Chapter one

Energy and Energy Balance

1-Introduction:

As an engineer designing a process, one of your principle jobs would be to a count carefully for the energy that flows into and out of each process unit and to determine the overall energy requirements for the process.

You would do this by writing (Energy Balance) for the process, in much may that you write material balance to account the mass flows to and from process and its units. One of the first things that chemical engineer needs to know about processes is the many different ways in which we may classify and operate the process.

2- Process Classification:

One of the first things that ChE's need to know about processes is the many different ways in which we may operate a process.

There are three major classifications of processes:

- **Batch Process**: In a batch process, material is placed in the vessel at the start and (only) removed at the end.
- --no material is exchanged with the surroundings during the process.

Batch Examples: fermentations, small-scale chemicals (pharmaceuticals)

• **Continuous Process**: In a continuous process, material flows into and out of the process during the entire duration of time.

Continuous Examples: pool filter, distillation processes

• Semi-batch Process: A semi-batch process is one that does not neatly fit into either of the other categories (i.e., it is a catch-all classification).

Semi-Batch Examples: washing machine, fermentation with purge.

3- Process Operation:

Each of the above classes of process may be further distinguished by their mode of operation with respect to time.

Continuous processes may be run:

- **Steady-State**: At steady-state, none of the process variables change with time (if we ignore small, random fluctuations).
- **Unsteady-State**: At unsteady-state, the process variables change with time. (One class of unsteady-state processes are oscillatory, where they process variables change with time in a regular way.

All other unsteady processes may be called Transient meaning that the process variables continuously evolve over time).

4- System Classification:

A "System" is an object or a collection of objects or process that an analysis is done on. The system has a definite boundary, called the system boundary that is chosen and specified at the beginning of the analysis. Once a system is defined, through the choice of a system boundary, everything external to it is called the **surroundings**. All energy and material that are transferred out of the system enter the surroundings, and vice versa.

- **Open System**: An open system is one where mass does move across the boundaries. In practice, this means that stuff goes in or out at some point during the process (not simply at the beginning and/or ending).
- **Close System**: closed tells us whether the system is isolated from its surroundings in terms of mass flow across the boundaries.

Our last classifications have to do with whether a system is isolated from its surroundings in terms of heat flow and whether it changes temperature.

- Adiabatic System: An adiabatic system is one where no thermal energy (heat) moves across the boundaries (in practice, this is accomplished through the use of insulation, so this is often also called an "insulated" system).
- **Isothermal system**: An isothermal system stays at a single constant temperature with respect to time.

State of a System:

Once a system is defined, a certain number of variables will specify its state fully. For example, one may need to provide the temperature, pressure, composition, total amount of material, velocity, and position in order to specify a system's "state." The exact information that is needed to specify the state of a system depends on the type of system and the analysis to be performed.

State Functions and State Properties

The state of a system can be changed, for example by increasing its temperature or changing its composition. Properties of the system, whose change depends only on the initial (before) and final states of the system, but not on the manner used to realize the change from the initial to the final state, are referred to as **state properties** or **state functions**. In other words, the change in a state function or state property *X*, between some final (state 2) and initial (state 1) situations, can be expressed as:

$$\Delta X = \underbrace{X_{\text{final}} - X_{\text{initial}}}_{\text{change in X}} \equiv X_{\text{state 2}} - X_{\text{state 1}}$$

5- Forms of Energy:

Energy is often categorized as:

- A. Kinetic Energy
- B. Potential Energy
- C. Internal Energy

Kinetic Energy

A system's kinetic energy is associated with directed motion (e.g. translation, rotation) of the system. Translation refers to straight line motion. The kinetic energy Ek of a moving object of mass m and travelling with speed u is given by,

 $\dot{E}_k = \frac{1}{2}\dot{m}u^2 \qquad (1.1)$

 E_k has units of energy, m⁻ has units of mass flow rate (mass/time), and u has units of velocity (length/time).

$$\frac{1}{2}\dot{m}v^2 \Rightarrow \left(\frac{\mathrm{kg}}{\mathrm{s}}\right) \left(\frac{\mathrm{m}}{\mathrm{s}}\right)^2 \left|\frac{\mathrm{N}}{\mathrm{kg}\,\mathrm{m/s^2}}\right| \frac{\mathrm{J}}{\mathrm{N}\cdot\mathrm{m}} \left|\frac{\mathrm{W}}{\mathrm{J/s}}\right| = \mathrm{W}$$

Potential Energy

Potential energy of a system is due to the position of the system in a potential field. The gravitational potential energy of an object of mass m at an elevation z in a gravitational field, relative to its gravitational potential energy at a reference elevation z_0 , is given by

The unit of the change in transport rate of potential energy is obtained as follows:

For closed system:

$$\Delta PE = mg(z - z_0) \Rightarrow m(kg)g(m/s^2)\Delta z(m) = N \cdot m = J$$

For open system:

$$\Delta PE = \dot{m}(kg/s)g(m/s^2)\Delta z(m) = N \cdot m/s = J/s = W$$

Internal Energy (U):

All the energy associated with a system that does not fall under the above definitions of kinetic or potential energy is internal energy. More specifically, internal energy is the energy due to all molecular, atomic, and subatomic motions and interactions. Usually, the complexity of these various contributions means that no simple analytical expression is available from which internal energy can be readily calculated. The internal energy will be represented by the symbol U.

Enthalpy (H):

The enthalpy H of a system is defined by

 $H = U + PV \tag{1.3}$

Where *P* is the pressure and *V* is volume. Let's think about the *PV* term. We know that *PA*, where *A* is the area subjected to a pressure *P*, is the force acting on that area. If a fluid inside a system is displaced through a distance *x* by the force *PA*, then the resultant work *W* done on the system can be calculated as the product of this force times the displacement. In other words, W = PAx. Now note that Ax = V, the volume swept out by the displacement. Thus, an alternate way to write the displacement work is W = PV. This type of work, where pressure results in the displacement of a fluid, will be referred to as **flow work**. If an amount of fluid of volume *V* is inserted into a system against a pressure *P*, the work required to accomplish this is *PV*. Enthalpy, therefore, can be viewed as the sum of the internal energy of this fluid volume added to the system plus the flow work performed on the system in order to insert the fluid. Enthalpy has units of energy (e.g. J, cal,BTU).

Energy Transferred to or from The system:Heat (Q):

Heat, Q, is the net amount of heat transferred to or from the system over a fixed time interval. A process may involve more than one specified form of heat transfer, of course, the sum of which is Q.

The rate of transfer will be designated by an overlay dot on Q thus the units of heat transfer per unit time, and the net heat transfer per unit mass would be designated by an overlay caret thus:

Heat (Q) is commonly defined as that part of the total energy flow across a system boundary (surrounding) that is caused by a temperature difference (potential) between the system and the surroundings (or between two systems). Because heat is based on the transfer of energy, heat cannot be stored. **Heat is positive when transferred to the system and negative when removed from the system.**

Heat transfer is usually classified in three categories: conduction, convection, and radiation. To evaluate heat transfer *quantitatively*, you can apply various empirical formulas to estimate the heat transfer rate. One example of such a formula is the rate of heat transfer by convection that can be calculated from

$$\dot{Q} = U^*A(T_2 - T_1)$$

where Q is the rate of heat transfer (such as joules per second), A is the area for heat transfer (such as square meters), $(T_2 - T_1)$ is the temperature difference between the surroundings at T_2 and the system at T_1 (such as in degrees Celsius), and U^* is an empirical coefficient usually determined from experimental data for the equipment involved; it might have the units of J/(s)(m²)(C).

• Work (W):

Work is a form of energy that represents a **transfer** of energy between the system and surroundings. Work cannot be stored. *Work is a path variable. Work is positive when the surroundings perform work on the system. Work is negative when the system performs work on the surroundings.* In this text, the symbol *W* refers to the net work done over period of time, *not* the *rate* of work. The latter is the **power**, namely, the work per unit time.

Many types of work can take place (which we will lump together under the notation *W*), among which are the following:

• Mechanical Work: Work that occurs because of a mechanical force that **moves the boundary** of a system. Sometimes the mechanical work called (PV Work) when a fluid expanded or compressed.

Then

• Shaft Work (W_s): Shaft work occurs when the system causes a shaft to turn against an external mechanical resistance. When a source of water outside the system circulates in the system and consequently causes a shaft to turn, the shaft work is positive. When a shaft in the system turns pump to pump water out of the system, the shaft work is negative.



Fig.1Shaft work. In the figure the force exerted on the impeller due to the water flow from the surroundings causes the shaft to rotate. Work is positive here–done by the surroundings on the system.

• Flow Work (W_f) : Flow work is performed on the system when a fluid is pushed into the system by the surroundings. For example, when a fluid enters a pipe, some work is done on the system (the water that already is in the pipe) to force the new fluid into the pipe. Similarly, when fluid exits the pipe, the system does some work on the surroundings to push the exiting fluid into the surroundings. Flow work will be described in more detail in the next subsection.



Fig 2: Flow work. Flow work occurs when the surroundings push an element of fluid into the system (sign is positive) or when the system pushes an element of fluid into the surroundings.

 $W = W_s + W_f$

6-Energy Balance on Closed System:

 $\begin{array}{l} \text{final system} \\ \text{energy} \end{array} - \begin{array}{l} \text{initial system} \\ \text{energy} \end{array} = \begin{array}{l} \text{net energy transferred to} \\ \text{the system (in - out)} \end{array}$

initial system energy = $U_i + E_{ki} + E_{pi}$ final system energy = $U_f + E_{kf} + E_{pf}$ energy transferred = Q - W

Then

$$(U_{\rm f} - U_{\rm i}) + (E_{\rm kf} - E_{\rm ki}) + (E_{\rm pf} - E_{\rm pi}) = Q - W$$

Or

$$\Delta U + \Delta E_{\mathbf{k}} + \Delta E_{\mathbf{p}} = Q - W \qquad (1.8)$$

This equation is the basic equation for the first law of thermodynamic for closed system, when applying this equation, we must be aware of the following points:

- If no temperature change, phase change, or no chemical reaction occur, and if the pressure change is less than 1 atm , then $\Delta U = 0$.
- For adiabatic process Q=0
- If the system is not accelerating , then $\Delta E_k = 0$
- If no change in height, then $\Delta E_p = 0$
- If there is no moving parts ,then W=0

• 7- Energy Balance for an Open System:

In open systems, material crosses the system boundary as the process occurs (e.g., continuous process at steady state). In an open system, work must be done on the system to push input fluid streams at a pressure P_{in} into the system, and work is done

on the surroundings to push output fluid streams at a pressure P_{out} out of the system, as shown in the schematic diagram in Figure



Fig.3 Energy balance for an open system.

Net rate of work done by the system is

$$\dot{W}_{\rm f} = \dot{W}_{\rm out} - \dot{W}_{\rm in} = P_{\rm out}\dot{V}_{\rm out} - P_{\rm in}\dot{V}_{\rm in}$$

For several input and output streams,

$$\dot{W}_{\rm f} = \sum_{\rm output} P_j \dot{V}_j - \sum_{\rm input} P_j \dot{V}_j$$

The total rate of work \dot{W} done by a system on its surroundings is divided into two parts:

$$\dot{W} = \dot{W}_{\rm s} + \dot{W}_{\rm f}$$

Where shaft work (W_s) is the rate of work done by the fluid on a moving part within the system (e.g., piston, turbine, compressor, and rotor), and flow work (\dot{W}_{t}) is the rate of work done by the fluid at the system outlet minus the rate of work done on the fluid at the system inlet. The general balance equation for an open continuous system under steady state in the absence of generation/consumption term is.

