latent heat. This is the change in specific enthalpy for the phase change at a constant temperature and pressure and this is different from the sensible heat. This can be obtained from the tables or using correlations. We have discussed the different correlations. You can go back and look up how we can estimate them. I had a short lecture on estimating latent heats themselves.

So please go and see how it can be done. So if you assume ideal gas behavior in case of vaporization, the internal change associated with vaporization can actually be calculated as $\Delta U_v = \Delta H_v - RT$. So in case of mixing or formation of solution at constant temperature and pressure, we tend to ignore it for ideal mixtures. So it is a good approximation to assume ideal mixtures for gases and for similar liquids and also for dilute solutions.

Whereas if you have dissimilar liquids like sulphuric acid and water then it is a non-ideal mixture and you need to get these values from tables. So these values would not just depend on temperature and pressure, it will also depend on the concentration of the components being mixed. So it is usually listed as R which represents the concentration. So we can actually use that value from the table and use it for performing calculations.

So when you have a reaction at constant temperature and pressure, you would have to account for the change in enthalpy either the heat of reaction can be given to you directly. If it is not given to you, then what you would do is you would calculate it using the heat of formation or heat of combustion by applying Hess's law. We have already looked at what Hess's law is and we can use that to get the heat of reaction.

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Heat of Reaction

- The enthalpy change for a process in which stoichiometric quantities of the reactants at given T and P react completely in a single reaction to form products at the same T and P
- $\Delta \hat{H}_r$ applies for stoichiometric quantities of each species
- For a reaction $2A + B \rightarrow 3C$, $\Delta \hat{H}_r (100^\circ\text{C}, 1 \text{ atm}) = -50 \text{ kJ/mol}$, enthalpy changes are -50 kJ/2 mol A consumed; -50 kJ/mol B consumed; -50 kJ/3 mol C formed

So heat of reaction is basically defined as the enthalpy change for a process in which stoichiometric quantities of a reactant at given temperature and pressure react completely in a single reaction to form products at the same temperature and pressure. So this definition has multiple informations which I have highlighted in the past. Again, please remember that here you have stoichiometric quantities of the reactants reacting to completion.

Which means the reaction has to go to completion and stoichiometric quantities as represented in the equation are actually taking part in the reaction and producing products as the stoichiometric

quantities and this has to be a single reaction. You cannot have multiple reaction, side reactions happening, okay? And another thing which you have to remember is the enthalpies of the initial and final conditions which are the enthalpy of the reactant and the product which are compared would be for the same temperature and pressure.

So products at the same temperature and pressure minus reactants at the same temperature and pressure will give you the change in enthalpy. So this difference in enthalpy is called as the heat of reaction. So this term we should understand also applies for the stoichiometric quantities of the species. Because when you have any enthalpy we usually tend to write it as kJ/mol or kJ/kg. So in case of heat of reaction when we say kJ/mol we have the question of per mole of what?

So if you have a reaction where $2A + B$ gives $3C$ and I give you that the heat of reaction is 50 kJ/mol what I mean is 50 kilo joules per 2 moles of A consumed or 50 kilo joules per mole of B consumed or 50 kilo joules per 3 moles of C formed. So actually I have given negative and I just said it positive but you understand that the concept is the same. So what you need to primarily understand is the numerical value given is for the number of moles based on the stoichiometric coefficient of a component reacting or being formed in the reaction.

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Internal Energy of Reaction

- Difference between the internal energy of the products and the reactants, if stoichiometric quantities of the reactants react to completely at a given T

$$\Delta \hat{U}_r(T) = \Delta \hat{H}_r(T) - RT \left(\sum_{\substack{\text{gaseous} \\ \text{products}}} |v_i| - \sum_{\substack{\text{gaseous} \\ \text{reactants}}} |v_i| \right)$$

And internal energy of a reaction is another term which is used for closed systems. So this is the difference between the internal energies of the products and the reactants if the stoichiometric

quantities of the reactants react completely at a given temperature and pressure. So here you would have the heat of reaction, so the internal energy of reaction would be equal to heat of reaction minus RT times the summation of the stoichiometric coefficients of gaseous products minus the summation of stoichiometric coefficients of gaseous reactants. So in cases where the same number of moles of gaseous reactants are there and as the gaseous products then this term in the brackets will go to 0 leaving the internal energy of the reaction to be equal to the heat of reaction.

