Al-Mustaqbal University / College of Engineering & Technology
Department of chemical engineering and petroleum industries
2ⁿᵈ Class
Subject: Principles of chemical engineering/ Code: UOMU012041
Lecturer: Dr. Abbas Khaleel Ibrahim Al-Gburi
2ⁿᵈ term – Lecture No.4 & Lecture Name: Internal energy and enthalpy calculations

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Internal energy and enthalpy calculations

Example 8.3 Internal Energy Calculation

Problem

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 (Example Figure 8.3.1).

Solution

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
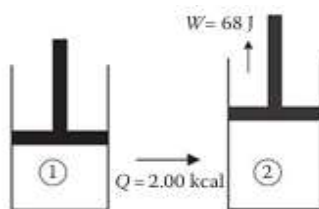
$$\Delta U = Q - W$$

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):

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

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

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

$$h = u + Pv \qquad (8.7)$$

EXAMPLE FIGURE 8.3.1
Heat added to a cylinder fitted with a piston.

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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 8.4 Enthalpy from Internal Energy

Problem

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,

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

$$= 6333 \ J/mol$$

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 ($\dot{H}$):

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

Email (abbas.khaleel.ibrahim@uomus.edu.iq)

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8.4 Enthalpy calculations

Change in enthalpy can occur because of change in temperature, change in phase, or mixing of solutions and reactions.

8.4.1 Enthalpy change as a result of temperature

Sensible heat is the heat transferred to raise or lower the temperature of a material in the absence of phase change. In the energy balance calculations, sensible heat change is determined by using a property of matter called the heat capacity at constant pressure, or just heat capacity (C_P). Units for C_P are (*J/mol. K*) or (*cal/g. °C*). Appendix A.2 lists C_P values for several organic and inorganic compounds. There are several methods for calculating enthalpy change using C_P values. When C_P is constant, the change in the enthalpy of a substance due to change in temperature at constant pressure is given by

$$\Delta H = mC_P(T - T_{ref}) \tag{8.22}$$

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

$$C_P = a + bT + cT^2 + dT^3 \tag{8.23}$$

Coefficients a, b, c, and d for a number of substances are given in Appendix A.2. In this case, the enthalpy change is

$$\Delta \dot{H} = \dot{m} \int_{T_{ref}}^{T} C_P \, dT = \dot{m} \int_{T_{ref}}^{T} \left(a + bT + cT^2 + dT^3 \right) dT \tag{8.24}$$

Sometimes, you need an estimate of specific enthalpy, specific internal energy, or specific volume at a temperature and a pressure that is between tabulated values. In this case, one can use a linear interpolation.

The following example demonstrates the determination of internal energy from heat capacity.

Example 8.14 Internal Energy and Heat Capacity

Problem

A closed rigid vessel that contains 200 kg of a fluid is heated from 20°C to 150°C. Calculate the heat required for this purpose. The constant volume heat capacity of the fluid is given by the following relation:

$$C_v \left(\frac{kJ}{kg \cdot °C} \right) = a + bT = 0.855 + 9.42 \times 10^{-4} T$$

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Solution

Known quantities: Mass of fluid, initial (20°C) and final temperature (150°C), heat capacity at constant volume as a function of temperature.

Find: Heat required to heat the content of the closed vessel.

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

$$Q - W = \Delta U$$

$W = 0.0$ (rigid vessel; no moving part), the change in internal energy is

$$Q = \Delta U$$

The change in internal energy is a function of heat capacity at constant volume; since the heat capacity is a function of temperature and mass, we multiply mass by heat capacity as follows:

$$\Delta U = m \int_{T_1}^{T_2} C_V \, dT$$

Substitute the heat capacity at constant volume:

$$\Delta U = m \int_{T_1}^{T_2} (0.855 + 9.42 \times 10^{-4} T) dT$$

Integrating the earlier equation as a function of initial and final temperature, we obtain

$$\Delta U = m \left[0.855(T_2 - T_1) + 9.42 \times 10^{-4} \left(\frac{T_2^2 - T_1^2}{2} \right) \right]$$

Substituting the values of initial (20°C) and final temperature (150°C),

$$Q = \Delta U = 200 \text{ kg} \left[0.855(150 - 20) + 9.42 \times 10^{-4} \frac{(150^2 - 20^2)}{2} \right]$$

$$\times \left[\frac{\text{kJ}}{\text{kg} \cdot {}^{\circ}\text{C}} \right] = 24,312 \text{ kJ}$$

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Example 8.15 Use of data from tables and reference state

Problem

The data shown in Table E8.15 are for a saturated fluid. Calculate Δh and Δu for the transition of saturated vapor from 10°C to −20°C.

Solution

Known quantities: Enthalpy, pressure, and temperature.

Find: Change of specific enthalpy and specific internal energy.

