

## Energy Balances on Closed Systems

A system is closed if mass does not cross the system boundary during the period of time covered by energy balance. Energy balance for a closed system written between two instants of time is

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

$\Delta U$  is change internal energy,  $\Delta E_k$  is change in kinetic energy and  $\Delta E_p$  is change in potential energy,  $Q$  is heat transferred to the system and  $W$  is work done by the system. We take heat lost to surroundings as -ve and heat transferred to the system as +ve.

If the system is adiabatic, there is neither gain by the system nor heat loss and  $Q$  is zero. If there are no moving parts, then  $W$  is zero.

## Energy Balances on Open Systems

A system is open if mass crosses the system boundary. For such a system, work must be done on the fluid mass to push it into the system and work is done by the fluid mass exiting the system. These two constitute the flow work and should be included in the energy balance. Work could also be done by the fluid mass on moving parts of the system (example: steam driving a turbine). This is called shaft work.

The net rate of work done by an open system on its surroundings includes the works discussed above:

$$\dot{W} = \dot{W}_s + \dot{W}_f$$

$\dot{W}_s$  is the shaft work and  $\dot{W}_f$  is the flow work.

To understand shaft work, consider a single-inlet and single-outlet system into which fluid enters at  $P_{in}$  ( $N/m^2$ ) at a volumetric flow rate of  $\dot{V}_{in}$  ( $m^3/s$ ) and leaves the unit at  $P_{out}$  ( $N/m^2$ ) at a volumetric flow rate of  $\dot{V}_{out}$  ( $m^3/s$ ).

Work required to push the mass in =  $P_{in} \dot{V}_{in}$

Work done by the fluid exiting the system =  $P_{out} \dot{V}_{out}$

The net rate of work done by the system =  $P_{in} \dot{V}_{in} - P_{out} \dot{V}_{out}$

The energy balance takes the following form:

$$\Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}_s$$

$\Delta \dot{H}$  is rate of change of enthalpy, a term defined below.  $\Delta \dot{E}_k$  is rate of change of kinetic energy and  $\Delta \dot{E}_p$  is rate of change of potential energy,  $\dot{Q}$  is rate at which energy is transferred to the system and  $\dot{W}_s$  is the rate at which work is done by the fluid on the system.

We define specific enthalpy (enthalpy per unit mass or mole) as:

$$\hat{H} = \hat{U} + P \hat{V}$$

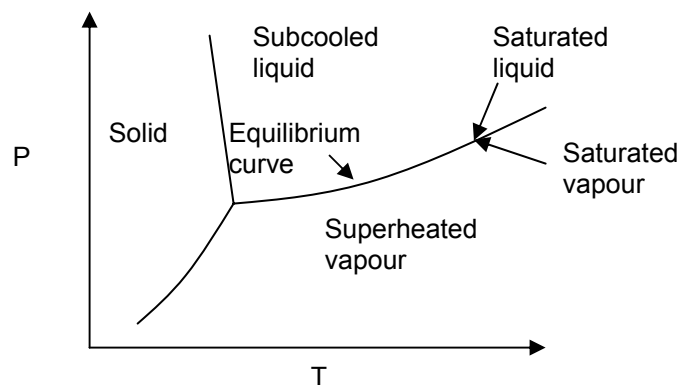
$\hat{U}$  is specific internal energy,  $P$  is pressure and  $\hat{V}$  is specific volume.

## Thermodynamic data

It is not possible to know or estimate the absolute values of internal energy and enthalpy. We need to find only the change in these properties to make an energy balance. Enthalpy and internal energy of species could be tabulated with respect to a reference state (temperature, pressure and phase). We will discuss how to generate the tables below after we talk about **steam tables**.

### Steam Tables

Single phase diagram for water is shown in Figure below. The values for  $T$  and  $P$  are not indicated; the Figure is meant for qualitative discussion.



Water exists as both vapour and liquid at temperatures and pressures corresponding to the vapour liquid equilibrium curve. At conditions on this curve, water could be a *saturated liquid* or a *saturated vapour* (if a superheated vapour is cooled slowly, it becomes saturated vapour when equilibrium curve is reached; similarly saturated liquid can be thought of).