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Hess's Law

- If the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, ..., then the heat of reaction $\Delta\hat{H}_{r1}^\circ$ can be obtained by performing the same operations on the heats of reactions $\Delta\hat{H}_{r2}^\circ, \Delta\hat{H}_{r3}^\circ, \dots$

- Heat of reaction from heats of formation

$$\Delta\hat{H}_r^\circ = \sum_i v_i \Delta\hat{H}_{fi}^\circ = \sum_{\text{products}} |v_i| \Delta\hat{H}_{fi}^\circ - \sum_{\text{reactants}} |v_i| \Delta\hat{H}_{fi}^\circ$$

- Heat of reaction from heats of combustion

$$\Delta\hat{H}_r^\circ = \sum_i v_i \Delta\hat{H}_{fi}^\circ = \sum_{\text{reactants}} |v_i| \Delta\hat{H}_{ci}^\circ - \sum_{\text{products}} |v_i| \Delta\hat{H}_{ci}^\circ$$

So Hess's law is applied while we perform calculations. So when we use heat of reaction, when we calculate heat of reaction from heat of formation and heat of combustion, we are actually applying Hess's law. Hess's law states that if the stoichiometric equation for reaction 1 can be obtained by algebraic operations which could be multiplication by constants, addition and subtraction on stoichiometric equations for reactions 2, 3 and so on.

Then the heat of reactions for the reaction 1 can actually be obtained by performing the same operation on the heats of reactions for reactions 2, 3 and so on. So it is just gives us a clarity on getting these values and heat of reaction can actually be obtained from the heat of formation using this equation where heat of reaction equals sigma for products where stoichiometric coefficient times the heat of formation is taken minus for the same for the reactants.

So heat of combustion can also be used when you have combustible components as part of the reaction. So the heat of reaction will be calculated the other way where it is reactants minus products. So you can use this equation to calculate the heat of reaction and we have done this a couple of times while we were performing the example problems.

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Heat of Formation and Heat of Combustion

- The standard heat of formation of a substance, $\Delta\hat{H}_f^\circ$, is the enthalpy change associated with the formation of 1 mole of the compound at a reference T and P (usually 25°C and 1 atm)
- The standard heat of combustion of a substance, $\Delta\hat{H}_c^\circ$, is the enthalpy change associated the combustion of 1 mole of that substance with oxygen to yield specified products, with both reactants and products at 25°C and 1 atm



So heat of formation and heat of combustion are two components which we have defined. These are basically heats of reactions for specific types of reactions. Heat of formation of a substance is basically the enthalpy change associated with the formation of 1 mole of a compound at a reference temperature and pressure from its elements as they occur in nature at 25 degree Celsius and 1 atmosphere.

So the standard heat of combustion of a substance is the enthalpy change associated with combustion of 1 mole of that substance with oxygen to yield specified products which are usually carbon dioxide, sulphur dioxide and so on. So here again the combustion has to go completion. You cannot have formation of carbon monoxides. So we have to assume that both reactants and products are at 25 degree Celsius while we account for the difference in enthalpies.

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Energy Balances on Reactive Processes

- Heat of reaction method

- Preferred when a single reaction with known heat of reaction is occurring
- Reference state should be the compounds and elements in the state they are involved in the reaction equation
- Accounts for the enthalpy change due to the reaction explicitly while calculating total change in enthalpy

$$\Delta\dot{H} = \sum_{rxn} \dot{\xi}_j \Delta\hat{H}_{rj}^{\circ} + \sum \dot{n}_{out} \hat{H}_{out} - \sum \dot{n}_{in} \hat{H}_{in}$$

So when we perform energy balances on reactive processes, we can use the heat of reaction method or the heat of formation method. Heat of reaction method is usually preferred when you have a single reaction with a known heat of reaction. The reference state would be the compounds and elements in the state as they are involved in the reaction equation. Again, please remember I am talking about the equation given, not the process itself.

So that is why we would be using the temperature and pressure and the phase as it appears in the equation, not as it appears in the process. This accounts for enthalpy change due to reaction explicitly when we calculate the total enthalpy change using this equation. So you have a third term which we usually do not have for nonreactive systems which is the sigma of psi i delta H ri. So this is basically the effect of reactions.

So if you have multiple reactions, there could be multiple extents of reaction which can be calculated and multiplied with the heats of reaction for the individual reactions and the summation of all that will account for the change in enthalpy associated with the reactions which are happening in the process. So this is taken care of explicitly while you perform the calculations.

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Energy Balances on Reactive Processes

- Heat of formation method
 - Preferred when the known heat of reaction is not readily available or when multiple reactions are occurring
 - Reference state should be the elements in their natural state as they would be involved in the formation reaction
 - Accounts for the enthalpy change due to the reaction implicitly by applying Hess's law



You also have the heat of formation method which is usually preferred when the heat of reaction is not available or when you have multiple reactions which are occurring. So the reference state which is used would be the elements as they occurred in their natural state as it would be involved in the formation reaction. So this accounts for enthalpy change due to reaction implicitly by applying Hess's law. We have already discussed how it applies Hess's law.

Please go back and refresh yourself on that concept if you are not confident about it. So with that we have come to the conclusion of a brief overview of all the concepts which we have learnt during the energy balance calculations and energy balance portion of this course. So we will perform a few example problems which highlight all these concepts and apply these concepts and this will help you fully understand and appreciate the aspects associated with energy balances. Thank you. See you in the next class.