The general energy balance for a process can be expressed in words as:

Accumulation of Energy in System = Input of Energy into System – Output of Energy from System

Rate of Energy Accumulation in System =

$$\sum_{\text{input streams}} \dot{m}_j \left(\hat{U}_j + \frac{u_j^2}{2} + gz_j \right) - \sum_{\text{output streams}} \dot{m}_j \left(\hat{U}_j + \frac{u_j^2}{2} + gz_j \right) + \dot{Q} - \dot{W}$$

Note that all terms in the above equation have units of energy/time. Also, recall the conventions with regard to the sign of the heat and work terms.

Enthalpy (H) is the sum of the internal energy (U) of fluid volume added to the system plus the flow work (PV) performed on the system in order to push the fluid in/out of the system:

$$\hat{H}_{j} = \hat{U}_{j} + P_{j}\hat{V}_{j}$$

rate of energy accumulation in system = $\sum_{\text{input streams}} \dot{m}_j \left(\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + gz_j \right) - \sum_{\text{output streams}} \dot{m}_j \left(\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + gz_j \right) + \dot{Q} - \dot{W}_s$

The rate of accumulation term can be broken down into rates of accumulation of kinetic, potential, and internal energies, and by using the fact

$$\dot{V}_{j} = \dot{m}_{j}\hat{V}_{j}.$$

$$\frac{dE_{k}}{dt} + \frac{dE_{P}}{dt} + \frac{dU}{dt} = \sum_{\text{input streams}} \dot{m}_{j}\left(\hat{H}_{j} + \frac{u_{j}^{2}}{2} + gz_{j}\right) - \sum_{\text{output streams}} \dot{m}_{j}\left(\hat{H}_{j} + \frac{u_{j}^{2}}{2} + gz_{j}\right) + \dot{Q} - \dot{W}_{s}$$

Integration of the above equation with respect to time, from an initial to a later (final) time yields,

$$(E_{\rm kf} - E_{\rm ki}) + (E_{\rm Pf} - E_{\rm Pi}) + (U_{\rm f} - U_{\rm i}) =$$

$$\sum_{\rm input \ streams} m_j \left(\hat{H}_j + \frac{u_j^2}{2} + gz_j\right) - \sum_{\rm output \ streams} m_j \left(\hat{H}_j + \frac{u_j^2}{2} + gz_j\right) + Q - W_s$$

Or

$$\Delta E_{\mathbf{k}} + \Delta E_{\mathbf{P}} + \Delta U = \sum_{\text{input streams}} m_j \left(\hat{H}_j + \frac{u_j^2}{2} + gz_j \right) - \sum_{\text{output streams}} m_j \left(\hat{H}_j + \frac{u_j^2}{2} + gz_j \right) + Q - W_s$$

Finally

$$\Delta \dot{H} = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j \hat{H}_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j \hat{H}_j$$
$$\Delta \dot{E}_k = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j u_j^2 / 2 - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j u_j^2 / 2$$
$$\Delta \dot{E}_p = \sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j g z_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j g z_j$$

Notice that if the process has a single output stream and single input stream and there is no accumulation of mass in the system so that $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$ then:

$$\Delta \dot{H} = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = \dot{m}\Delta \hat{H} \qquad (1.10)$$

Example 1: Internal Energy Calculation

A cylinder fitted with a movable piston is filled with gas. An amount of 2.00 kcal of heat is transferred to the gas to raise the gas temperature 100°C higher. The gas does 68 J of work in moving the piston to its new equilibrium position. Calculate the change in internal energy of the system.

Solution:

$$W = 68 J$$

$$\uparrow$$

$$Q = 2.00 \text{ kcal}$$
(2)

Known quantities: The difference in gas temperature (100° C), work done by the system (+68 J), and heat added to the system (+2.00 kcal).

Find: Change in internal energy.

Analysis: Use the energy balance equation for a closed system.

System: Gas in the system, closed system

$$\Delta U + \Delta KE + \Delta PE = Q - W$$

Assumption: No change in kinetic and potential energy; accordingly, both are set to zero. The equation is reduced to

$$\Delta U = Q - W$$

Substitute the values of Q and W to calculate the change in internal energy (make sure units are consistent). The heat is added to the system (positive value) and the work is done by the system (positive value as well):

$$\Delta U = \left(2.0 \text{ kgal}\right) \left[\frac{1000 \text{ cal}}{\text{ kgal}} \frac{1 \text{ J}}{0.239 \text{ cal}}\right] - 68 \text{ J} = 8300 \text{ J}$$

The change in internal energy $\Delta U = 8.30$ kJ.

The specific enthalpy (h = H/m) can be calculated using the following equation:

$$H = U + PV$$

Substituting the values of specific internal energy (u = U/m), pressure (P), and specific volume (v) in the earlier equations gives the specific enthalpy h.

Example 2: Enthalpy from Internal Energy

The specific internal energy of helium at 25°C and 1 atm is 3.80 kJ/mol, and the specific molar volume under the same conditions is 25 L/mol. Calculate the specific enthalpy of helium at this temperature and pressure, and the rate at which enthalpy is transported by a stream with a molar flow rate of 250 kmol/h.

Solution

Known quantities: Internal energy, pressure, temperature, molar volume, molar flow.

Find: Specific molar enthalpy (*h*), rate of enthalpy transport (\dot{H}).

Analysis: Follow the specific enthalpy definition. The specific enthalpy of helium is given by : h = u + Pv

Substituting the values of specific internal energy, pressure (P), and specific volume (v) in the earlier equations,

$$h = \left(3800 \frac{\text{J}}{\text{mol}}\right) + (1 \text{ atm})\left(25 \frac{\text{L}}{\text{mol}}\right) \left[\frac{1 \text{ m}^3}{1000 \text{ L}} \frac{1.01325 \times 10^5 \frac{\text{N}}{\text{m}^2}}{1 \text{ atm}} \frac{\text{J}}{\text{N} \cdot \text{m}}\right]$$

= 6333 J/mol

The enthalpy transport rate (\dot{H}) is calculated by multiplying the molar flow rate (\dot{n}) with the specific molar enthalpy (h):

$$\dot{H} = \dot{n} \times h$$

Substitute the values of molar flow rate (\dot{n}) and specific enthalpy (h) to find the enthalpy transport rate (\dot{H}):

$$\dot{H} = \left(250 \,\frac{\mathrm{kmol}}{\mathrm{h}}\right) \times \left(6333 \,\frac{\mathrm{J}}{\mathrm{mol}}\right) \left[\frac{1000 \,\mathrm{mol}}{\mathrm{kmol}} \frac{\mathrm{kJ}}{1000 \,\mathrm{J}}\right] = 1.58 \times 10^6 \,\mathrm{kJ/h}$$

8- Obtaining Enthalpies:

Obviously, whenever we do an energy balance we are going to need to get values for enthalpy, H. The enthalpy is a function of T and P and will have different values for different fluids. The methods that you will encounter as we go along include:

Methodology for getting H:

- Look up enthalpies from charts or tables for specific fluids
- Look up enthalpy departure functions from CSP
- Calculate from equations of state

There is no such thing as absolute enthalpy; enthalpy is always measured relative to some reference state. So when values are obtained from a chart, remember that they are values *relative to a reference* point. Often the reference point will be the enthalpy of the solid at its melting point or some other fixed reference point. Fortunately, we have outlet minus inlet in the energy balance so that we will always be calculating a difference in enthalpy between the inlet and outlet fluid states. This means that the reference can be neglected because it always cancels out. Thus,

$\Delta H = H_{out} - H_{in} = (H_{out} - H_{ref}) - (H_{in} - H_{ref}) = (H_{out} - H_{in}) - (H_{ref} - H_{ref})$

For the examples below, if water as the working fluid. We can obtain enthalpies for water and steam from the steam tables. Enthalpies are obtained from steam tables by looking up each individual point for a given T and P. If the system has two phases in equilibrium, then we need the properties of saturated water and saturated steam. These can be obtained from the saturated tables. Recall that for a pure fluid, we only need specify either T<u>or</u> P, not both, when we are in the two-phase region.

Enthalpies for water can be found in Tables B.5, B.6 and B.7 in your textbook or from steam tables book. Also steam tables are used to determine the temperature, specific internal energy, and specific enthalpy of saturated steam and superheated steam. Water exists as both vapor and liquid at temperatures and pressures corresponding to the vapor liquid equilibrium curve. At conditions on this curve, water could be a *saturated liquid* or a *saturated vapor* (if a superheated vapor is cooled slowly, it becomes saturated vapor when equilibrium curve is reached; similarly, saturated liquid can be thought of). The phase diagrams (P-T diagram) and (P-V diagram) of water are shown in Fig.4 and Fig.5

Enthalpies for water can be found in Tables B.5, B.6 and B.7 in your textbook. We spend just a moment here to familiarize you with how to look up enthalpies in these tables.

<u>1. Saturated Steam: Temperature Table B.5</u>

If you need properties for either saturated liquid or saturated vapor, you can use Table B.5. This table has the following structure:

Τ	Р	V (water)	V (steam)	U (water)	U (steam)	H (water)	ΔH (evaporation)	H (steam)
50	0.1234	0.001012	12.05	209.2	2443.6	209.3	2382.9	2592.2
60	0.1992	0.001017	7.678	251.1	2456	251.1	2358	2609

These columns have the following meanings:

• 2nd column: P is the vapor pressure for the saturated liquid at the given temperature [bar]

- 3rd column: V(water) is the specific volume (reciprocal density) for the saturated water at this temperature $[m^3/kg]$
- 4th column: V(steam) is the specific volume of the saturated vapor $[m^3/kg]$
- 5th column: U(water) is the internal energy per unit mass of the saturated liquid [kJ/kg]
- 6th column: U(steam) is the internal energy per unit mass of the saturated vapor [kJ/kg]
- 7th column: H(water) is the enthalpy per unit mass of the saturated liquid [kJ/kg]
- 8th column: ΔH (evaporation) is the enthalpy of vaporization to convert one kg of liquid to vapor at this temperature [kJ/kg]. Note that it is the difference between the enthalpy of the vapor and the enthalpy of the liquid.
- Final column: H(vapor) is the enthalpy per unit mass of the saturated vapor [kJ/kg]

2. Saturated Steam: Pressure Table B.6

Table B.6 is the same as Table B.5, but the data are organized according to systematic intervals in pressure rather than temperature. The columns have the same meaning as before. An example from this table is:

Р	Т	V (water)	V (steam)	U (water)	U (steam)	H (water)	ΔH (evaporation)	H (steam)
0.050	32.9	0.001005	28.2	137.8	2420.6	137.8	2423.8	2561.6
0.060	36.2	0.001006	23.74	151.5	2425.1	151.5	2416.0	2567.5

3. Superheated Steam: Table B.7

Two properties are required to specify the state of a single-phase fluid. So if you want properties of superheated steam (at a temperature above its two-phase, saturation temperature) you have to find the value at the specific temperature and pressure desired. As an example, suppose I need the enthalpy of steam at 300°C and 80 bar. The temperature is given across the top of the table and the pressure is listed down the left most column. I can then read the value as shown in the isolated portion of the table given below.

If you want to calculate the enthalpy change of saturated steam from 305 to 307 K by linear interpolation from steam tables, you would carry out the following computation:

If H at 305K =2558.9 kJ/kg

And H at 310 K = 2567.9 kJ/kg

What is the enthalpy at 307K

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$$\hat{H}_{307} = \hat{H}_{305} + \frac{H_{310} - H_{305}}{T_{310} - T_{305}} (T_{307} - T_{305})$$
$$= 2558.9 + \frac{2567.9 - 2558.9}{310 - 305} (307 - 305) = 2562.5$$

P vs T Diagram: Water Supercritical fluid Critical point 218.3 atm Liquid Solid D Find: 760 mm Hg Triple Condensing-boiling 17.535 mm Hg Freezing-melting Gas Vapor Freezing-sublimation 4.58 mm Hg 3 mm Hg -5 0.0098 20 100 130 374.3 T(°C) (a) H20







Fig.5: P-V and P-T diagram of water with notification.