Properties of water, saturated steam and superheated steam have been tabulated and are made available as **steam tables**. This is done so that the properties can be looked up from the tables instead of calculating them every time. **You should get used to knowing how to read these tables.**

These tables are available in Hostel 10 photocopy shop. Look at them as they are described.

Table B.5 lists properties of saturated liquid water and saturated steam at temperatures from 0.01 °C (the triple point temperature) to 102°C. The following properties can be determined.

**Column 2.** The pressure (bar) corresponding to the given temperature on the equilibrium curve—by definition, the vapour pressure of water at the given temperature. The temperature at a given pressure corresponds to boiling point of water at that pressure.

**Columns 3 and 4.** The specific volumes of liquid water and saturated steam at the given temperature.

**Columns 5 and 6.** The specific internal energies of saturated liquid water and saturated steam at the given temperature *relative to reference state of liquid water at the triple point*.

**Columns 7—9.** The specific enthalpies of saturated liquid water (column 7) and saturated steam (Column 9). Column 8 gives the difference between enthalpies of saturated steam and saturated water. The difference is *heat of vapourization*.

Table B.6 gives same properties as Table B.5 but for a broader range of temperature and pressures. These two Tables are called saturated steam tables.

Table B.7 is a superheated steam table and it provides specific volume, specific internal energy and specific enthalpy at any temperature and pressure. The values in parentheses below the pressures listed in column 1 are boiling point temperature. Columns 2 and 3 list the properties of saturated water and steam at that pressure.

## Process Paths

We said that enthalpy and internal energy are state properties. In other words, the change in enthalpy of a species depends only on the final and initial states and not on how the final state is reached from the initial state, i.e., they are path independent. When Tables of internal energy and specific enthalpy are unavailable, we should estimate it by constructing process path from a reference state to final state.

Process path involve one of the following:

1. Changes in pressure at constant temperature and state of aggregation (phase).
2. Changes in temperature at constant pressure and state of aggregation (phase).
3. Changes in phase at constant temperature and pressure.
4. Mixing of liquids or dissolving of gas in a liquid or a solid.
5. Chemical reaction.

We will now calculate changes in enthalpy and internal energy associated with each of the above paths.

**Changes in P at constant T:** For ideal gases, both  $\Delta \hat{U}$  and  $\Delta \hat{H}$  are zeros. For solids and liquids,  $\Delta \hat{U} = 0$  but  $\Delta \hat{H} = \Delta P \hat{V}$ .

**Changes in T at constant P:** For ideal gases, solids and liquids,  $\Delta \hat{U} = \int_{T_1}^{T_2} C_v dT$  and

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p dT.$$

$C_v$  and  $C_p$  are functions of temperature for gases, usually given as polynomial functions. For liquid and solids, they are usually constants.

Kopp's rule: For liquid and solids, at or near 20°C, specific heats may be estimated from specific heats of elements that constitute them. For example,

$$C_p[\text{CaCO}_3] = C_p[\text{Ca}] + C_p[\text{C}] + 3C_p[\text{O}]$$

Specific heats of elements are given at the end of the text book in Table B.10

For mixtures, use the following formula to find specific heat capacity

$$(C_p)_{\text{mixture}}(T) = \sum_{i=1}^n y_i C_{p_i}(T)$$

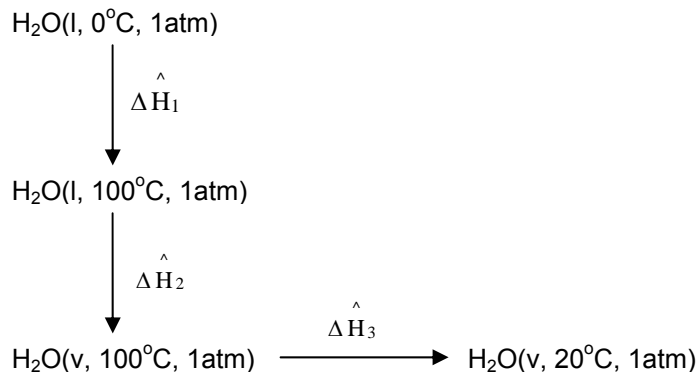
Where  $(C_p)_{\text{mixture}}$  is heat capacity of the mixture,  $y_i$  is the mass or mole fraction of  $i^{\text{th}}$  species,  $C_{p_i}$  is heat capacity of  $i^{\text{th}}$  species and  $n$  is number of species.

