CH365 Chemical Engineering Thermodynamics

Lesson 6
Enthalpy, Heat Capacity, and Open Systems – Part 1

Professor Andrew Biaglow
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Summary of Constant-V and Constant-P Processes

$$dU = dQ + dW \qquad \text{p. 40, top equation}$$

$$dW = -PdV \qquad \text{1.3, p. 10}$$

$$dU = dQ - PdV \qquad \text{2.7}$$

Constant V $dV = 0$ $\Rightarrow$ $dU = dQ$ $\Rightarrow$ $Q = \Delta U$

dV=0   2.8   2.9

Enthalpy

U, P, and V are state functions

$\therefore$ H is also a state function

  units are energy per mole
    or energy per mass

$$H \equiv U + PV$$

eq. 2.11, Lesson 5

$$P \ [=] \ Pa \ [=] \ \frac{N}{m^2}$$

$$PV \ [=] \ \frac{N}{m^2} \cdot \frac{m^3}{mol} \ [=] \ \frac{N \cdot m}{mol} \ [=] \ \frac{J}{mol}$$

mol or kg

$$dH = dU + d(PV)$$

eq. 2.13, p. 41

$$\Delta H = \Delta U + \Delta(PV)$$

eq. 2.14, p. 41

Example 2.6

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 100 degC and constant pressure of 101.33 kPa. The specific volumes of liquid and water vapor at these conditions are 0.00104 and 1.673 m³ kg⁻¹. For this change, heat in the amount of 2,256.9 kJ is added to the water.

system: 1kg of water

$$\Delta H = Q = +2,256.9 \text{ kJ}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V \qquad V_1 = 0.00104 \, \frac{m^3}{kg} \qquad V_2 = 1.673 \, \frac{m^3}{kg}$$

$$P\Delta V = 101.33 \text{ kPa} \times (1.673 - 0.00104) \text{ m}^3$$
$$= 169.4 \text{ kPa} \cdot \text{m}^3$$
$$= 169.4 \, \frac{kN}{m^2} \, m^3$$
$$= 169.4 \text{ kJ}$$

1 kN·m = 1 kJ

$$\Delta U = +2,256.9 - 169.4 = 2087.5 \text{ kJ}$$

Check:
steam table, p.699
U=2087.5 kJ kg⁻¹

Heat Capacity

Energy per mole per degree or energy per mass per degree

Simplest model consistent with Joule's' experiments:

Heat added is proportional to temperature change

$$dQ = C \cdot dT$$

$$C \equiv \frac{dQ}{dT}$$

Problem - Q is a "path" function; we want a "state" function

Constant V

$$dQ = dU \qquad \text{eq. 2.8}$$

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{eq. 2.15} \qquad = \frac{C}{n}$$

$$dU = C_V dT \qquad \text{eq. 2.16}$$

$$\Delta U = \int_{T_1}^{T_2} C_V dT \qquad \text{eq. 2.17}$$

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT \qquad \text{eq. 2.18}$$

U, T, and V are state functions
$\therefore C_V$ is also a state function

Constant P

$$dQ = dH \qquad \text{eq. 2.11}$$

$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{eq. 2.19} \qquad = \frac{C}{n}$$

$$dH = C_P dT \qquad \text{eq. 2.20}$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT \qquad \text{eq. 2.21}$$

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT \qquad \text{eq. 2.22}$$

H, T, and P are state functions
$\therefore C_P$ is also a state function

For the calculation of property changes, an actual process may be replaced by any other process which accomplishes the same change in state.

Supplement - Problem 2.6 (L4)

One mole of a gas in a closed system undergoes a four-step thermodynamic cycle. Use the data given in the following table to determine the numerical values for the missing quantities, i.e., determine a-h.

Step	ΔU^t/J	Q/J	W/J
12	-200	5800	-6000
23	-4000	-3800	-200
34	-500	-800	300
41	4700	200	4500
12341	0	1400	-1400

- Example 2.7 is similar to Problem 2.6 from the end-of chapter problems, but with two steps instead of four.

- In problem 2.6, we completed the rows and columns (red entries) using summations across the rows and columns and the concept of state functions.
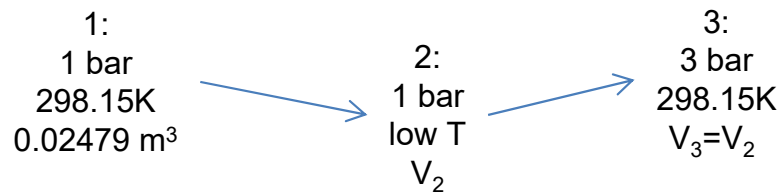
Example 2.7

Air at 1 bar and 298.15 K (25 degC) is compressed to 3 bar and 298.15 K by two different mechanically reversible processes:

    (a) Cooling at constant pressure followed by heating at constant volume.

    (b) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

$$C_V = 20.785 \text{ and } C_P = 29.100 \text{ J mol}^{-1} \text{ K}^{-1}$$

Assume also for air that PV/T is a constant, regardless of the changes it undergoes. At 298.15 K and 1 bar, the molar volume of air is 0.02479 m³ mol⁻¹.