Example 3:

What is the enthalpy of steam at 1 atm that has a 90% quality?

Solution:

Quality is the fraction or percentage of a two-phase stream (steam + liquid water) that is steam. For a two-phase system, we know that we have saturated liquid and saturated vapor in equilibrium. Therefore, we turn to the pressure table for saturated steam, Table B.6.

At 1 atm, $h_L = 419.1$ kJ/kg and $h_V = 2675.4$ kJ/kg (as obtained from Table B.6).

The total enthalpy of the mixture is therefore,

 $H = m_{\rm L}h_{\rm L} + m_{\rm V}h_{\rm V}.$

This can also be written in terms of the specific enthalpy (per kg of mixture) by dividing both sides by the total mass of the mixtures. This gives:

 $h = H/m = w_L h_L + w_V h_V = (0.1 \text{ kg}) (419.1 \text{ kJ/kg}) + (0.9 \text{ kg}) (2675.4 \text{ kJ/kg}) = 2449.8 \text{ kJ/kg}$

Or sometimes written as:

$$H = x H_L + (1 - x) H_G$$

Since: $H_G - H_L = \Delta H_{vap}$(1.11)

Then $H = H_L + x \Delta H_{vap}$(1.12)

Example 4: Use of a Steam Table

Use steam tables in the appendix to determine the temperature, specific internal energy, and specific enthalpy of saturated steam at 3.0 bar. What is the state of the steam at 10 bar and 400° C? (i.e., is it saturated or superheated steam?)

Solution

Known quantities: *Case 1*: 3 bar, saturated steam, *Case 2*: 10 bar, 400°C.

Find: Specific enthalpy (*h*) and specific internal energy (*u*), specific volume (*v*). The state of steam at 10 bar and 400°C.

Analysis: Two properties are needed to be able to use saturated steam table and superheated steam table in the appendix.

Case 1: At 3 bar, steam is saturated: use saturated steam table (Appendix A.3). The temperature is 133.5°C, specific enthalpy is 2724.7 kJ/kg, and specific internal energy is 2543 kJ/kg.

Case 2: At 10 bar and 400°C: At 10 bar the saturated temperature is 179.9°C, and since the steam is at 400°C, this temperature is higher than the saturated temperature at 10 bar. Therefore, the state of water is superheated steam, and hence, the superheated steam table (Table A.5) is used.

Specific enthalpy is 3264 kJ/kg, specific internal energy is 2958 kJ/kg, and specific volume is 0.307 m³/kg.

• Steps in Solving Energy Balance Problems:

In order to apply the energy balance to common engineering situations. The general procedure is below:

- Draw and label the diagram
- Decide which terms are negligible in the general energy balance equation
- Simplify the energy balance by dropping out negligible terms
- Solve as much of the mass balance as possible
- Plug masses into the energy balance and solve it

Simplification of the energy balance equation for your particular problem is a key step that you should always do. There are very few cases where every term in the general energy balance equation would be significant to the problem. Try these examples to get a handle on when certain terms can be discarded.



• Energy Balance for Open Systems with Multiple Inputs and Multiple Outputs

The general energy balance for an open system is

$$Q - \dot{W_{\rm s}} = \Delta \dot{H} + \Delta KE + \Delta PE$$

The change in the rate of enthalpy for multiple streams is

$$\Delta \dot{H} = \sum \dot{H}_{\rm out} - \sum \dot{H}_{\rm in}$$

Setting enthalpy transport rate (H^{\cdot}) in terms of specific enthalpy h,

$$\Delta \dot{H} = \sum \dot{m}_{\rm out} h_{\rm out} - \sum \dot{m}_{\rm in} h_{\rm in}$$

Example 5: Energy Balance for an Open System: The Steam Turbine

Steam flowing at a rate of 10 kg/h enters a steam turbine at a velocity of 50 m/s and leaves at a point 5 m below the inlet at a velocity of 300 m/s. The heat loss from the turbine is estimated to be 10 kW, and the turbine delivers shaft work at a rate of 70 kW. Calculate the change in enthalpy transport rate of the process.

Solution

Known quantities: Steam flow rate, inlet and exit velocity, heat loss, and work delivered.

Find: Change in enthalpy transport rate.

Analysis: Use the general energy balance equation for an open system.

System: Steam turbine as open system

The energy balance for an open system has been derived as

$$\dot{Q}-\dot{W}_{\rm s}=\Delta\dot{H}+\Delta KE+\Delta P\dot{E}$$

In this example, heat is lost (negative value) from the system: Q=-10kW=-10kJ/s

The shaft work is delivered (positive value) by the system:

$$W_{\rm s} = 70 \, \rm kW = 70 \, \rm kJ/s$$

The change in kinetic energy

$$\Delta KE = \frac{1}{2}\dot{m}\left(\upsilon_2^2 - \upsilon_1^2\right)$$

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Substitute the values of mass flow rate (\dot{m}), inlet (v_1), and exit (v_2) velocities, and use conversion factors (make sure units are consistent):

$$\Delta KE = \frac{1}{2} \left(10 \, \frac{\text{kg}}{\text{h}} \, \frac{\text{h}}{3600 \, \text{s}} \right) \left(300^2 - 50^2 \right)$$
$$\times \left(\frac{\text{m}}{\text{s}} \right)^2 \left| \frac{\text{N}}{\text{kg m/s}^2} \left| \frac{\text{J}}{\text{N} \cdot \text{m}} \right| \frac{\text{kJ}}{1000 \, \text{J}} = 0.12 \, \text{kJ}$$

Change in potential energy

$$\Delta PE = \dot{m}g(z_2 - z_1)$$

Substitute the values of mass flow rate (\dot{m}), and inlet and exit heights from the surface of the earth (z_1 , z_2):

$$\Delta PE = 10 \frac{\text{kg}}{\text{h}} \frac{\text{h}}{3600 \text{ s}} \times 9.81 \frac{\text{m}}{\text{s}^2}$$
$$\times (-5-0) \text{m} \left| \frac{\text{N}}{\text{kg m/s}^2} \right| \frac{\text{J}}{\text{N} \cdot \text{m}} \left| \frac{\text{kJ}}{1000 \text{ J}} \right| = -0.00014 \text{ kJ}$$

The change in potential energy is almost negligible compared to the magnitudes of heat and work.

Substitute the values of Q, W_s , and changes in kinetic and potential energies in the energy balance equation for an open system:

$$\Delta H + \Delta KE + \Delta PE = Q - W_{\rm s}$$

$$\Delta \dot{H} + 0.12 \,\frac{\text{kJ}}{\text{s}} - 0.00014 \,\frac{\text{kJ}}{\text{s}} = -10 \,\frac{\text{kJ}}{\text{s}} - \left(70 \,\frac{\text{kJ}}{\text{s}}\right)$$

The change in enthalpy transport rate is

$$\Delta \dot{H} = -80.12 \text{ kJ/s}$$

Example 6: Turbine Work

Steam at a rate of 1500 kg/s enters a turbine at 40 bar and 400°C. It comes out of the turbine as wet steam at 4 bar. The turbine operates adiabatically and produces 1000 MW of work. What is the temperature of the steam leaving the turbine? What is the mass fraction of vapor in the stream leaving the turbine?

Solution

Known quantities: Steam mass flow rate (1500 kg/s), inlet conditions (40 bar and 400°C), exit steam conditions (4 bar, wet steam).

Find: Mass fraction of vapor in the stream leaving the turbine.

Assumptions: No change in kinetic and potential energy.

Analysis: Use steam tables to find inlet and exit enthalpy and the first law for an open system. Inlet and exit steam enthalpies: Saturated steam (Table A.4), superheated steam (Table A.5).

Inlet steam conditions: at 40 bar and 400°C: the enthalpy of the incoming steam is 3216 kJ/kg (Table A.5).

Exit steam conditions: at 4 bar: steam is either wet or saturated (Table A.4).

Since the steam leaving the turbine is a vapor–liquid mixture, it must be saturated. From Table A.4, for saturated steam at 4 bar the enthalpies of the liquid and vapor are 604.7 and 2737.6 kJ/kg, respectively, and the temperature is 143.6°C.

The general energy balance applied to this process, after neglecting the potential and kinetic energy terms and bearing in mind that the turbine is adiabatic, can be expressed as

$$\Delta \dot{H} = -\dot{W}_{\rm s}$$

Rearranging the earlier equation,

$$-\dot{W}_{\rm s} = \Delta \dot{H} = \dot{H}_{\rm out} - \dot{H}_{\rm in} = \dot{m}(h_{\rm out} - h_{\rm in})$$

Substituting known values of shaft work, mass flow rate, and inlet specific enthalpy, since the turbine is producing work, the sign of W_s is +:

$$-W_{\rm s} = -1000 \text{ MW} = -1 \times 10^6 \frac{\text{kJ}}{\text{s}} = 1500 \frac{\text{kg}}{\text{s}} (h_{\rm out} - 3216) \frac{\text{kJ}}{\text{kg}}$$

The specific enthalpy of the exit steam is

$$h_{\rm out} = 2549.3 \, \rm kJ/kg$$

Let *x* be the mass fraction of the steam that is in the vapor phase, then

$$h_{\rm out} = 2549.3 \, \frac{\rm kJ}{\rm kg} = h_{\rm f} + x h_{\rm fg} = 604.7 \, \frac{\rm kJ}{\rm kg} + x \big(2133.0 \, \rm kJ/\rm kg \big)$$

The steam quality is $x=0.912 \rightarrow$ The wet steam is 91.2 wt% vapor. The wet contains 91.2% water vapor and 8.80 wt% liquid water.

Example 6: Heat Exchanger

Steam at a rate of 60 kg/h, at 200°C, and 1 bar enters the tube side of a shell and tube heat exchanger. The steam is used to heat cold water flowing on the shell side; the steam leaves as saturated liquid. Neglect pressure drop of the steam on the tube side and the water on the shell side of the heat exchanger. How much heat must be transferred from the steam to the water side?

Solution

Known quantities: Mass flow rate (60 kg/h), inlet temperature and pressure (200°C, 1 bar), exit conditions (saturated water, 1 bar).

Find: Heat transfer rate from steam to water.

Assumptions: Pressure drop across the boiler is neglected, so exit pressure is at 1 bar.

Analysis: Use steam tables to find inlet and exit enthalpy.

Basis: 60 kg/h of feed steam. The schematic diagram of the problem is shown below.



Inlet: (1 bar, 200°C): *h*1 = 2875 kJ/kg

Using saturated steam table,

Outlet: (1 bar, saturated water):

$$h_2 = h_f \Big|_{at \, 1 \, bar} = 417.5 \, kJ / kg$$

No change in steam mass flow rate:

$$\dot{m} = \dot{m}_{\rm in} = \dot{m}_{\rm out} = 60 \text{ kg/h}$$

The general energy balance equation for an open system is

$$\Delta \dot{H} + \Delta KE + \Delta PE = \dot{Q} - \dot{W}_{\rm s}$$

The following simplifying assumptions for the condenser are used:

No shaft work: $W_s = 0$.

No change in elevation. The inlet and outlet lines are at the same level: $\Delta PE = 0$.

