Chapter 5 Energy Balances

(Refs: Geankoplis sect 1.6; Felder, Chts 7-9; Himmelblau, Cht 4, 5th ed)

1. Introduction

Our world in the 21st century is experiencing a rapid increase in energy consumption and decrease in natural fuel resources. This situation is a threat to sustainable growth of the world economy and also to the natural environment (since fossil fuel consumption is a major source of CO2 generation and cause of global warming). The skyrocketing fuel price and high energy cost impose a severe constraint on the profitability of industrial processes. Saving and efficient use of energy is becoming more and more important.

Since energy consumption is a major portion of the total expenses in most process plants, efficient energy utilisation is crucial for the profitability of process plants. In the design, selection and operation of a process, you often need to estimate the amounts of energy required and/or generated in the process by computing **energy balances** on the whole process as well as each individual process included. Following are a few examples of the common problems involving energy balances:

- A highly exothermic chemical reaction A→ B takes place in a reactor. If a 75% conversion of A is to be achieved, and at what rate must heat be removed from the reactor to maintain a constant temperature?
- 2) To heat up certain amount of water to a desired temperature with a burner, how much fuel do you need, given the composition of the fuel?
- 3) To concentrate a solution by evaporation, calculate the amount of steam (1.72 bar saturated) required?
- 4) Heat is generated in a fermenter from microbial metabolism and mechanical agitation (friction). Estimate the cooling requirement for the fermenter, the flow rate and outlet temperature of cooling water.

This part covers the basic concepts of energy balances for chemical, biochemical and separation processes. In energy balance calculations, you often need to use the *thermodynamic* properties of materials, including *heat capacity, enthalpy, heat of reaction* and *heat of formation*, especially the properties of water and steam, fuels and combustion gases. **These properties can usually be found out from the Appendices of the textbooks and references for this subject**. Although the broad topic of energy balances covers all kinds of energy, such as kinetic, potential and internal energies of material, work and heat, this chapter will focus on the balance of **heat energy**.

2. Basic Concepts

2.1. System and surroundings

As defined in the part of material balances, a **system** is an *arbitrary* portion or the whole of a process, around which we set up a **boundary** for the balance calculations. The materials and processes outside the system boundary are called the **surroundings** of the system. There are two types of system, **open system** and **closed system**. An open system is one that has material flowing across the boundary (entering/exiting the system); and a closed system is one without

material crossing its boundary. In this subject, we only deal with open systems and systems which can be treated as open systems.

2.2. Properties of a system

- 1. Specific properties. A specific property of a system is the property per unit mass or per unit mole, such as specific volume v (m³/kg, ft³/lb) and specific enthalpy \hat{H} (J/mol, Btu/lb). Obviously, a specific property is independent of the amount of material in the system (similar to a concentration or a density term).
- 2. **State.** State here mainly refers to the *thermodynamic state* of a system with a given set of properties of material in the system at a given time. The variables or conditions required to *fix* a state usually include temperature, pressure, phase and composition. When the state of a system is fixed, all its *specific* properties are fixed.
- 3. State (or point) property or variable is a property whose value depends only on the state of the system (such as internal energy and enthalpy). To calculate the change of a state property, you may assume any intermediate steps for your convenience from the initial to the final points, since the net change always equals the final value minus the initial (e.g, $\Delta H = H_2 H_1$).

For **multi-phase systems**, the properties of materials can only be specified or fixed when an *equilibrium state* is established among different phases. Such an equilibrium state (as well as the properties of materials) changes with the temperature, pressure and composition.

2.3. Types of energy

Before doing energy balance, you should know the definition, dimension and common units of energy, specific energy and power, enthalpy and heat capacity.

• The energy components of a system

The total energy E of a system or an object is made up of three components, including

1. **Kinetic Energy** (E_K): Energy due to the motion of a body relative to a reference at rest $(E_K = \frac{1}{2} mv^2/g_c)$.

Ex.1. Kinetic energy of a flowing fluid (Ex.21.2 Himmelblau) Water is pumped from a storage tank through a tube of 3.0 cm inside diameter at the rate of 0.001 m³/s. What is the kinetic energy per kg water in the tube?