**Phase changes at constant T & P:** For solid to liquid transformation, use latent heat of fusion,  $\Delta \hat{H}_m$  and for liquid to vapour, use latent heat of vapourization,  $\Delta \hat{H}_v$ .

$\Delta \hat{H}_v$  is a function of temperature and is independent of pressure (found from experiments). That is the amount of heat required to vapourize water at 100°C and 20°C is significantly different but the heat needed at 100°C at two pressures, say 760 mm Hg and 76 mm Hg is essentially same.

How do we calculate  $\Delta \hat{H}_v$  at 20°C, if  $\Delta \hat{H}_v$  at 100°C is known? We will use liquid water at 0°C and 1 atm as reference.

Construct a process path as shown below:



Estimate change in specific enthalpies associated with each step and then add them up to get specific enthalpy at water vapour at 20°C and 1 atm with respect to liquid water at 0°C and 1 atm.

## Procedure for Energy Balance Calculations

1. Make material balance calculations and find flow rates (or masses) of all streams.
2. Write the generalized energy balance equation and cancel all the terms that are either zeros or can be neglected.
3. Choose reference states for each species involved. By reference state we mean T, P and the phase of the species. A proper choice of the reference states enables easy calculation of enthalpies and hence, energy balances.
4. Construct an inlet-outlet enthalpy table with mass or molar flow rates for open systems and initial-final amounts of species and internal energies for closed systems.
5. Estimate the specific enthalpies or internal energies and insert the values in the Table constructed in step 4. You need to construct process paths to determine specific enthalpies and internal energies.
6. Solve the simplified energy balance equation in step 2 for the unknown.

## Psychrometric Charts

The following can be read from the psychrometric charts.

**Dry-bulb temperature:** This is the x-axis of the chart. It is the temperature of air measured by a thermometer.

**Absolute humidity:** This is the y-axis of the chart in the units of kg H<sub>2</sub>O/kg dry air.

**Relative humidity:** Curves on the chart indicating percentages. The uppermost curve indicating 100% represents saturation curve.