Since we do not know anything about the diameters of the inlet and exit pipes, same pipe diameters are used for inlet and exit streams; accordingly, there is no change in velocity, and change in kinetic energy is negligible: $\Delta KE = 0$.

The simplified form of the energy balance is therefore

$$\dot{Q} = \Delta \dot{H} = \dot{H}_{out} - \dot{H}_{in}$$

The rate of enthalpy transport (\dot{H}) as a function of specific enthalpy (h),

$$\Delta \dot{H} = \dot{m} \Delta h$$

Replacing enthalpy change rate ($\Delta \dot{H}$) with specific enthalpy (Δh) at constant mass flow rate,

$$Q = \dot{m}\Delta h = \dot{m}(h_{\rm out} - h_{\rm in})$$

Substituting the values of mass flow rate and exit and inlet specific enthalpy in the earlier equation,

$$Q = \left(60 \frac{\text{kg}}{\text{h}}\right) \left(417.5 - 2875\right) \frac{\text{kJ}}{\text{kg}} = -147,450 \text{ kJ/h}$$

The value of heat transfer is negative; that is, heat is transferred from the system (steam) to the surrounding (cold water).

Example 8: Heat Added to a Boiler

Liquid water is fed to a boiler at 23°C under a pressure of 10 bar, and is converted at constant pressure to saturated steam. Calculate Δh for this process and the heat input required for producing 15,000 m³/h of steam at the exit conditions. Assume that the inlet velocity of liquid entering the boiler is negligible and that the steam is discharged through a 0.15 m ID (inner diameter) pipe. Inlet and exit pipes are at the same level.

Solution

Known quantities: Water inlet conditions (23°C under a pressure of 10 bar), exit steam conditions (10 bar, saturated steam), exit steam volumetric flow rate (15,000 m^3/h), exit pipe diameter (0.15 m).

Find: Change in specific enthalpy (Δh) .

Analysis: The reboiler is an open system, and the general energy balance equation is



Since the reboiler does not deliver shaft work, no change is seen in elevation between inlet and exit steams (change in potential energy is zero); the energy balance equation reduces to

$$Q_{\rm s} = \dot{m}\Delta h + \Delta KE$$

The change in specific enthalpy:

Since no value of specific enthalpy is available at 23°C and 10 bar, the value is taken at 23°C (saturated water):

$$h_1\Big|_{\text{at 23°C, 10 bar}} = 96.2 \text{ kJ/kg}$$

The specific enthalpy value for the exit conditions at 10 bar, saturated steam is

$$h_2\Big|_{\text{at 10bar, sat'd steam}} = 2776.2 \text{ kJ}/\text{kg}$$

The change in specific enthalpy is

$$\Delta h = h_2 - h_1$$

Substitute the values of inlet and exit specific enthalpy:

$$\Delta h = 2776.2 \,\frac{\text{kJ}}{\text{kg}} - 96.2 \,\frac{\text{kJ}}{\text{kg}} = 2680 \,\text{kJ}/\text{kg}$$

The discharge mass flow rate (\dot{m}_2) is calculated at the exit steam because exit steam volumetric flow rate and diameter of discharge pipe are given. The density is calculated from the inverse of specific volume ($\rho = 1/v$). The specific volume (v) at 10 bar, saturated steam is 0.1943 m³/kg (used

$$\dot{m}_2 = \rho \times \dot{V} = \frac{1}{0.1943 \text{ m}^3/\text{kg}} \times 15,000 \frac{\text{m}^3}{\text{h}} \times \frac{\text{h}}{3600 \text{ s}} = 21.45 \text{ kg/s}$$

The inlet velocity is negligible as given in the problem statement. The exit velocity is calculated from the discharge volumetric flow rate divided by pipe cross sectional area:

$$\upsilon_2 = \frac{\dot{V}_2}{\frac{\pi D^2}{4}} = \frac{\frac{15,000 \text{ m}^3/\text{h}}{\pi (0.15)^2}}{\frac{\pi (0.15)^2}{4} \text{ m}^2} \times \frac{\text{h}}{3600 \text{ s}} = 235.79 \text{ m/s}$$

The simplified general energy balance equation becomes

$$Q = \dot{m}\Delta h + \Delta KE = \dot{m}\Delta h + \frac{1}{2}\dot{m}(\upsilon_2^2 - \upsilon_1^2)$$

Substitute the values of mass flow rate, specific enthalpy, and velocity:

$$Q = 21.45 \frac{\text{kg}}{\text{s}} \times \left(2680 \frac{\text{kJ}}{\text{kg}}\right) + \frac{1}{2} \times 21.45 \frac{\text{kg}}{\text{s}} \left\{ \left(235.79 \frac{\text{m}}{\text{s}}\right)^2 - 0 \right\}$$
$$\times \frac{\text{kJ}}{1000 \text{ J}} = 58,082 \text{ kJ/s}$$

The sign of the heat transfer across system boundaries is positive; that is, heat is transferred from the surroundings to the system.

Example 9: Mixing

Hundred kilograms per hour of a saturated steam at 1 bar is mixed with superheated steam available at 400°C and 1 bar to produce superheated steam at 300°C and 1 bar. Calculate the amount of superheated steam produced at 300°C, and the required mass flow rate of the 400°C steam.

Solution

Known quantities: Stream 1: mass flow rate, saturated steam, 1 bar. Stream 2: 400°C and 1 atm. Stream 3: superheated steam produced at 300°C, 1 bar.

Find: Volumetric flow rate of stream 2.

Assumptions: No change in kinetic and potential energy, no shaft work.



Analysis: Use open system energy balance with multiple inputs, single output. The process flow sheet is shown in Example Figure 8.20.1.

The general energy balance for an open system after applying the assumptions is reduced to

$$\Delta H = 0$$

For two inputs, single output,

$$\Delta \dot{H} = \dot{H}_3 - \dot{H}_1 - \dot{H}_2 = 0$$

Putting the equation in terms of mass flow rate and specific enthalpy,

$$\Delta \dot{H} = \dot{m}_3 h_3 - \dot{m}_1 h_1 - \dot{m}_2 h_2 = 0$$

Overall mass balance for the mixing system is

$$\dot{m}_1 + \dot{m}_2 = \dot{m}_3 \Rightarrow 100 \frac{\text{kg}}{\text{h}} + \dot{m}_2 = \dot{m}_3$$

The specific enthalpy of stream 1 is

$$h_1 \Big|_{1 \text{ bar, sat'd steam}} = 2675.4 \text{ kJ/kg}$$

$$h_2 \Big|_{1 \text{ bar, } 400^{\circ}\text{C}} = 3278 \text{ kJ/kg}$$

The specific enthalpy of stream 3 is

$$h_3|_{1 \text{ bar, } 300^{\circ}\text{C}} = 3074 \text{ kJ/kg}$$

The general energy balance for the mixing process is

$$\dot{m}_1\hat{H}_1 + \dot{m}_2\hat{H}_2 = \dot{m}_3\hat{H}_3$$

Substituting the values,

$$100 \frac{\text{kg}}{\text{h}} \left(2675.4 \frac{\text{kJ}}{\text{kg}} \right) + \dot{m}_2 \left(3278 \frac{\text{kJ}}{\text{kg}} \right) = \dot{m}_3 \left(3074 \text{ kJ/kg} \right)$$

From the material balance equation,

$$\dot{m}_2 = \dot{m}_3 - 100$$

Substitute the value of \dot{m}_2 in the earlier equation:

$$100 \text{ kg/h}(2675.4 \text{ kJ/kg}) + (\dot{m}_3 - 100)(3278 \text{ kJ/kg}) = \dot{m}_3(3074 \text{ kJ/kg})$$

Solving for \dot{m}_3 ,

$$100 \text{ kg/h}(2675.4 - 3278) \text{ kJ/kg} = \dot{m}_3(3074 \text{ kJ/kg}) - m_3(3278 \text{ kJ/kg})$$

Rearranging,

$$\frac{100 \times (2675.4 - 3278) \frac{\text{kJ}}{\text{h}}}{(3074 - 3278) \frac{\text{kJ}}{\text{kg}}} = \dot{m}_3$$

The rounded values of the mass flow rates of streams 3 and 2 are

$$\dot{m}_3 = 295 \text{ kg/h}$$
 and $\dot{m}_2 = 195 \text{ kg/h}$

9- Mechanical Energy Balance:

This balance is for isothermal flow (constant *T*) of an incompressible fluid (ρ is constant - for liquids) through a piping system, so there is one stream coming in and one stream going out ($m_{in} = m_{out} = m$). The mechanical energy balance is most useful for processes in which changes in the potential and kinetic energies are of primary interest, rather than changes in internal energy or heat associated with the process. Thus, the mechanical energy balance is mainly used for purely mechanical flow problems that is, problems in which heat transfer, chemical reactions, or phase changes are not present.

First, we assume the steady-state condition so that all terms on the left-hand side become zero. Second, we assume that the system has only a single inlet and a single outlet. Let us start with the general energy balance equation:

$$\dot{Q} - \dot{W}_{s} = \left(\dot{U}_{out} + K\dot{E}_{,out} + P\dot{E}_{,out} + P_{out}\dot{V}_{out}\right) - \left(\dot{U}_{in} + K\dot{E}_{,in} + P\dot{E}_{,in} + P_{in}\dot{V}_{in}\right)$$

Rearrange the earlier equation by taking the mass flow rate (m) as a common factor. In this case, the internal energy and volumetric flow rate will become specific internal energy and specific volumetric flow rate, respectively:

$$\dot{Q} - W_{\rm s} = \dot{m} \left(u_{\rm out} + \frac{v_{\rm out}^2}{2} + gz_{\rm out} + P_{\rm out}v_{\rm out} - u_{\rm in} - \frac{v_{\rm in}^2}{2} - gz_{\rm in} - P_{\rm in}v_{\rm in} \right)$$

In this equation, subscript "in" refers to the inlet section, and subscript "out" to the outlet port. Now, we divide the entire equation by (m^{\cdot}) , and express the specific volume (volume/mass) as $v = 1/\rho$, where ρ is the density (mass/volume) of the flowing material. Assuming incompressible flow rate, so that the density is constant, $v_{in} = v_{out} = 1/\rho$. Also, we define $\Delta u = u_{out} - u_{in}$ and $\Delta P = P_{out} - P_{in}$. With these changes, the general energy balance equation becomes

$$\frac{-W_{\rm s}}{\dot{m}} = \frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + \Delta u - \frac{Q}{\dot{m}}$$

The term $\Delta u - Q/m$ in the absence of chemical reactions, phase changes, or other sources of large amounts of heat transfer will generally represent heat generated due to the viscous friction in the fluid. In such situations, this term is called the friction loss and we will write it as *F*. With this last change, the general energy balance represents the usual form of the mechanical energy balance:

$$\frac{-\dot{W}_{\rm s}}{\dot{m}} = \frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + F$$

In many instances, the amount of energy lost to viscous dissipation in the fluid is small compared to magnitudes of the other terms in the general energy balance equation. In such a case, F = 0. Moreover, many common flows such as fluid flow through a pipe do not have any appreciable shaft work associated with them; accordingly, $\dot{W} = 0$. For such frictionless flows with no shaft work, the mechanical energy balance simplifies to **Bernoulli's equation**:

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z = 0 \qquad (1.13)$$

Or

$$\frac{P_2 - P_1}{\rho} + \frac{v_2^2 - v_1^2}{2} + g(z_2 - z_1) = 0 \qquad (1.14)$$

Bernoulli's equation has a wide range of application, despite its simplifying assumptions. Finally, it is often necessary to relate the volumetric flow rate V. or the massflowrate m. through a pipe or other conduit to the average fluid velocity u. The relations are:

$$\dot{V} = Au$$

 $\dot{m} = \dot{V} \rho = \rho A u$

Where (*A*) is the cross-sectional area of the flow.