Solution: kinetic energy $E_k = \frac{1}{2} mv^2$, tube dia. D = 3.0 cm, m = 1 kg. Cross-section area of tube A = $\frac{1}{4} \pi D^2 = \frac{1}{4} \pi (3.0/100 \text{ m})^2 = 7.0686 \times 10^{-4} \text{ m}^2$ Average velocity of water $v = Q/A = 0.001 \text{ m}^3/(7.0686 \times 10^{-4} \text{ m}^2) = 1.415 \text{ m/s}$ $KE \ per \ kg = E_k/m = \frac{1}{2} v^2 = \frac{1}{2} (1.415 \text{ m/s})^2 = 1.00 \text{ m}^2/\text{s}^2 = 1.00 \text{ J/kg}.$

2. **Potential Energy** (E_P) : Energy due to the position of a body in a potential field (such as gravitational or electromagnetic field) relative to a given reference. One kind of potential energy is the one due to gravity on a body of mass m, $E_P = mgh$ where h is the level *relative* or *above* the reference.

Ex. 2. Potential energy change of water (Ex.21.3Himmelblau) Water is pumped from a storage tank (tank 1) to another tank (2) which is 40 ft above tank 1. Calculate the potential energy increase with each lb of water pumped from tank 1 to tank 2. Express the answer in btu/lb.

Solution: PE increase per lb = $E_P / m = gh = (9.806 \text{ m/s}^2) (40 \text{ m/}3.2808) = 119.54 \text{ m}^2/\text{s}^2 = 119.544 \text{ J/kg} = (119.544 \text{ btu}/1055.6)/2.2046 \text{ lb} = 0.0514 \text{ btu}/\text{lb}.$

3. **Internal Energy** (U): Internal energy is a macroscopic measure of the molecular, atomic, and subenergies. Internal energy can not be measured directly and can only be calculated from other variables. The internal energy of a system depends almost entirely on the chemical composition, state of aggregation, and temperature of the system material.

These different energy components can be converted from one to another within the system, and the system can exchange energy with its surroundings in the form of heat and work.

• The transfer energy terms

- 1. Heat (Q): Energy transfer as a result of the temperature difference between the system and its surroundings. If a system and its surroundings are at the same temperature (or if the system is perfectly insulated), then Q = 0 and the system is termed adiabatic.
- 2. Work (*W*): Energy transfer via a moving mechanical part, such as a turbine, an impellor of a pump ($W_s =$ Shaft work), or by moving the system boundary against a pressure (Flow work $W_f = \Delta(pV)$).

Note that heat and work refer only to the energy being *transferred* but *not possessed* by the system, unlike the kinetic, potential and internal energies which are properties of the system material.

According to the **law of energy conservation**, if there is an increase or decrease in the total energy of the system, the system must have either received or given out work or heat from/to the surroundings, so that

$$\Delta E = \Delta (U + E_K + E_P) = Q + W \qquad (1)$$

This is the *general energy balance equation* and will be discussed in more details later.

Fig.5.1 illustrates the energy transfer and conversion process in a steam or heat engine. An input of heat (Q) from fire (surrounding) to water (system) causes an increase in the water temperature and conversion to steam (ΔU). The hot and high pressure steam expands (W_f) to push a piston and its shaft (W_s) turns the wheel (ΔE_K).



2.4. Dimension and common units of energy

The dimension of energy including heat and work is Force times Distance, *F-L*, commonly measured by units such as Joules (1 J = 1 N.m), kJ, cal, kcal, ft-lb_f, and btu (British thermal unit). The energy per unit time is power with the dimension of *F-L/θ*, representing the rate of energy or energy per unit time, with common units of W, kW, btu/h, horsepower (hp).