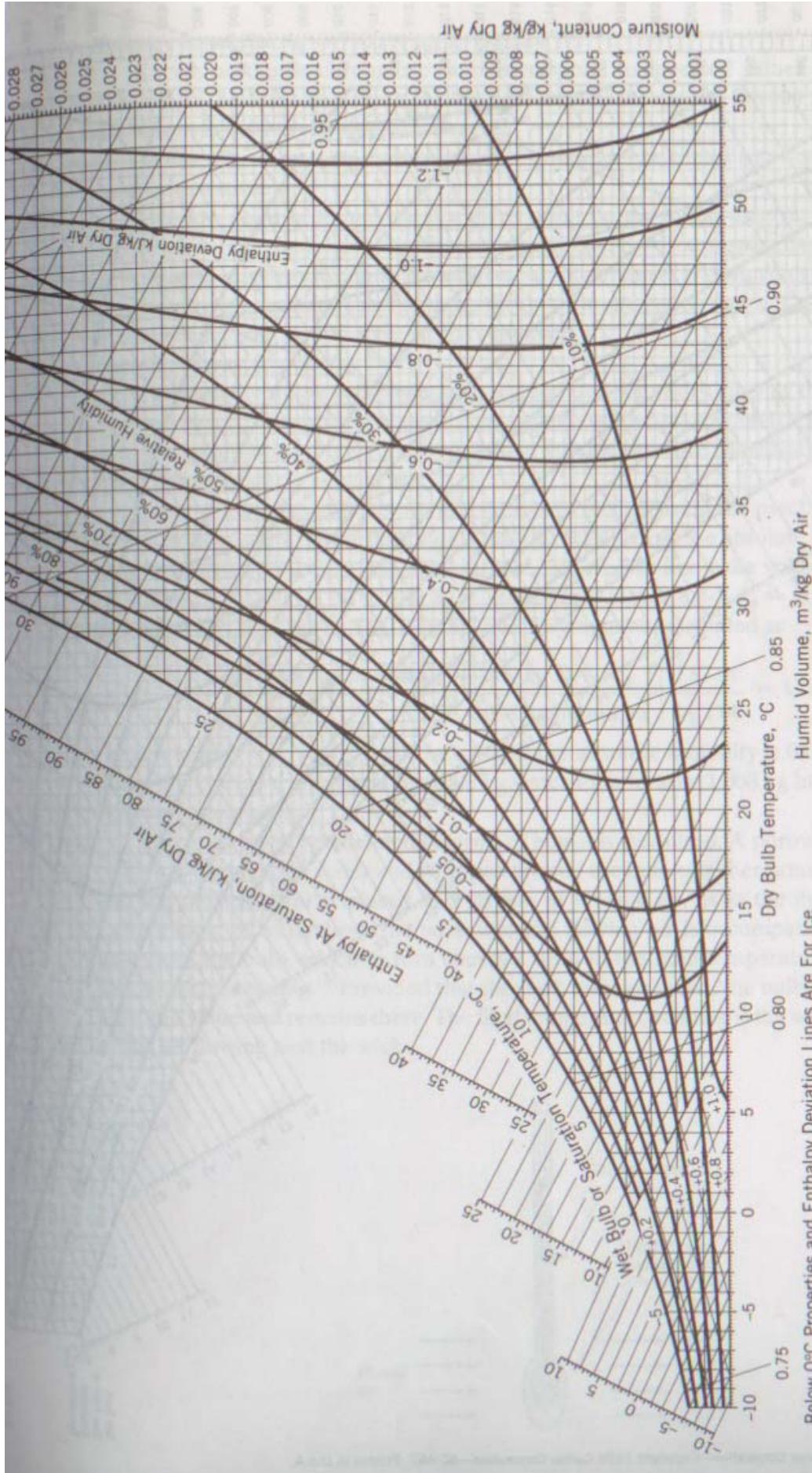
**Dew point:** This is the temperature to which humid air must be cooled to saturate it. Suppose dry bulb temperature is 25°C and relative humidity is 20%. Locate this point on the chart and then move horizontally to 100% saturation curve. The temperature corresponding to 100% saturation is dew point temperature.

**Humid volume:** This is reported in the chart in the units of m<sup>3</sup>/kg dry air. Lines of constant humid volume (0.9, 0.85, 0.80 etc) are shown on the chart.

**Wet-bulb temperature:** This is the temperature indicated by a thermometer to which a wet cotton wick has been attached. If this thermometer is kept in a room containing humid air and it is made sure that the wick is always wet, the temperature of thermometer falls because water evaporates into the humid air. As the temperature drops, heat is transferred from the room air to the wick, which tends to rise the temperature of the wick. When equilibrium is attained, the temperature of the thermometer is less than the room temperature. The final temperature of the wick is called wet-bulb temperature. This temperature is always less than or equal to dry-bulb temperature. The smaller the difference between the temperatures, the more humid is the air; the larger the difference, the less humid is the air.

If you want to know, wet-bulb temperature for a given dry-bulb temperature and relative humidity, do the following. Locate the point corresponding to dry-bulb temperature and relative humidity and then move diagonally to reach the 100% saturation curve. A vertical line from the saturation curve gives the wet-bulb temperature. Of the three values, dry-bulb, wet-bulb and relative humidity, if two are known, the third can be found from the chart.

**Specific enthalpy of air:** The diagonal scales on the left side of the chart indicate the specific enthalpy of a unit mass of dry air plus the water vapour it contains at saturation.



Below 0°C Properties and Enthalpy Deviation Lines Are For Ice

**Figure 8.4-1** Psychrometric chart—SI units. Reference states: H<sub>2</sub>O (L, 0°C, 1 atm), dry air (0°C, 1 atm). (Reprinted with permission of Carrier Corporation.)

The reference states are for dry air (0°C, 1 atm) and for water (liquid, 0°C, 1 atm).