Example 10: Mechanical Energy Balance Equation

A water supply tank is capable of delivering 0.3 m3/s of water for firefighting purposes in a chemical plant. The water supply is to come from a lake, the elevation of the surface of the lake is 800 m and the elevation of the factory is 852 m from sea level. The water discharge pipe is located at a depth of 100 m from the surface of the lake. The frictional losses in the water line to the plant are given by the relation (0.01 m/s²) *L*, where *L* is the length of the pipe line. The water line to the supply tank has an inner diameter of 0.15 m and a length of 8000 m. How much energy must a pump deliver to the water?

Solution

Known quantities: Discharge line volumetric flow rate, initial and final elevation, friction losses, length and diameter of the pipe. **Find :** Pump horsepower.

Assumption: Pressure drop is neglected because the pressure at both ends of line is atmospheric.

Analysis: Use the mechanical energy balance equation:

$$\frac{\Delta P}{\rho} + \frac{\Delta v^2}{2} + g\Delta z + F = \frac{-\dot{W_s}}{\dot{m}}$$

The pressure at both ends of the line is atmospheric, so $\Delta P = 0$. The velocity at the inlet of the lake is zero but the velocity out of the discharge end of the pipe is

$$v_2 = \dot{V} \times \frac{1}{\frac{\pi D^2}{4}} = \left(0.3 \frac{\text{m}^3}{\text{s}}\right) \times \frac{1}{\frac{\pi (0.15 \,\text{m})^2}{4}} = 17 \,\text{m/s}$$

The mass flow rate

$$\dot{m} = \dot{V} \times \rho = \frac{0.3 \text{ m}^3}{\text{s}} \times \frac{1000 \text{ kg}}{m^3} = 300 \text{ kg/s}$$

The elevation change is from 800 m (800–100 to the lake) to 852 to the factory, or the difference is equivalent to 152 m. So the mechanical energy balance becomes

$$\frac{0}{\rho} + \frac{\left(17\frac{m}{s}\right)^2 - 0}{2} + 9.81\frac{m}{s^2}(152\text{ m}) + 0.01\frac{m}{s^2}(8000\text{ m}) = \frac{-\dot{W}_s}{300\text{ kg/s}}$$

Solving for shaft work,

$$-\dot{W}_{\rm s} = 514,686 \text{ W} \times \frac{\text{hp}}{746} = 690 \text{ hp}$$

Homework Problems:

1- Suppose you are operating a steam turbine where the steam leaving the turbine is at 5 bar. This steam contains 95 wt% vapors. If the shaft work produced by the turbine is 1100 kJ/kg and the high pressure, high temperature steam enters the turbine at 100 bar (abs), what is the temperature of the steam entering the turbine? If water at 10°C is supplied to the steam boiler to generate steam, how much heat is required per kilogram of steam produced? You may assume that heat losses from the turbine are negligible. **Answer: (3700 kJ/kg)**

2- Steam at 60 bar and 500°C enters an adiabatic turbine at a steady flow rate of 1 kg/s; the turbine outlet stream is at 1 bar and 400°C. The inlet and exit streams of the turbine are at the same height and the pipes have the same diameter of 0.15 m. How much work can be obtained from an adiabatic, continuous-flow turbine? (-144 kJ/s)

3- A large tank that is filled with water is open to the atmosphere. Water is taken from the tank, passed through a pump, and then delivered to the hoses of a firefighting extinguisher in a chemical factory. It is desired to deliver 69.5 lbm of water per second at a pressure of 200 psi (gauge). If there is a negligible elevation change between the water level in the tank and the discharge of the pump, no changes in the diameter of the pipes and hoses, and if the pump has an efficiency of 65.0%,

how much work must be supplied to the pump in order to meet the pressure and discharge rate specifications? (89.7 hp)

4- A power plant (800 MW) burns natural gas to boil water producing saturated steam (100% quality) at 70 bar. This steam is expanded in a turbine to steam at 100°C and 1 bar. The steam enters the turbine at 10 m/s and exits 5 m below the entrance point level at 100 m/s. The turbine is connected to an electrical generator by a shaft. The efficiency of the turbine is 60%. What is the mass flow rate of steam to the turbine (kg/h)? (**5.05×10⁷ kg/h**)

5- Air at 100 kPa and 10°C enters a compressor and is brought to 1000 kPa and 50°C. The constant pressure heat capacity of air is 1.01 kJ/kg K. If 15 kg/min of air are to be compressed, determine the power requirement of the compressor. State your assumptions. (12.625 kW)

6- A volume of 734 cm³ of liquid acetone is contained in a closed (vertical) cylinder fitted with a movable frictionless piston at 10°C. The acetone is heated via heating coil inserted inside the cylinder to vapor at 500°C. The piston area is 50.0 cm², and the piston weighs 200 kg. The heat of vaporization of acetone at its normal boiling point (56.0°C) is 30.2 kJ/mol. Assume the cylinder is perfectly insulated and no heat is lost to the surroundings. If the heat is provided by superheated steam at 550°C and 1.0 bar, the final condition of the steam is saturated at 100°C. How much steam is needed? (**1.0 kg**)

7- Propane gas at 40°C and 250 kPa enters an adiabatic heat exchanger and exits the heat exchanger at 240°C. The flow rate of propane is 100 mol/min. The saturated steam with a flow rate of 6 kg/min at 5 bar (absolute) enters the heat exchanger. The discharge wet steam (contains vapor and liquid) is at 3 bar. Calculate the exit steam quality and temperature. (0.86, 133.5°C)

8- Wet steam at 20 bar with 97% quality is passed through a throttling valve and expands to 1 bar pressure. Calculate the temperature of the steam that departs from the adiabatic expansion valve. $(132.25^{\circ}C)$

9- Hundred kilograms per hour of wet steam at 20 bar with 97% quality is passed through a throttling valve and expands to 10 bar pressure. Calculate the temperature of the steam that departs from the adiabatic expansion valve and the quality of steam. (179.9°C, 0.982)

10-Water (100 kg/s) passes through the gate of a dam and falls on a turbine 10 m below, which turns a shaft connected to a generator. The fluid velocity on both sides of the dam is negligible, and the water undergoes insignificant pressure and temperature changes between the inlet and outlet. Calculate the work generated by the turbine. (9.81 kW)

Reference books:

1. Richard M. Felder and Ronald W. Rousseau, "Elementary Principles of Chemical Processes", Third Edition, (2006).

2. David M. Himmelblau and James B. Riggs, "Basic Principles and Calculations in Chemical Engineering", Seventh Edition, (2004).

Chapter Two

Energy Balances on Nonreactive Processes

1- Calculating Changes in Enthalpy and Internal Energy:

 H° and U° are state functions meaning that their values only depend on the state of the system, and not on the path taken to arrive at that state. To do energy balance you must be able to evaluate (H) for fluid between inlet and outlet conditions from tabulated data. We can also evaluate H from heat capacity data because we are inserted in the change in enthalpy between inlet and outlet. Specific (or molar) enthalpies and internal energies are examples of "state functions", meaning they depend only on the initial and final states (or states of the outlet and inlet streams) for a system and not on the actual "process path" independent of how the material in the system got from state 1 to state 2.

$$\Delta \hat{H} = \hat{H}_2 - \hat{H}_1$$

 $\Delta \boldsymbol{U}^{\boldsymbol{\wedge}} = \boldsymbol{U}_{\boldsymbol{2}}^{\boldsymbol{\wedge}} - \boldsymbol{U}_{\boldsymbol{1}}^{\boldsymbol{\wedge}}$

• *H* is a function of two independent variables for a pure fluid. We may therefore write H = H(T,P) which gives the total differential

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_P \,\mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \,\mathrm{d}F$$

Define

$$C_{p} = \left(\frac{\partial H}{\partial T}\right)_{p} \tag{2.1}$$

The **constant pressure heat capacity** C_p is a small quantity of heat added isobarically divided by the corresponding temperature rise. Note that if the pressure is constant, C_P can also be thought of as the change in enthalpy with respect to *T*.



We learn from chemical engineering thermodynamics that this value taken as 0 for gases and equal to V for solids and liquids. It is exactly zero for <u>ideal gases</u>, and approximately equal to V for solids and liquids.

Thus, we will use:

And $dH = \int_{T_1}^{T_2} C_P \, dT + \int_{P_1}^{P_2} V \, dP$ (For liquids and solids)(2.3)

(Used when the variables *T* and *P* are known for the process).

• Also U is a function of two variables: U = U(T, V). We may therefore write (by taking the total differential of U):

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V} dT + \left(\frac{\partial U}{\partial V}\right)_{T} dV$$

The first partial is defined as the constant volume heat capacity C_V

$$C_{\mathcal{V}} = \left(\frac{\partial U}{\partial T}\right)_{\mathcal{V}} \tag{2.4}$$

The constant volume heat capacity is a small quantity of heat added isochorically divided by the corresponding temperature rise. Note that if the volume is constant, no *PV* work is done and C_V is also the change in internal energy with respect to *T*.

$$\left(\frac{\partial U}{\partial V}\right)_{T} = ?$$

We learn from chemical engineering thermodynamics that this value taken as zero. It is in fact identically 0 for an *ideal gas* and close to zero for liquids and solids.

Thus, we will use:

 $dU = \int_{T1}^{T2} C_V \, dT$ (2.5)

And H = U + PV (Evaluation of U and H when T and V are known)

2-Hypothetical Process Paths:

To evaluate changes in enthalpy or internal energy, we can make up any process path we want to simplify the calculations. There are six types of paths for which we will learn to calculate enthalpy changes ΔH^{2} :

- 1. changes in P at constant T
- 2. changes in T at constant P
- 3. changes in T at constant V
- 4. changes in phase at constant T and P (e.g., heats of vaporization)
- 5. mixing at constant T and P (heats of mixing)
- 6. chemical reactions at constant T and P (heats of reaction)
 - Changes in P at Constant T (no phase change or reactions)

Ideal gases: $\Delta \hat{U} = \Delta \hat{H} = 0$

Real gases:

$$\Delta \hat{U} \neq 0, \quad \Delta \hat{H} \neq 0$$

Must evaluate from

- 1. enthalpy departure charts and equation of state
- 2. tabulated data

Liquids and solids: $\Delta \hat{U} \approx 0$, $\Delta \hat{H} \approx \hat{V} \Delta P$



Ideal gas: Isothermal expansion

Fig.1 Isothermal expansion



Fig.2 Expansion and compression of a gas is a type of this process.

• Changes in T and Constant P (no phase change or reactions):

Sensible heat: Sensible heat is heat added to a system that results in a change in temperature. The rate of change of specific enthalpy H° of a substance with T, while the pressure p on the substance is kept fixed, is called the heat capacity at constant pressure.

$$C_p(T) = \left(\frac{\partial \hat{H}}{\partial T}\right)_p$$

 C_p is in general a function of *T*. Given the function $C_p(T)$, the change in enthalpy of a substance as its temperature is raised from T_1 to T_2 at constant pressure is

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T) dT$$

Then

$$Q = \Delta H$$

Heat capacities for most substances vary with temperature where the values of C_P vary for the range of the change in temperature. Heat capacities are tabulated as polynomial functions of temperature such as

$$C_p = a + bT + cT^2 + dT^3$$
(2.6)

Where *a*, *b*, *c* and *d* are constants.

The units of heat capacity could be (J/ (kg °C), (J/ (mol °C), etc.)