Common units for heat capacities and their relationships are,

 $\frac{cal}{g \cdot {}^{o}C} = \frac{kcal}{kg \cdot {}^{o}C} = \frac{Btu}{lb \cdot {}^{o}F}, \quad \frac{cal}{g \bmod \cdot {}^{o}C} = \frac{kcal}{kg \bmod \cdot {}^{o}C} = \frac{Btu}{lb \bmod \cdot {}^{o}F}$

and, $kJ/kg^{-o}C$ and kJ/kg mol-^oC (1 kcal = 4.184 kJ).

2.5. Enthalpy and heat capacity

The enthalpy (H) of an object or the material in a system is defined as

$$H = U + pV \tag{2}$$

where p = pressure and V = volume of the material. Since U, p and V are all properties of the system, H is also a property of the system.

Internal energy and enthalpy have no absolute values, and only their changes can be calculated. Usually the values given at certain conditions are *relative to a reference* (difference). For example, in the steam table, the reference is liquid water at 0°C. The calculation of enthalpy changes will not be affected by the choice of reference if the enthalpies are based on the same reference.

Heat capacity of a substance is the amount of energy required to increase the temperature of unit quantity of the substance by one degree. The most useful heat capacity is C_p , the heat due to temperature change under constant pressure. For most practical cases, heat capacity of a material C_p is defined as,

$$\hat{H}_{2} - \hat{H}_{1} = \int_{T_{1}}^{T_{2}} C_{p} dT$$
(3)

where \hat{H}_1 and \hat{H}_2 are the specific enthalpies at T_1 and T_2 , respectively.

Heat capacity is also a physical property of material, and can be used to calculate the enthalpy change with temperature, called the *sensible heat*. Integration is needed since heat capacity is a function of temperature. If the **mean heat capacity** over the temperature interval of T_2 - $T_1 C_{pm}$ is given, however, the enthalpy change over this temperature range may be calculated by

$$\hat{H}_{2} - \hat{H}_{1} = C_{pm}(T_{2} - T_{1})$$
(4)

For combustion gases at low pressures, you can find the mean heat capacities at various temperatures from Table 1.6-1 of Geankoplis p15, and Table 8.3-1 and Table 8.3-2 of Felder's book, p350-351. Notice that all the mean heat capacities in these tables are based on the reference temperature $T_{ref} = 25^{\circ}$ C (77°F), i.e.

$$C_{pm(T)} = \frac{\hat{H}_T - \hat{H}_{25} \circ C}{T - 25^{\circ} C}$$

Therefore, the enthalpy of a gas at T is given by $\hat{H}_T = C_{pm}(T - 25^{\circ}C) + \hat{H}_{25^{\circ}C}$

By setting the reference state to 25°C (so that $H_{25C}^{\circ} = 0$), the specific enthalpy of the gas at temperature *T* is given by $\hat{H}_T = C_{pm}(T - 25^{\circ}C)$.

Specific heat is sometimes encountered in some textbooks as the alternative name of heat capacity. To be precise, it should be considered as the ratio of the heat capacity of a substance to that of a reference (similar to specific gravity). Since water is usually used as the reference substance which has a heat capacity of 1.0 cal/g-°C, the numerical values of heat capacity and specific heat are about the same if the same units are chosen.

2.6. Steam tables: Properties of water (A.2-9, A.2-10 of Geankoplis)

Steam tables are tabulated data of thermodynamic properties of water at different temperatures, pressures and states, such as enthalpy and internal energy. Since water and steam are most widely used in process plants as heat transfer media, these tables are very useful for plant design as well as for our subject on energy balances.

The terms related to the states of water:

- Saturated liquid, liquid about to vaporize (bubble point) or liquid in liquid-vapor system
- Saturated vapor, vapor about to condense (dew point) or vapor in liquid-vapor system
- Superheated steam, steam at a temperature higher than the saturation temperature
- Sub cooled liquid, liquid at a temperature lower than the saturation temperature
- Quality, the mass fraction of vapor in a liquid-vapor system.

To better understand the various states of waters, you may refer to Felder, Cht 6, p224-245, and Himmelblau Cht 3 or 4. (Some diagrams showing the phase transition and equilibrium between saturated, sub-cooled and superheated states are shown at the end of this chapter).