Analysis: The reference is liquid at −40°C, because the enthalpy at this temperature is zero. Change in specific enthalpy (Δh) and change in specific internal energy (Δu) for the transition of saturated CH_3Cl vapor from 10°C to −20°C can be calculated as

$$\Delta h = h_{-20°C} - h_{10°C} = 456 - 470 = -14 \text{ kJ/kg}$$

The change in specific internal energy starts using $h = u + Pv$ and $\Delta h = \Delta u + \Delta(Pv)$.

Rearranging for Δu,

$$\Delta u = \Delta h - \Delta(Pv) = \Delta h - \left\{ (Pv)_{-20} - (Pv)_{10} \right\}$$

TABLE E8.15
Properties of Saturated Methyl Chloride

State	T (°C)	P (atm)	v (m³/kg)	h (kJ/kg)
Liquid	−40	0.47	0.001	0.00
Vapor	−20	1.30	0.310	456
Vapor	10	3.54	0.120	470

To calculate the change in internal energy,

$$\Delta u = -14\frac{\text{kJ}}{\text{kg}} - \{1.30 \times 0.312 - 3.54 \times 0.12\}\left(\text{atm} \times \frac{\text{m}^3}{\text{kg}}\right)$$
$$\times \left(\frac{101.325 \text{ kN/m}^2}{1 \text{ atm}}\right)\left(\frac{\text{kJ}}{\text{kN} \cdot \text{m}}\right)$$

The rounded result of change in internal energy is

$$\Delta u = -12 \text{ kJ/kg}$$

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8.4.2 Constant heat capacity

Keeping P constant and letting T change, we can get the expression for the constant P part as $\Delta h = \int C_P dT \approx C_P \Delta T$ (at constant P). It is not necessary to know the reference state to calculate $\Delta \dot{H}$ for the transition from one state to another. Δh from state 1 to state 2 equals $h_2 - h_1$ regardless of the reference state upon which h_1 and h_2 were based. If different tables are used, one must make sure they have the same reference state. h and u are state properties; their values depend only on the state of the species, temperature, and pressure and not on how the species reached its state. When a species passes from one state to another, both Δu and Δh for the process are independent of the path taken from the first state to the second one.

Example 8.16 Constant Heat Capacity

Problem

What is the change in the enthalpy of 100 g/s acid heated in a double pipe heat exchanger from 20°C to 80°C, if the average heat capacity at constant pressure is 0.50 cal/g.°C?

Solution

Known quantities: Mass of acid, constant heat capacity, initial and final temperatures.

Find: Change in enthalpy.

Analysis: Use change in enthalpy with const heat capacity.

The change in enthalpy as a function of specific heat is given by

$$\Delta \dot{H} = \int_{T_1}^{T_2} \dot{m} C_P \, dT$$

Since the heat capacity (C_P) is constant, the earlier equation is simplified to

$$\Delta \dot{H} = \dot{m} C_P (T_2 - T_1)$$

Substitute the values of mass flow rate, heat capacity at constant pressure, and difference in temperature (the reference temperature is 20°C):

$$\Delta \dot{H} = \left(100 \, \frac{g}{s}\right)\left(0.5 \, \frac{cal}{g \, ^{\circ}C}\right)(80 - 20)^{\circ}C = 3000 \, cal/s$$

The change in enthalpy transport rate is

$$\Delta \dot{H} = 3.0 \, kcal/s$$

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Example 8.17 Heat added to a boiler

Problem

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 (Example Figure 8.17.1). Inlet and exit pipes are at the same level.
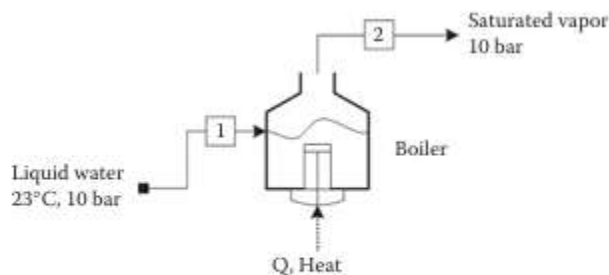
Solution

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 m³/h), exit pipe diameter (0.15 m).

Find: Change in specific enthalpy (Δh).

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

$$Q - W_s = \dot{m}\Delta h + \Delta KE + \Delta PE$$

EXAMPLE FIGURE 8.17.1
Production of saturated steam.

Since the boiler 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

$$Q_s = \dot{m}\Delta h + \Delta KE$$

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):

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

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

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

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 saturated steam table, Appendix A.3):

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

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:

$$v_2 = \frac{\dot{V}_2}{\frac{\pi D^2}{4}} = \frac{15{,}000 \text{ m}^3/\text{h}}{\frac{\pi(0.15)^2}{4} \text{ m}^2} \times \frac{\text{h}}{3600 \text{ s}} = 235.79 \text{ m}/\text{s}$$

The simplified general energy balance equation becomes

$$Q = \dot{m}\Delta h + \Delta KE = \dot{m}\Delta h + \frac{1}{2}\dot{m}(v_2^2 - v_1^2)$$

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

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

$$\times \frac{\text{kJ}}{1000 \text{ J}} = 58{,}082 \text{ kJ}/\text{s}$$

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