For nitrogen at a constant pressure of 1 atm, the heat capacity C_p is

$$C_p(\text{kJ/(mol °C)}) = 0.02900 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3$$

A few sources exist for equations expressing Cp as a function of T, and charts exist on which C_p is plotted as a function of temperature. As shown in Fig.1.



Fig.3: Heat capacity curves for the combustion gases at 1 atm

 C_p values for mixtures. When dealing with heat capacities of mixtures, the most accurate method is to look up C_p values from tables or other experimental information, if available. Lacking such data, if one is willing to neglect corrections to C_p that derive from mixing of the different components of the mixture, the overall heat capacity of the mixture $C_{p,mix}$ can be approximated as the sum of heat capacity contributions from the separate components of the mixture,

$$C_{p,mix}(T) = \sum_{\substack{all \\ mixture \\ components}} x_i C_{p,i}(T)$$

Where $C_{P,mix}$ is heat capacity of the mixture, x_i is the mass or mole fraction of ith species, C_{Pi} is heat capacity of ith species and n is number of species This mole-fraction average relation is exact for ideal gas mixtures, and approximately correct for many liquid solutions.





Fig.4: Heating and cooling process at constant pressure.

• changes in T at constant V

Here, we use the heat capacity at constant volume, defined by:

$$C_V(T) = \left(\frac{\partial \hat{U}}{\partial T}\right)_{V}$$

The change in specific internal energy as the system temperature is raised from T_1 to T_2 at constant volume is

$$\Delta \hat{U} = \int_{T_1}^{T_2} C_V(T) dT$$

Using the general energy balance for a closed system, no change in kinetic and potential energies as the system is a rigid vessel:

 $Q - W = \Delta U$

W = 0 (rigid vessel; no moving part), the change in internal energy is

$$Q = \Delta U$$

Example 1: Chlorinated diphenyl is heated from 303 K to 503 K in an indirectly fired heater at a rate of 3500 kg/h. Calculate the heat to be supplied to the fluid in the heater. The heat capacity of the fluid in this temperature range is given by the equation

$$C_{P} = 0.751 + 1.465 \times 10^{-3}T, \text{ kJ/kg} \rightarrow \text{K}$$

$$Q = m \left(\int_{T_{1}}^{T_{2}} C_{P} dT \right)$$

$$= \left[\int_{T_{1}}^{T_{2}} (0.751 + 1.465 \times 10^{-3}T) dT \right]$$

$$= m \left[0.751T + \frac{1.465 \times 10^{-3} \times T^{2}}{2} \right]_{T_{1}}^{T_{2}}$$

$$= m \left[0.751(T_{2} - T_{1}) + \frac{1.465 \times 10^{-3}}{2} \times (T_{2}^{2} - T_{1}^{2}) \right]$$

$$= 3500 \left[0.751(503 - 303) + \frac{1.465 \times 10^{-3}}{2} \times (503^{2} - 303^{2}) \right]$$

$$= 3500 \left[0.751 \times 200 + \frac{1.465 \times 10^{-3}}{2} \times 161200 \right]$$

$$= 938976.5 \text{ kJ/h}$$

= 260.82 kW

Example 2: Flue gases leaving the stack of a boiler at 520 K have the following molar composition.

 $CO_2 = 11.4\%$: $H_2O = 13.0\%$: $O_2 = 2.3\%$: and $N_2 = 73.3\%$.

Calculate the heat lost in 1 kmol of gas mixture above 298 K.

Data:

Component	Cp (kJ/kmol . K)		
CO_2	41.62		
H ₂ O	34.33		
O_2	30.14		
N_2	29.31		

Solution: Basis: 1 kmol of gas mixture.

$$C_{Pm(\text{mix})}^{\circ} = \sum x_i \cdot C_{Pm_i}^{\circ}$$

= 0.114 × 41.62 + 0.130 × 34.33 + 0.023 × 30.14 + 0.733 × 29.31
= 4.745 + 4.463 + 0.693 + 21.484
= 31.385 kJ/kgmol – K

$$Q = m - C_{Pm(\text{mix})}^{\circ} (T - T_0)$$

where

Q = Amount of heat lost (kJ) m = 1 kgmol $C_{Pm(mix)}^{\circ}$ = Mean molal heat capacity (kJ/kgmol \rightarrow K) T = 520 K $T_0 = 298$ K Therefore, $Q = 1 \times 31.385 \times (520 - 298) = 6967.47$ kJ. **Example 3:** A stream flowing at a rate of 30 kmol/h containing 30% (mole) N_2 and 70% (mole) H_2 . This is to be heated from 300 K to 470 K. Calculate the amount of heat transferred using the data given below.

$$C_{PN_2}^{\circ} = 29.57 - 5.43 \times 10^{-3}T + 13.17 \times 10^{-6}T^2$$
, kJ/kgmol \rightarrow K
 $C_{PH_2}^{\circ} = 28.65 + 1.02 \times 10^{-3}T - 0.15 \times 10^{-6}T^2$, kJ/kgmol \rightarrow K

Solution: Basis: 30 kmol/h of N₂ and H₂ gas mixture.

$$\begin{split} x_{N2} &= 0.30 \\ x_{H2} &= 0.70 \\ C_{P \text{mix}}^{\circ} &= \sum C_{Pi}^{\circ} \cdot x_{i} \\ &= x_{N_{2}} \cdot C_{PN_{2}}^{\circ} + x_{H_{2}} \cdot C_{PH_{2}}^{\circ} \\ &= 0.30 \times (29.57 - 5.43 \times 10^{-3}T + 13.17 \times 10^{-6}T^{2}) + 0.70 \times (28.63 + 1.02 \times 10^{-3}T - 0.15 \times 10^{-6}T^{2}) \\ &= (8.87 - 1.63 \times 10^{-3}T + 3.95 \times 10^{-6}T^{2}) + (20.04 + 0.71 \times 10^{-3}T - 0.11 \times 10^{-6}T^{2}) \\ &= 28.91 - 0.92 \times 10^{-3}T + 3.84 \times 10^{-6}T^{2} \end{split}$$

$$Q = m \int_{T_1}^{T_2} C_{P \min}^{\circ} dT$$

= $m \left[\int_{T_1}^{T_2} (28.91 - 0.92 \times 10^{-3}T + 3.84 \times 10^{-6}T^2) dT \right]$
= $m \left[28.91T - \frac{0.92 \times 10^{-3}}{2}T^2 + \frac{3.84 \times 10^{-6}}{3}T^3 \right]_{T_1}^{T_2}$
= $30 \left[28.91(470 - 300) - \frac{0.92 \times 10^{-3}}{2}(470^2 - 300^2) + \frac{3.84 \times 10^{-6}}{3}(470^3 - 300^3) \right]$
= $30[4914.70 - 60.21 + 98.33]$
= 30×4952.82
= 148584.6 kJ/h
= 41.27 kW.

• changes in phase at constant T and P (Processes Involving Phase Changes)

Latent heat: Latent heat is the enthalpy change that accompanies a change in phase of a substance at a constant *T* and *p*. *Latent heat of vaporization* $\Delta H^{\gamma}vap$ (which is the negative of the *latent heat of condensation*) refers to the enthalpy change per unit amount of liquid when that liquid is vaporized (units: energy/amount, where amount could be given in a mass or a molar basis). Similarly, *latent heat of melting* ΔH^{γ}_m (equivalently, *heat of fusion*, which is also the negative of the *heat of solidification*) refers to the amount of heat (change in enthalpy) that must be added to a unit amount of material to cause it to melt. Contributions to latent heats include changes in molecular level interactions as well as changes in specific volume that accompany the phase change.

Latent heats are, in general, functions of P and T. However, they depend much more strongly on T than on P. Therefore, when calculating heat associated with a change of phase, it is important to ensure that the latent heat value used for the calculation is that for the actual T at which the phase transformation occurs.

Latent heats are often available from a table (e.g. Table B.1 and the steam tables). However, they can also be estimated or calculated in various ways. There are some estimation methods:

1. Trouton's Rule:

For a very rough approximation of $\Delta H^{\uparrow}_{vap}$ at the boiling point of a liquid at 1 atm (i.e. at the normal boiling point),

$\Delta \hat{H}_{v}$ (kJ/mol) $\approx 0.088 T_{b}$ (K)	(nonpolar liquids)
$\Delta \hat{H}_{v}$ (kJ/mol) $\approx 0.109 T_{b}$ (K)	(water, low molar weight alcohols)

2- Watson Correlation:

Watson's correlation can be used to estimate $\Delta H^{\uparrow} vap$ at one temperature from its known value at another temperature,

$$\Delta \hat{H}_{\nu}(T_2) = \Delta \hat{H}_{\nu}(T_1) \left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38}$$

2. Clapeyron Equation:

If $\Delta H^{\uparrow} vap$ does not vary appreciably with *T* and the gas behaves ideally, then one can use the Clausius-Clapeyron equation for this purpose. When $\Delta H^{\uparrow} vap$ depends on *T* (the usual case), the Clapeyron equation needs to be used instead. If ideal gas behavior applies, the Clapeyron equation can be expressed as

$$\frac{d\ln p}{d(1/T)} = -\frac{\Delta \hat{H}_{v}}{R}$$

Where P^* the vapor pressure and R is is the gas constant.

Phase transitions occur from the solid to the liquid phase and from the liquid to the gas phase, and vice versa. During these transitions very large changes in the value of the enthalpy (and internal energy) of a substance occur, changes called latent heat changes, **because they occur without any noticeable change in temperature**. For a single phase, the enthalpy varies as a function of the temperature, as illustrated in Fig.2. The enthalpy changes that take place within a single phase are usually called sensible heat changes.



Fig.5: the overall enthalpy change includes the sensible heats (the enthalpy changes within a phase) plus the latent heats (the enthalpy changes of the phase transitions).





Fig.6: the overall enthalpy change includes the sensible heats (the enthalpy changes within a phase) plus the latent heats (the enthalpy changes of the phase transitions).



Fig.7: P-T diagram including phase changes.

Example 4(8.1-1): Energy Balance on a Condenser



STEP 1: Perform required material balance calculations. -None are required in this example because there is no material balance involved in this process.

STEP 2: Write and simplify the energy balance. For open steady-state system:

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

• Delete any of the terms that are either zero or negligible in process system.

-No moving parts and no energy is transferred in the system: $\dot{W}_{2} = 0$

-No significant vertical distance separates the inlet and outlet ports:

$\Delta \dot{E}_k \approx 0$ $\Delta \dot{E}_p \approx 0$

-Phase changes and nonnegligible temperature changes occur: So, the energy balance become:

$$\dot{Q} = \Delta \dot{H} = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$$

STEP 3: Choose reference states for acetone and nitrogen.

The reference states may be chosen for computational convenience, since the choice has no effect on the calculated value of $\Delta \dot{H}$. We will arbitrarily choose the inlet stream condition for nitrogen (65°C, 1 atm) as the reference state for this species and one of the two outlet stream conditions for acetone (1, 20°C, 5 atm) as the reference state for acetone, which will enable us to set the corresponding values for $\Delta \dot{H}$ in the enthalpy table equal to zero instead of having to calculate them.

N₂ (g, 25°C, 1 atm): convenient (Table B.8)

Ac (l, 20°C, 5 atm): choose from one of the process stream.

STEP 4: Construct an inlet-outlet enthalpy table.