To find enthalpy of saturated air, from the 100% saturation line at a given dry-bulb temperature, follow the line to enthalpy scale.

**Enthalpy deviation:** The curves with negative values associated with them (-0.1, -0.2, -0.4 etc) give enthalpy deviation. For a given state of the air, locate the point on the chart and then find its enthalpy deviation. If this added to enthalpy of saturated air, we obtain enthalpy of the air in the given state. Note you may have to interpolate if the point does not fall on the drawn curves for enthalpy deviation.

## MIXING AND SOLUTION

When two liquids are mixed or when a gas dissolves in a liquid or in a solid heat could be liberated. During mixing, some bonds are broken and some are formed. Breaking of bonds requires energy and formation releases energy. If the latter is greater than the former, heat is evolved.

Formally, heat of solution is difference in enthalpy of the solution at a T and P and the total enthalpy of the solute and the solvent at the same T and P. If HCl(g) is dissolved in water then the heat of solution is  $\Delta H = H_{\text{HCl(aq)}} - (H_{\text{HCl(g)}} - H_{\text{H}_2\text{O(l)}})$

The heat of solution is defined as the change in enthalpy when one mole of a solute is dissolved in r moles of a solvent at a constant T. As r becomes very large,  $\Delta H$  is called heat of solution at infinite dilution. Table B.11 in the Appendix of the text book provides heats of solution when HCl(g), H<sub>2</sub>SO<sub>4</sub>(l) and NaOH(s) are dissolved in water as a function of r at 25°C.

Let's consider an example. You are making 20 wt% H<sub>2</sub>SO<sub>4</sub> at 40°C by adding requisite amounts of water and sulphuric acid, both at 25°C, and want to find the amount of heat liberated.

Material balances are easy to make on the basis of 1 kg of solution. Now, you should construct an inlet-outlet enthalpy table. Choose references as water and sulphuric acid, both at 25°C. Inlet enthalpies of water and sulphuric acid are zero.

Process path to find enthalpy of H<sub>2</sub>SO<sub>4</sub> (aq) at 40°C.

Step 1:  $22 \text{ H}_2\text{O} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_2\text{SO}_4 \text{ (aq) at } 25^\circ\text{C}$

Step 2: heat the solution to 40°C.