3. Energy Balances for Open and Steady-State Systems

3.1. The balance equation

An **open system** by definition has material flow cross its boundaries as the process occurs (referring to Fig. 5.2). Starting with the general energy balance equation (1), for open systems, we may further divide the work into two types, a *flow work* which is due to the expansion/contraction of the system boundary against a pressure, $W_f = p_1V_1 - p_2V_2$ and a *shaft work* which is by moving mechanical parts such as a pump, W_s . By substituting $W_s + p_1V_1 - p_2V_2$ for W



Fig. 5.2 An open or fluid flow system where T=temperature, p=pressure, u=velocity and z =level relative to the reference plane, and the subscript 1 for inlet and 2 for outlet.

and **H** for U + pV, eq.(1) is converted to

$$\Delta H + \Delta E_K + \Delta E_P = Q + W_s \qquad (5)$$

where ΔH , ΔE_K , ΔE_P = Total energy at output (point 2) - Total energy at input (point 1), e.g., $\Delta H = H_2 - H_1$, Q = Heat transferred to the system from the surroundings (-Q for heat transferred out from the system to its surroundings), W_s = Shaft work done to the system (by a moving mechanical parts such as a pump and a turbine).

The energy balance equation (5) means that the increase (or decrease) in the total energy of the material after passing through the system is equals to the heat and work received (or lost) by the system.

The general energy balance equation can be simplified for specific cases. In this part we mainly consider enthalpy change and heat transfer, neglecting E_K , E_P and W_s (mechanical energy terms). So that, eq.(5) is reduced to

$$\Delta H = Q \tag{6}$$

Therefore, the heat received or lost by the system accounts for the enthalpy change of the material.

3.2. Calculation of Enthalpy Changes

Heating a material may cause a temperature increase and/or phase transition (melting, boiling and sublimation). Similarly, cooling a material may cause a temperature decrease and/or phase transition (freezing and condensation). The part of heat responsible for the temperature change is referred to as *Sensible Heat* and the part for phase transition is *Latent Heat*. All these heats can be related to enthalpy changes according to Eq.(6).

- Sensible heat

- 1) Use of heat capacity equations or mean heat capacities: Eq.(3) and Eq.(4)
- 2) Use of enthalpy tables or charts to find \hat{H}_1 and \hat{H}_2 : $\Delta \hat{H} = (\hat{H}_2 \hat{H}_1)$

- Latent heat, λ

The enthalpy change associated with the transition of a unit amount (mass of mole) of a substance from one phase to another at constant temperature and pressure is known as the latent heat of that phase change.

- Use of enthalpy tables to find \hat{H} at two different states, $\lambda = \Delta \hat{H}$

E.g. for vaporization: $\lambda = \Delta \hat{H}_{v} = (\hat{H}_{v} - \hat{H}_{l}) (\Delta \hat{H}_{v} = \text{heat of vaporization})$

- Common cases and methods of enthalpy change calculation:

- (1) Combustion gases including fuels, air and the waste flue gases: use heat capacity table (Table 1.6-1, Geankoplis).
- (2) Water and steam: use steam tables.
- (3) Less common materials, Solids and liquids: usually by heat capacity provided; Gases: by mean heat capacity or specific enthalpy provided.

Ex.3. Sensible Heat. Calculate the enthalpy change of 150 g formic acid from 40°C to 85°C at 1 atm. From Table B.5 (Doran), C_p for formic acid in the temperature range of interest is 0.524 cal g⁻¹ °C⁻¹. $\Delta H = m \times Cp \times (T_2-T_1) = 150 \times (0.524) \times (85-40) = 3537$ cal or 3.537 kcal

(In this example, C_p value is assumed as a constant for the temperature range or equal to C_{pm} .)

Ex.4. Water and steam (Problem 23.5 Himmelblau) Use the SI property data for water to calculate the change of enthalpy that occurs when 5 kg of water at 70°C in a closed vessel of 0.50m3 in volume are heated to 453.1 K and 1000 kPa. Also determine the final quality of the steam in the vessel. Is the steam saturated or superheated?