References: Ac (l, 20°C, 5atm); N₂ (g, 25°C, 1atm)

	In	let	Outlet		
Substance	\dot{n}_{in}	\hat{H}_{in}	n _{out}	\hat{H}_{out}	
Ac (v)	66.9	\hat{H}_1	3.35	\hat{H}_2	
Ac (l)	-	-	63.55	0	
N ₂	33.1	\hat{H}_3	33.1	$\hat{H}_{_{4}}$	

STEP 5: Calculate all unknown specific enthalpies. In this step we need to find

H_1, H_2, H_3 and H_4

• For changes in pressure (ΔP) at constant T

$$\Delta \hat{H} = \hat{V} \Delta P$$

• For changes in temperature (ΔT) at constant P

$$\Delta \widehat{H} = \int_{T_1}^{T_2} C_p (T) dT$$

Ac(1): $C_n\left(\frac{kJ}{k}\right) = 0.123 + 18.6 \times 10^{-5}T$ ŀ

Ac(v):
$$C_p\left(\frac{kJ}{\text{mol}\cdot^{\circ}C}\right) = 0.123 + 18.0 \times 10^{-17} T$$

Ac(v): $C_p\left(\frac{kJ}{\text{mol}\cdot^{\circ}C}\right) = 0.07196 + 20.10 \times 10^{-5} T - 12.78 \times 10^{-8} T^2 + 34.76 \times 10^{-12} T^3$

where T is in $^{\circ}C$.

- For changes in phases at constant P and T, Use heat of vaporization or heat of melting at normal boiling point and normal melting point, respectively. (can be obtained from Table B.1
- The process path involved for determination of H1

Ac(l, 20°C, 5 atm)
$$\xrightarrow{\Delta \hat{H}_{1g}}$$
 Ac(l, 20°C, 1 atm) $\xrightarrow{\Delta \hat{H}_{1b}}$ Ac(l, 56°C, 1 atm)
 $\xrightarrow{\Delta \hat{H}_{1c}}$ Ac(v, 56°C, 1 atm) $\xrightarrow{\Delta \hat{H}_{1d}}$ Ac(v, 65°C, 1 atm)
 $\downarrow \downarrow$
 $\hat{H}_1 = \Delta \hat{H}_{path}$
 $= \Delta \hat{H}_{1a} + \Delta \hat{H}_{1b} + \Delta \hat{H}_{1c} + \Delta \hat{H}_{1d}$
 $= \hat{V}_{Ac(l)}(1 \text{ atm} - 5 \text{ atm}) + \int_{20^{\circ}C}^{56^{\circ}C} (C_p)_{Ac(l)} dT + (\Delta \hat{H}_v)_{Ac} + \int_{56^{\circ}C}^{65^{\circ}C} (C_p)_{Ac(v)} dT$
 $= (0.0297 + 4.68 + 30.2 + 0.753) \text{ kJ/mol}$
 $= 35.7 \text{ kJ/mol}$

*Use the same manner to obtain the values for \ddot{H}_2 , \ddot{H}_3 and \ddot{H}_4

• insert all specific enthalpies into inlet-outlet enthalpy table

References: Ac(1, 20°	'C, 5 atm)	$N_2(g, 2)$	25°C, 1 at	m)
-----------------------	------------	-------------	------------	----

Substance	$\dot{n}_{ m in}$ (mol/s)	$\hat{H}_{ m in}$ (kJ/mol)	n _{out} (mol/s)	$\hat{H}_{ m out}$ (kJ/mol)
Ac(v)	66.9	35.7	3.35	32.0
Ac(l)			63.55	0
N_2	33.1	1.16	33.1	-0.10

STEP 6: Calculate $\Delta \dot{H}$

$$\Delta \dot{H} = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$$

= (3.35 mol/s)(32.0 kJ/mol) + [(63.55)(0) + (33.1)(-0.10) - (66.9)(35.7) - (33.1)(1.16)] kJ/s= -2320 kJ/s

EXAMPLE 8.3-5: Energy Balance on a Gas Preheater

EXAMPLE 8.3-6: Energy Balance on a Waste-Heat Boiler

EXAMPLE 8.4-4: Partial Vaporization of a Mixture

• Mixing at Constant T and P (Heats of Mixing):

When two liquids are mixed, the final enthalpy is not necessarily the sum of the pure component enthalpies. This is because the unlike interactions between molecules is most likely different than the like interactions. Thus, if the A-B interactions are stronger than the A-A and B-B interactions, then the mixing process will be exothermic (heat will be released because the more tightly bound A-B interactions are at a lower energy). Again, what we want is the *change* in enthalpy that occurs when the mixing occurs.

Let us examine the situation of the change in enthalpy upon mixing two liquid streams **isothermally** as shown in the diagram at the right. n_1 moles of liquid 1 are mixed with n_2 , and the product liquid mixture leaves the mixer at the same temperature as the two inlet streams. We will have to supply or remove a certain amount of heat, Q, in order to maintain the isothermal process.



The energy balance for this process can be written as

 $Q = \Delta H$ $Q = (n_1 + n_2) h_m - n_1 h_1 - n_2 h_2$

Where $h_1 = \text{enthalpy of stream 1}$ $h_2 = \text{enthalpy of stream 2}$ $h_m = \text{enthalpy of mixture and sometimes called } h_3$

If we write this in terms of the heat absorbed or released per mole of product solution, we obtain

 $Q/m = h_{\rm m} - x_1 h_1 - x_2 h_2 = \Delta h_{\rm mix}$

This heat release or gain per mole of product solution for isothermal mixing is called the *Heat of Mixing*, Δh_{mix} . It may be either negative (exothermic - heat given off or positive (endothermic - heat absorbed because the mixture has a higher enthalpy than the pure components).

The enthalpy of the mixture is the sum of the pure component enthalpies (weighted by their mole fractions) plus the heat of mixing:

• Ideal Mixtures:

An ideal mixture is one in which the interactions in the mixture are the same as for the two pure components. Thus, for an ideal mixture,

$h_m = x_1h_1 + x_2h_2$ (ideal mixture) $\Delta h_{mix} = 0$ (ideal mixture)

There are many mixtures that mix ideally or nearly ideally. All gases mix virtually ideally, because the interactions are small between gas molecules. Even in liquids, the interactions may be very similar between the components such that the heat of mixing is small. For example, the heat of mixing of hexane and heptane would be nearly zero. When ideal mixing can be assumed, one simply adds the contributions from the pure components to obtain the enthalpy of the mixture.

• Nonideal mixtures:

Liquids that can associate, form hydrogen bonds, or even break bonds as solvation occurs will often have fairly large heats of mixing. For example, the mixing of H_2SO_4 and H_2O produces so much heat that you must be careful to add the acid to the water very slowly so that it doesn't get hot enough to vaporize some of the water.

 h_1 , h_2 , and h_m are determined for different mole ratio(r) by using Table B.11 on page 653 of your text lists heats of mixing for HCl, NaOH, and H_2SO_4 with water. That same table is also reproduced and available through the course tool links.

HCl(g)	NaOH(s)	H ₂ SO ₄
kJ/mol	kJ/mol	kJ/mol
HCl	NaOH	H_2SO_4
		-15.73
-26.22		-28.07
		-36.90
-48.82		-41.92
-56.85	-28.87	-48.99
-61.20	-34.43	-54.06
-64.05	-37.74	-58.03
-69.49	-42.51	-67.03
-71.78	-42.84	
		-72.30
-72.59	-42.72	
-73.00	-42.59	
-73.26	-42.51	-73.34
-73.85	-42.34	-73.97
-74.20	-42.26	
	HC1(g) kJ/mol HC1 -26.22 -48.82 -56.85 -61.20 -64.05 -69.49 -71.78 -72.59 -73.00 -73.26 -73.85 -74.20	HCl(g) kJ/mol HClNaOH(s) kJ/mol NaOH26.2226.2248.8248.8256.85-28.87-61.20-34.43-64.05-37.74-69.49-42.51-71.78-42.8472.59-42.72-73.00-42.59-73.26-42.51-73.85-42.34-74.20-42.26

Integral Heats of Mixing at 25°C

Example 5:

What is the heat duty for a mixer that mixes 9.2 moles of H_2O with 1 mole of 0.2 mole fraction H_2SO_4 if the inlet and outlet streams are all to be at 25°C?



The energy balance for this system is $Q = \Delta H = n_3 h_3 - n_1 h_1 - n_2 h_2$

We need to find the enthalpy of each stream <u>relative to a reference enthalpy</u>. We can do this because we are always interested in a difference in enthalpies and so the reference will always cancel out. But, we must be sure that we choose the same reference for each stream so that the cancellation really does occur. In this case, we choose the pure components at 25° C as the reference enthalpy relative to which we will find the values of all the streams.

Stream 1:

Stream 1 is a mixture of sulfuric acid and water at 25°C. It's enthalpy relative to the pure references is simply the heat of mixing for this mixture since the pure enthalpies are identically zero by definition of the reference:

Therefore, we find r for this mixture in the following way, where A represents acid and W water:

 $x_{\rm A} = n_{\rm A}/(n_{\rm W} + n_{\rm A}) = 0.2 = n_{\rm A}/1 \text{ mol} ====> n_{\rm A} = 0.2 \text{ mol and } n_{\rm W} = 0.8 \text{ mol}$ so $r = n_{\rm W}/n_{\rm A} = (0.8 \text{ mol})/(0.2 \text{ mol}) = 4.0$

From Table B.11, we therefore obtain $h_1 = -54.06 \text{ kJ/mol A}$

Stream 2:

This stream is pure water which is the reference state. Therefore, relative to the reference state,

 $h_2 = 0$

Stream 3:

We now do a mass balance to find *r* for the outlet stream. The acid balance tells us that 0.2 moles of A end up in the mixture and the water balance says that 9.2 + 0.8, or 10 mol of water ends up in the final mixture. Thus, $r = n_W/n_A = (10 \text{ mol})/(0.2 \text{ mol}) = 50$ From Table B.11, we obtain $h_3 = -73.34$ kJ/mol A

Now we complete the energy balance to obtain: Q = (0.2 mol A)(-73.34 kJ/mol A - (-54.06 kJ/mol A) = -3.9 kJ

On the previous problem we limited the mixing process to the case where the **temperature was the same for the inlet and outlet streams.** We can now relax that restriction and allow the temperature to be different in each of the streams. We will still use the heat of mixing, which is still defined as the change in enthalpy for the isothermal mixing process, but we can add to this the sensible heat changes associated with the change in temperature of each stream.

Example 6: Components A and B that are continuously fed to a mixer. The inlet temperatures of A and B are respectively T_1 and T_2 . Set up equations that would allow

you to calculate the outlet temperature of the mixture, T, for a specified heat gain/loss, Q. In so doing, assume the heat of mixing is only known at 25°C.



Solution:

First, we choose a reference state for each component. Let's choose the reference state to be the following:

References: pure A at T1 and pure B at T2

The energy balance then becomes:

 $Q = (n_A + n_B)h_{mix}(T) - n_A h_A(T1) - n_B h_B(T2) = (n_A + n_B)h_{mix}(T) - 0 - 0$

Note that the two pure component streams are identically zero because they are in the reference state. Now we must calculate h_{mix} at *T*, the outlet temperature of the mixer, relative to the <u>same reference</u> defined above.