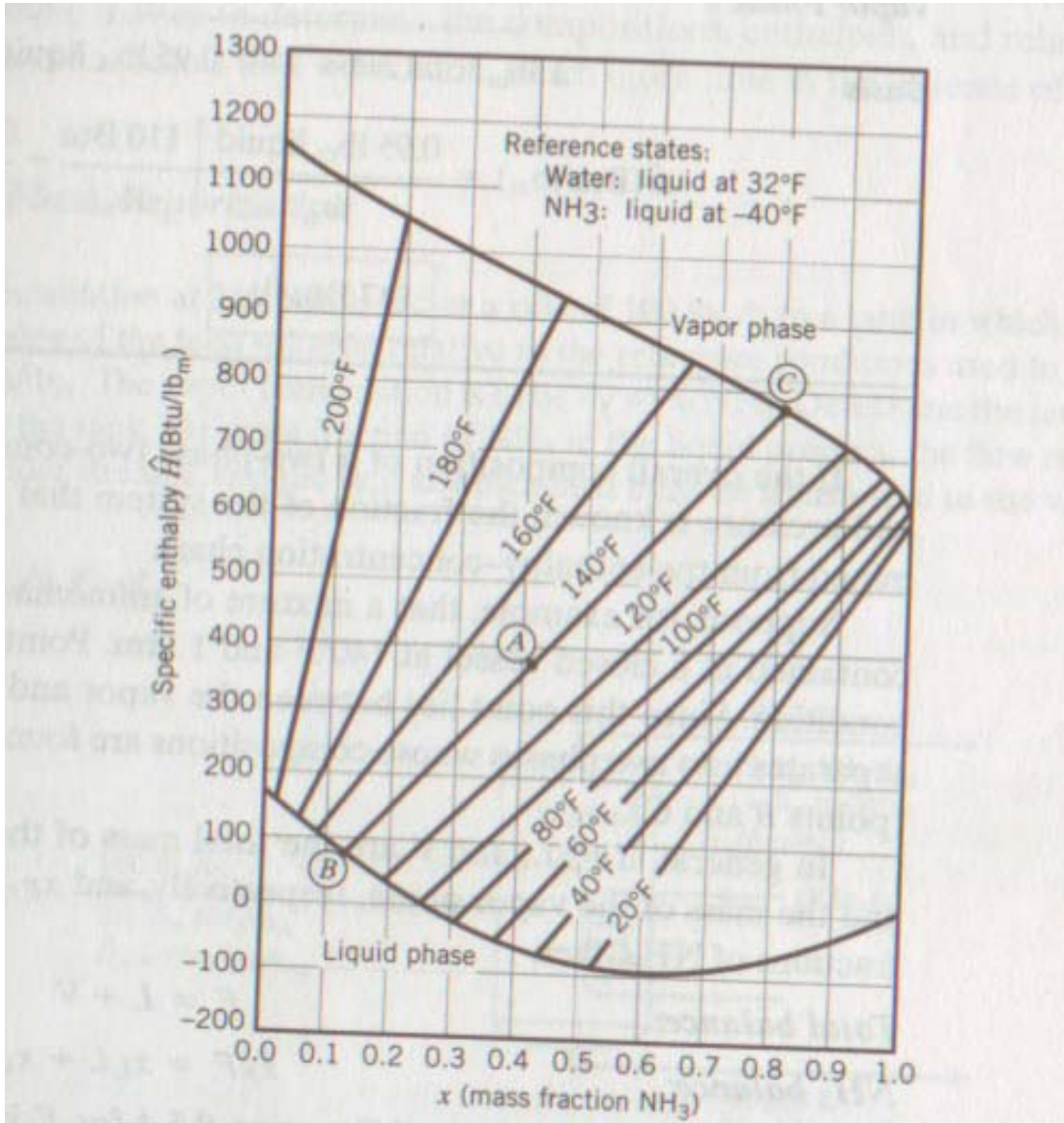
After determining  $\Delta H$  for both steps add them up to find enthalpy of H<sub>2</sub>SO<sub>4</sub> (aq) at 40°C. Now, complete the energy balance to determine the heat liberated.

## Enthalpy concentration chart for vapour liquid equilibrium calculations

For convenience, enthalpy concentration charts are prepared that allow us to do energy balances easily. These charts obviate the need of calculating specific enthalpies at different T. The enthalpies values could be read from the chart. The text book enthalpy concentration chart for a single phase system. It is not discussed here. We will look at two phase systems involving a liquid phase and a vapour phase.

The diagonal lines in the Figure below are tie lines. Their intersection with the lower curve gives liquid phase composition and with the upper curve gives vapour phase composition. The two phases are in equilibrium. We can read the specific enthalpies of vapour and liquid phases from the chart. Always note the reference states of the species when you are using the charts.

In the chart shown below for  $\text{NH}_3\text{-H}_2\text{O}$  system at 1 atm, at  $80^\circ\text{F}$ , liquid phase has about 30 mole% ammonia and vapour phase has about 95 mole%. The specific enthalpy of liquid phase is about -25 Btu/lb<sub>m</sub> and that of vapour phase is about 650 Btu/lb<sub>m</sub>. You could use these values in energy and mass balances.





## REACTIVE SYSTEMS

You carry out the six steps indicated for non-reactive systems, with a modification to the enthalpy term in the general energy balance equation.

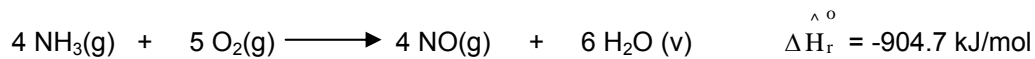
When reactions occur, the change in enthalpy term in general energy balance equation is evaluated as follows:

$$\dot{\Delta H} = \dot{\xi} \Delta H_r^{\circ} + \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in} \quad \text{for single reaction}$$

$$\dot{\Delta H} = \sum \dot{\xi} \Delta H_r^{\circ} + \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in} \quad \text{for multiple reactions}$$

$\Delta H_r^{\circ}$  is standard heat of reaction, which is difference between total enthalpy of products and total enthalpy of reactants at 25°C when stoichiometric quantities of reactants react to produce products. The units of  $\Delta H_r^{\circ}$  are kJ/mol. It is important to know what we mean by mole here.