Ans: Enthalpy change $\Delta H = 7520 \text{ kJ}$; Quality of steam (mass of steam/total mass) x = 0.51.

Ex. 5. Enthalpy change in downstream processing of gluconic acid (Doran). Concentrated fermentation liquid containing 20% (w/w) gluconic acid from an evaporator has a flow rate of 2000 kg/h and a temperature 90 °C. It needs to be cooled to 6 °C in a heat exchanger with cooling water. The cooling water has a flow rate 2700 kg/h and an initial temperature 2 °C. If the cooling water leaves the heat exchanger at 50 °C, what is the rate of heat loss from gluconic acid solution to the surroundings? Assume the heat capacity of gluconic acid is $0.35 \text{ cal/g-°C}^{-1}$.



Solution: Heat lost by gluconic acid = heat gained by water

 $[2000(0.2) \times (0.35 \times 4.184 \times 1000/1000) \times (90-6) + 2000 \times (0.8) \times (376.92-25.2)] + Q$

 $= 2700 \times (209.33 - 8.37) \times 611955.84 + Q = 542565$

Q = -69390.84 kJ/h

Negative sign means heat loss by the system to surrounding.

Hence, heat loss to the surroundings is 69390.84 kJ/h.

More energy balance examples: Felder: Ex7.4-2 (general balance), Ex 7.6-3 (m + E bal). From Himmelblau: Ex4.24 (Heat exchg, steam heating biomass); Ex.4.18 (Enthalpy chg of ice to water vapour, using steam tables).

4. Energy Balances involving Chemical Reactions

4.1. Heat of reaction

Large enthalpy changes, which may be positive or negative, are associated with many chemical

reactions. If ΔH is positive for a reaction process (endothermic), heat must be added to keep the temperature from dropping; if ΔH is negative (exothermic), heat is emitted from the reactor. The heat of reaction or enthalpy $\Delta \hat{H}_r(T, p)$ is the *specific* enthalpy difference between the reactants and products at specified states. For example, for the reaction

$$CaC_2 + 2 H_2O(1) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$
 (1=liquid, s=solid, g=gas)

The heat of reaction at 25°C and a total pressure of 1 atm: $\Delta \hat{H}_r$ (25°C, 1 atm) = -125.4 kJ/mol.

The negative sign signifies an exothermic reaction (heat releasing) and it will be positive if the reaction is endothermic (heat absorbing). Note that the value of a heat of reaction depends on the reaction temperature and pressure and the states of aggregation (gas, liquid, or solid) of the reactants and products. Therefore, these conditions must be specified for a given heat of reaction.

4.2. Standard heat of reaction and heat of formation

The heat of reaction at a reference state, usually 25°C and 1 atm, is referred to as the **standard** heat of reaction, denoted by $\Delta \hat{H}_r^{o}$. A *formation reaction* of a compound is the reaction in which the compound is formed from its atomic constituents as they normally occur in nature (e.g., O₂ rather than O). The standard heat of such a reaction is the *standard heat of formation*, $\Delta \hat{H}_f^{o}$ of the compound. Based on this definition, the standard heat of formation of an element is zero. Standard heat of reaction, if not given, may be computed from the standard heats of formation of the reactants (based on Hess's law),

$$\Delta \hat{H}_{r}^{o} = \sum_{\text{products}} v_{i} (\Delta \hat{H}_{f}^{o})_{i} - \sum_{\text{reactants}} v_{i} (\Delta \hat{H}_{f}^{o})_{i}$$
(7)

where v_i is the stoichiometric coefficient of the *i*th species participating in the reaction and $(\Delta \hat{H}_f^{o})_i$ its standard heat of formation of this species. The standard heats of formation of all elements should be set equal to zero in this formula. (Geankoplis, A.3-1 Heats of formation)

The **standard heat of combustion** $\Delta \hat{H}_c^o$ of a substance is the heat of reaction of that substance with oxygen to yield specific products, such as C+O₂=CO or CO₂, H₂+ $\frac{1}{2}$ O₂= H₂O. (Geankoplis A.3-2 Heats of combustion).