To do this, we think of the most convenient path to get from the reference state to the final state and evaluate the corresponding change in enthalpy for that path. In this case, because we only know the heat of mixing at 25°C, the best path is the one that involves mixing at 25°C. Thus, we can change the temperature of A from T₁ (its reference T) to 25°C and change the temperature of B from T₂ (its reference T) to 25°C, and then do the mixing isothermally at 25°C, followed by a change in the mixture temperature from 25°C to the outlet temperature, *T*. We may diagram this process of going from A and B to the mixture as:



Thus, we would find $h_{mix}(T)$ relative to the references as

$$h_{\text{mix}}(T) = x_{\text{A}}[h_{\text{A}}(25) - h_{\text{A}}(T_{1})] + x_{\text{B}}[h_{\text{B}}(25) - h_{\text{B}}(T_{2})] + [h_{\text{m}}(25) - x_{\text{A}}h_{\text{m}}(25) - x_{\text{B}}h_{\text{m}}(25)] + [h_{\text{m}}(T_{3}) - h_{\text{m}}(25)]$$

$$= x_{A} \int_{T_{1}}^{25} Cp_{A}dT + x_{B} \int_{T_{2}}^{25} Cp_{B}dT + \Delta h_{\text{mix}}(25) + \int_{T_{2}}^{T} Cp_{m}dT$$

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This equation can now be put into the energy balance above to give the heat.

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, the **Heat of Solution**.

Table B.11 in the Appendix of the text book provides heats of solution when HCl(g), $H_2SO_4(l)$ and NaOH(s) are dissolved in water as a function of r at 25°C.

Example 7: Application of Heat of Solution Data

Hydrochloric acid is an important industrial chemical. To make aqueous solutions of it in a commercial grade (known as *muriatic acid*), purified HCl(g) is absorbed in water in a tantalum absorber in a steady-state continuous process. How much heat must be removed from the absorber by the cooling water per 100 kg of product if hot HCl(g) at 120° C is fed into water in the absorber? The feed water can be assumed to be at 25° C, and the exit product HCl(aq) is 25% HCl (by weight) at 35° C. The cooling water does not mix with the HCl solution.



The system will be the HCl and water (not including the cooling water).

Basis: 100 kg of product : Ref. temperature: 25° C

From simple material balances the kilograms and moles of HCl in and out, and the
water in and out, are as listed below

Component	kg	Mol. wt.	kg mol	Mole Fraction
HCl	25	36.37	0.685	0.141
H ₂ O	75	18.02	4.163	0.859
Total	100		4.848	1.000

Cp for the product is approximately 2.7 J/(g)($^{\circ}$ C)

The heat of solution is -65,442 J/mol HCl for the ratio of HCl/H2O = 6.077.

 $Q = \Delta H$ $Q = H_{out} - H_{in} + \Delta H_{solution}$ $Q = m_{product} \int_{25}^{35} Cp_{product} dT - m_{HCL} \int_{25}^{120} Cp_{HCL gas} dT + \Delta H_{solution}$ $Q = -46.586 \ kJ$

3- The Humidity (Psychrometric) Chart:

The air-water system is so important in industry (for humidification. air conditioning, and drying process) that special charts, called psychrometric or humidity chart has been developed to provide enthalpies of air –water mixture for use in energy balance. The following terms used in psychrometric chart (Fig.3):

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

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.

Dew point temperature: 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

Absolute humidity: This is the y-axis of the chart in the units of kg H_2O/kg dry air.

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

Humid volume: This is reported in the chart in the units of m^3/kg dry air. Lines of constant humid volume (0.9, 0.85, 0.80 etc) are shown on 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 vapor it contains at saturation.

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 drybulb 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.

The enthalpy H^{\uparrow} of air that is not saturated with water vapor is obtained by summing the saturation enthalpy and the enthalpy deviation,

$$\hat{H} = \hat{H}_{sat} + \hat{H}_{dev}.$$

The specific enthalpy per mass of dry air (not air plus water vapor) for a saturated air-water vapor mixture:



Fig .8: The Humidity (Psychrometric) Chart.



Fig.9. Representation of the wet-bulb process on H-T chart



Fig.10. A skeleton humidity (psychrometric) chart showing typical relationships of the temperatures, dew point, wet- and dry-bulb temperatures, relative humidity, specific humid volume, humidity enthalpy, and adiabatic cooling/wet-bulb line

Example 8:

A solution of sugar in water is concentrated from 5% sugar to 20% sugar by weight using an **<u>adiabatic</u>** humidification process. The sugar stream leaving the humidifier is at the same temperature as the sugar stream entering. Moist air with a dry bulb temperature of 45°C and a dew point of 4°C is fed to the humidifier. The air leaving the humidifier is saturated. Using the psychrometric chart, find:

(a) h_a for the inlet air stream, (b) kg of dry air/kg sugar solution, (c) volume of wet air fed to humidifier per kg of sugar solution.

Solution:

The labeled flow diagram for this process is shown below. Note that some of the water evaporates from the sugar-water stream. Where does the heat of vaporization for this water come from? It comes from the sensible heat of cooling the air, so the air is expected to leave at a colder temperature.



a) The dew point of the air coming in is $T_{dp} = 4^{\circ}C$ so that means the absolute humidity of the air is $h_a = 0.005$ kg H₂O/kg BDA. (This is found by moving horizontally over from $T_{dp} = 4^{\circ}C$ clear over to the axis on the right hand side and reading off h_a . Since the process takes place adiabatically, it must satisfy the energy balance expression. These adiabatic lines have been plotted on the psychrometric charts for you. For H₂O, the adiabatic saturation curve through a given state corresponds with constant wet bulb lines. This is a coincidence only for the H₂O + air system.

To find the outlet air humidity, first find the inlet air point as the intersection of T_{db} = 4°C and T_{dp} = 45°C. Then follow the adiabatic line (which is the same as the T_{wb} = 20.5°C line) all the way back to saturation. Then find the absolute humidity of this point by moving horizontally over to the right again. This gives

$h_a = 0.0154 \text{ kg H}_2 \text{O/kg BDA}$

b) Now we do some material balances:

Sugar balance: (Basis: 1 kg sugar soln.)

0.05 kg = 0.2P P = 0.25 kg

Water balance:

0.95 kg + $m_{BDA}h_{a,in}$ = (0.8)(0.25 kg) + $m_{BDA}h_{a,out}$

or 0.75 kg = $m_{\text{BDA}}(h_{a,2} - h_{a,1})$

Thus,

$\underline{m}_{BDA} = 72.1 \text{ kg BDA/kg soln.}$

(c) Reading directly from the chart we obtain:

 $V = 0.91 \text{ m}^{3}/\text{kg BDA}$ or

 $V = (0.91 \text{ m}^3)(72.1) = 65.6 \text{ m}^3 \text{ air/kg soln.}$

Example 9: Psychrometric Chart

Humid air at 28°C has a dew point of 8°C. Using the psychrometric chart provided, determine the following: relative humidity, absolute humidity, wet-bulb temperature, dry-bulb temperature, humid volume, specific enthalpy, and mass of air that contains 2 kg of water, and volume occupied by air that contains 2 kg of water.

Solution

Known quantities: Humid air at 28°C has a dew point of 8°C. Air contains 2 kg of water, and volume occupied by air that contains 2 kg of water.

Find: Relative humidity, absolute humidity, wet-bulb temperature, dry-bulb temperature, humid volume, specific enthalpy.

Analysis: Use psychrometric chart. Humid air at 28°C has a dew point of 8°C. Using the psychrometric chart provided, determine the following:

1. Relative humidity = 30%.

2. Absolute humidity = 0.007 kg water/kg dry air.

3. Wet-bulb temperature = 16.5° C. Follow the constant enthalpy line from the intersection of the dry-bulb and dew point temperatures.

- 4. Dry-bulb temperature = 28° C.
- 5. Humid volume = 0.86 m3/kg.
- 6. Specific enthalpy = 46 kJ/kg 0.3 kJ/kg = 45.7 kJ/kg.
- 7. Mass of air that contains 2 kg of water:

$$2 \text{ kg H}_2\text{O} \frac{\text{kg dry air}}{0.007 \text{ kg H}_2\text{O}} = 285.7 \text{ kg dry air}$$

8. Volume occupied by air that contains 2 kg of water:

 $\frac{0.86 \text{ m}^3}{\text{kg dry air}} \frac{\text{kg dry air}}{0.007 \text{ kg H}_2\text{O}} 2 \text{ kg H}_2\text{O} = 245.7 \text{ m}^3$

Homework Problems:

1- Liquid methanol at 25°C is heated and vaporized for use in a chemical reaction. How much heat is required to heat and vaporize 10 mol/s of methanol to 600°C.

Answer: (744 kJ/s)

2- Methanol is heated by condensing steam in a concentric double pipe heat exchanger as depicted in Problem Figure 8.5.1. Methanol flowing through the inner pipe at 64.0 kg/s enters at 20°C and exits at 60°C. Steam enters the outer pipe at 350°C and 80 bar (absolute) and leaves the heat exchanger as saturated water at 1.0 bar. Assume that the outer pipe is well insulated and no heat is lost to the surroundings. Determine the mass flow rate of the steam. Answer :(2.57 kg/s).



3- Calculate the heat rate required to heat 32.04 kg/s of liquid methyl alcohol (CH₃OH) at 5°C and 1 atm to vapor at 500°C and 1 atm. The heat of vaporization of methanol at 64.7°C and 1 atm is 35.27 kJ/mol. **Answer: (69.0 MW)**.

4- A liquid stream (10 kg/min) flows through a heat exchanger in which it is heated from 25° C to 80° C. The liquid specific heat is 4.18 kJ/kg K. The inlet and outlet pipes have the same diameter, and there is no change in elevation between these points. Calculate the heat required. (**38.3 kW**)

5-Saturated steam at 300°C is used to heat a counter currently flowing stream of methanol vapor from 65°C to 260°C in an adiabatic heat exchanger. The flow rate of

the methanol is 6500 standard liters per minute, and the steam condenses and leaves the heat exchanger as liquid water at 90°C.

(a) Calculate the required flow rate of the entering steam in m3/min.

(b) Calculate the rate of heat transfer from the water to the methanol (kW).

(c) Suppose the outlet temperature of the methanol is measured and found to be 240° C instead of the specified value of 260° C. List five possible realistic explanations for the 20° C difference.

6-Benzene vapor at 480°C is cooled and converted to a liquid at 25°C in a continuous condenser. The condensate is drained into 1.75-m3 drums, each of which takes 2.0 minutes to fill. Calculate the rate (kW) at which heat is transferred from the benzene in the condenser.

7- A gas stream containing 8.0 mole % CO and 92.0 mole% CO₂ at 500 $_{\circ}$ C is fed to a waste heat boiler. In the boiler, heat is transferred from this gas stream to a water stream, which is fed to the boiler at 25 $_{\circ}$ C in a ratio of 0.200 mole feed water per mole of hot gas. The water is heated by the gas so that it forms saturated steam at 5.0 bar. The boiler operates adiabatically, with all heat lost by the gas stream going to heat the water stream. What is the temperature of the exiting gas?

The heat capacities for CO and CO₂ are:

 $C_{p,CO} = 0.02895 + 0.4110 \times 10^{-5}T + 0.3548 \times 10^{-8}T^2 - 2.220 \times 10^{-12}T^3$ $C_{p,CO2} = 0.03611 + 4.223 \times 10^{-5}T - 2.887 \times 10^{-8}T^2 + 7.464 \times 10^{-12}T^3$

8- Saturated steam at a gauge pressure of 2.0 bar is to be used to heat a stream of ethane. The ethane enters a heat exchanger at 16° C and 1.5 bar gauge at a rate of $795m^{3}$ /min and is heated at constant pressure to 93° C. The steam condenses and leaves the exchanger as a liquid at 27° C. The specific enthalpy of ethane at the given pressure is 941 kJ/kg at 16° C and 1073 kJ/kg at 93° C.

(a) How much energy (kW) must be transferred to the ethane to heat it from 16° C to 93° C?

(b) Assuming that all the energy transferred from the steam goes to heat the ethane, at what rate in m^{3}/s must steam be supplied to the exchanger? If the assumption is incorrect, would the calculated value be too high or too low?