Consider an example.



This means that if 4 moles of  $\text{NH}_3(\text{g})$  react with 5 moles of  $\text{O}_2(\text{g})$  to make 4  $\text{NO}(\text{g})$  and 6  $\text{H}_2\text{O}(\text{v})$  at 25°C, the difference between total enthalpy of products and total enthalpy of reactants is 904.7 kJ/mol.

**CHOOSE AS REFERENCES MOLECULAR SPECIES AT T AND P WHERE HEAT OF REACTION IS SPECIFIED. STANDARD HEAT OF REACTION IS ESTIMATED AT 25°C AND 1 ATM; SO, CHOOSE THIS AS THE REFERENCE. P HAS NEGLIGIBLE EFFECT OF HEAT OF REACTION. THE PHASES OF THE SPECIES SHOULD BE SAME AS THE PHASE IN THE REACTION AT 25°C.**

$\dot{\xi}$  is extent of reaction for a species defined as  $\frac{|\dot{n}_{A,out} - \dot{n}_{A,in}|}{|v|}$ ,  $v$  is stoichiometric coefficient of

the species. Always calculate  $\dot{\xi}$  before finding  $\dot{\Delta H}$ .

$\Delta H_r^{\circ}$  can be obtained in many ways.

$$\Delta H_r^{\circ} = \sum \left( v \Delta H_f^{\circ} \right)_{\text{products}} - \sum \left( v \Delta H_f^{\circ} \right)_{\text{reactants}} \quad \text{where } \Delta H_f^{\circ} \text{ is standard heat of formation of a}$$

species. You could use Hess's law to calculate  $\Delta H_f^{\circ}$ .

$$\Delta H_r^{\circ} = \sum \left( v \Delta H_c^{\circ} \right)_{\text{reactants}} - \sum \left( v \Delta H_f^{\circ} \right)_{\text{products}} \quad \text{where } \Delta H_c^{\circ} \text{ is standard heat of combustion of a}$$

species.

In the above example of ammonia oxidation, suppose ammonia and oxygen enter the reactor at 50°C, 1 atm and the products emerge at 300°C, 1 atm. We choose references as NH<sub>3</sub> (g), O<sub>2</sub>(g), NO(g) and H<sub>2</sub>O(v) all at 25°C and 1 atm.

Now, construct inlet-outlet enthalpy table and find enthalpies of all species. You should, by now, be able to do it. Then, use the equation at the beginning of REACTIVE SYSTEMS section, to

evaluate  $\dot{\Delta H}$ . What we essentially are doing is: bringing the reactants from 50°C to 25°C, reacting them at 25°C to generate products and then heating up the products to 300°C. We follow this path because standard heat of reaction is available at 25°C. This method is called **Heat of Reaction** method.

There is another method called **Heat of Formation** method, which is recommended if multiple reactions occur. You could also use the equation for multiple reactions at the beginning of REACTIVE SYSTEMS section, but **Heat of Formation** method works out to be simple.

When you use **Heat of Formation** method,  $\dot{\Delta H} = \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in}$ .

What we do is choose as references elemental species that make up the reactants and products at 25°C and 1 atm in the phase in which they appear in the heat of formation. We then construct inlet-outlet enthalpy table and find enthalpies of all molecular species.

Enthalpy of each molecular species is found by the following process path:

Make the molecular species from the elemental species at 25°C and subject the molecular species to isobaric and isothermal conditions to take it to the inlet/outlet conditions. The first step of making molecular species involves standard heat of formation. When you do this for all species and then use the equation,  $\dot{\Delta H} = \sum \dot{n}_{out} \dot{H}_{out} - \sum \dot{n}_{in} \dot{H}_{in}$ , you are automatically accounting for the heat of reaction term.