Ex.6. Heat of reaction (Problem 25.3 Himmelblau) The corrosion of aluminum in water is normally prevented by the tightly adhering oxide layer that forms on the aluminum. If this layer were absent, as when aluminum is amalgamated with mercury in an anaerobic atmosphere, the following reaction occurs. $2Al(s) + 6H2O(l) \rightarrow 2A1(OH)3(s) + 3H2(g)$

To get the heat of formation of A1(OH)3(s), the reaction is carried out with stoichiometric quantities of reactants, and after complete reaction occurs you find that heat was liberated. After applying the

energy balance, you found $\Delta \hat{H}_r^{o}$ per 2 moles of A1 was -837.0 kJ. What is the heat of formation of A1(OH)3(s)?

Ans: $\Delta \hat{H}_{f}^{o} = -1276 \text{ kJ/g mol A1(OH)3(s)}$

4.3. Energy balances on reactive systems

Considering a system in which the changes in kinetic energy, potential energy are negligible and no work is involved, the balance equation Eq.(6) applies, and the enthalpy change can be represented by,

$$Q = \Delta H = \frac{n_{AR}}{v_A} \Delta \hat{H}_r^o + \sum_{output} n_i \hat{H}_i - \sum_{input} n_i \hat{H}_i \qquad (8)$$

where $\Delta \hat{H}_r^o =$ standard heat of reaction; $n_{AR} =$ moles of A actually reacted; $v_A =$ stoichiometric coefficient of A in the reaction equation; $n_i \hat{H}_i =$ the enthalpy of a component relative to the reference state (25°C and 1 atm) ($n_i =$ mole, and $\hat{H}_i =$ specific enthalpy).

In Eq.(9), the first term on the right accounts for the enthalpy changes due to chemical reactions, and the 2nd term Σ - Σ for the enthalpy change due to physical changes, such as temperature increase (sensible heat) and phase transition (latent heat). If there is no phase transition involved between the reference temperature 25°C and the actual temperature of *i*th substance T_i (no latent heat), \hat{H}_i (25°C to T_i) may be calculated by

$$\hat{H}_i = \int_{25^o C}^{T_i} C_{pi} \, dT$$

or if the mean heat capacity is known, by

$$\hat{H}_i = C_{pmi} (T_i - 25^{\circ} C)$$

Therefore, \hat{H}_i is the enthalpy change of the *i*th substance when its temperature is changed from 25°C to T_i . If a component is at 25°C (the ref. state), its enthalpy is zero. For combustion reactions, the C_{pm} of combustion gases can be found in Table 1.6-1 of Geankoplis.

Examples on reactive systems: Geankoplis: Ex 1.7-2 (Heat and material bal. in combustion), 1.7-3 (Oxidation of Lactose, use ΔH_c^{o}); Felder: Ex 9.5-1 (Ammonia oxidation); Doran: Ex 5.7 and 5.8 (Cooling for ethanol fermentation, and citric acid production).

Summary (Chapter 5 Energy Balances)

Refs: Geankoplis sec.1.6, Felder, Chapters 7-9; Himmelblau, Cht 4, 5th ed/Cht 5, 6th ed.

- 1. Concepts of energy balances, properties and specific properties; Energy components of system material: internal (U), potential (E_P) , kinetic (E_K) and pressure (pV) energy; Transfer energies, work (W) and heat (Q); Shaft work W_f and flow work W_S .
- 2. Enthalpy and heat capacity, calculation of enthalpy changes with or without phase transition.
- 3. Use of steam tables and thermodynamic data, understand the terms of saturated liquid or vapour (steam) and superheated vapour (steam). For most cases, the effect of pressure may be neglected in the calculation of enthalpy changes of liquid water.
- 4. Energy balances with chemical reactions: heats of reaction, formation and combustion;
- 5. Simultaneous mass and energy balances.



(Based on Himmelblau 5th ed. pp290-291; Felder and Rousseau 2nd ed, pp226-