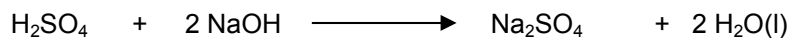
#### **Difference between heat of reaction method and heat of formation method.**

**Heat of Reaction method:** Bring reactants from inlet conditions to 25°C, react them at 25°C to make products at 25°C and then take the products to outlet conditions. Add the enthalpy changes in the three steps.

**Heat of Formation method:** Bring reactants from inlet conditions to their constituent elements at 25°C, taking the elements at 25°C to outlet conditions. Add the enthalpy changes in the two steps.

#### **Thermochemistry of Solutions**

If solutions of acid and base are mixed they react to make products. To perform energy balances on such systems, we consider the following example in which 20 wt% sulphuric acid reacts with 10 wt% sodium hydroxide.



Basis: 1 kg of sulphuric acid solution.

If required quantities of acid and base are taken, it is easy to find that we need 1.632 kg of NaOH solution and 289.8 g of Na<sub>2</sub>SO<sub>4</sub> are made and 36.73 g of water are generated.

We calculate  $r = \text{moles of solvent/mole of solute}$ .

$r$  for H<sub>2</sub>SO<sub>4</sub> = 21.78 (Verify) and for NaOH = 20.

Choose references as H<sub>2</sub>SO<sub>4</sub> (aq,  $r = 21.78$ ) and NaOH (aq,  $r = 20$ ), Na<sub>2</sub>SO<sub>4</sub> (aq,  $r = 62.7$ ), H<sub>2</sub>O (l) all at 25°C

Construct inlet-outlet enthalpy table.

Evaluate enthalpies of all inlet and outlet species. Note that reference is 25°C and if reactants and products enter or leave at any other temperature, you need to account for it.

$$\text{The heat of reaction is } \Delta H_r = \left( \Delta H_f^0 \right)_{\text{Na}_2\text{SO}_4(\text{aq})} + 2 \left( \Delta H_f^0 \right)_{\text{H}_2\text{O}(\text{l})} - \left( \Delta H_f^0 \right)_{\text{H}_2\text{SO}_4(\text{aq})} - 2 \left( \Delta H_f^0 \right)_{\text{NaOH}(\text{aq})}$$

To estimate standard heat of formation for aqueous solutions, use the following:

$$\left( \Delta H_f^0 \right)_{\text{solution}} = \left( \Delta H_f^0 \right)_{\text{solute}} + \Delta H_s^0$$

That is, the heat of formation of aqueous solution = heat of formation of the solute (sulphuric acid, NaOH etc) + heat of dilution. Remember: heat of dilution depends on  $r$  (moles of solvent/moles of solute).

$$\text{In the above example, } \left( \Delta H_f^0 \right)_{\text{H}_2\text{SO}_4(\text{aq})} = \left( \Delta H_f^0 \right)_{\text{H}_2\text{SO}_4} + \Delta H_s^0 (r = 21.78). \text{ Similarly, find standard}$$

heats of formation of all aqueous solutions, then find heat of reaction.

### Adiabatic Flame Temperature

When the heat liberated upon combustion of a fuel is entirely used in raising temperature of the products, the product temperature would be highest and it is called adiabatic flame temperature. Actual product temperature would always be less than this because of unavoidable heat losses.

How do we determine adiabatic flame temperature?

Write energy balance on a furnace in which a fuel or a mixture of fuels is being burned.

If changes in kinetic and potential energies are negligible and, and heat losses are zero, then the general energy balance equation reduces to:

$$\dot{\Delta H} = n_f \Delta H_c^0 + \sum_{\text{out}} nH(T_{\text{ad}}) - \sum_{\text{in}} nH(T_{\text{feed}})$$

Shaft work is zero for furnaces. If heats of combustion are available at 25°C, choose as reference 25°C and 1 atm. The phase of the species should be the phase in which it appears in heat of combustion reaction. Construct inlet-outlet enthalpy table and evaluate all specific enthalpies.

Note: The outlet enthalpies will be functions of temperature. In fact, they would be fourth order polynomials in T because specific heat is a third order polynomial in T. You could use Excel spreadsheet or any other computer program to solve for T.