<div align="center">

1:
1 bar
298.15K
0.02479 m³

2:
1 bar
low T
V_2

3:
3 bar
298.15K
$V_3=V_2$

</div>

system: 1 mol of air in a piston

$$V_3 = V_1 \cdot \frac{P_1}{P_3} = 0.02479 \cdot \left(\frac{1}{3}\right) = 0.008263 \text{ m}^3 = V_2$$

Example 2.7, part (a)

Air at 1 bar and 298.15 K (25 degC) is compressed to 3 bar and 298.15 K by two different mechanically reversible processes:

(a) Cooling at constant pressure (to V_2) ...

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad T_2 = T_1 \cdot \frac{V_2}{V_1} = 298.15 \cdot \left(\frac{0.008263}{0.02479}\right) = 99.38K$$

$$W_{12} = -P\Delta V = -1\,bar \cdot \frac{10^5 Pa}{bar} \cdot \frac{1N/m^2}{Pa} \cdot (0.008263 - 0.02479)\frac{m^3}{mol} = 1,653\,\frac{J}{mol} \text{ (compressed, work +)}$$

$$Q_{12} = \Delta H_{12} = C_P \Delta T_{12} = (29.100) \cdot \frac{J}{mol \cdot K} \cdot (99.38 - 298.15)K = -5,784\,\frac{J}{mol} \qquad \text{(cooled, heat -)}$$

$$\Delta U_{12} = \Delta H_{12} - \Delta(PV)_{12} = \Delta H_{12} - P\Delta(V)_{12} = -5,784 - 1 \cdot (10^5) \cdot (0.008623 - 0.02479) = -4,131\,\frac{J}{mol}$$

... followed by heating at constant volume ($V_2 = V_3$).

(ΔH_{23} not needed) $\qquad \Delta U_{23} = Q_{23} = C_V \Delta T = (20.785) \cdot (298.15 - 99.38) = 4,131\,\frac{J}{mol} \qquad W_{23} = 0 \quad$ (why zero?)

Overall 1-3:
$$\Delta U_{13} = \Delta U_{12} + \Delta U_{23} = -4,131 + 4,131 = 0\,\tfrac{J}{mol}$$

$$Q_{13} = Q_{12} + Q_{23} = -5,784 + 4,131 = -1,653\,\tfrac{J}{mol}$$

$$W_{13} = W_{12} + W_{23} = 1653 + 0 = 1,653\,\tfrac{J}{mol}$$

$$\Delta H_{13} = \Delta U_{13} + \Delta(PV)_{13}$$

$$P_1V_1 = P_3V_3 \Rightarrow \Delta(PV) = 0$$

$$\Delta H_{13} = \Delta U_{13} = 0\,\tfrac{J}{mol}$$

Example 2.7, part (b)

Air at 1 bar and 298.15 K (25 degC) is compressed to 3 bar and 298.15 K by two different mechanically reversible processes:

(b) Heating at constant volume (at V_1) ...

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad T_2 = T_1 \cdot \frac{P_2}{P_1} = 298.15 \cdot \left(\frac{3}{1}\right) = 894.45 \text{K}$$

$$Q_{12} = \Delta U_{12} = C_V \Delta T_{12} = (20.785) \cdot (894.45 - 298.15) = 12,394 \text{ J / mol} \qquad W_{12} = 0 \quad \text{(why zero?)}$$

$$V \Delta P_{12} = 0.02479 \cdot \frac{\text{m}^3}{\text{mol}} \cdot (3 \text{ bar} - 1 \text{ bar}) \cdot \frac{10^5 \text{ Pa}}{\text{bar}} \cdot \frac{1 \text{ N / m}^2}{\text{Pa}} = 4,958 \text{ J / mol}$$

$$\Delta H_{12} = \Delta U_{12} + V \Delta P_{12} = 12,394 + 4,958 = 17,352 \text{ J / mol}$$

... followed by cooling at constant pressure (at P_3).

$$Q_{23} = \Delta H_{23} = C_P \Delta T_{23} = (29.100 \frac{\text{J}}{\text{mol} \cdot \text{K}}) \cdot (298.15 - 894.45) \text{ K} = -17,352 \text{ J / mol}$$

$$W_{23} = -P \Delta V_{23} = -(0.008263 - 0.02479) \cdot \frac{\text{m}^3}{\text{mol}} \cdot 3 \text{ bar} \cdot \frac{10^5 \text{ Pa}}{\text{bar}} \cdot \frac{1 \text{ N / m}^2}{\text{Pa}} = 4,958 \text{ J / mol}$$

$$\Delta U_{23} = \Delta H_{23} - \Delta (PV)_{23} = \Delta H - P \Delta (V)_{23} = -17,354 - (3 \times 10^5) \cdot (0.008263 - 0.02479) = -12,394 \text{ J / mol}$$

Overall 1-3:
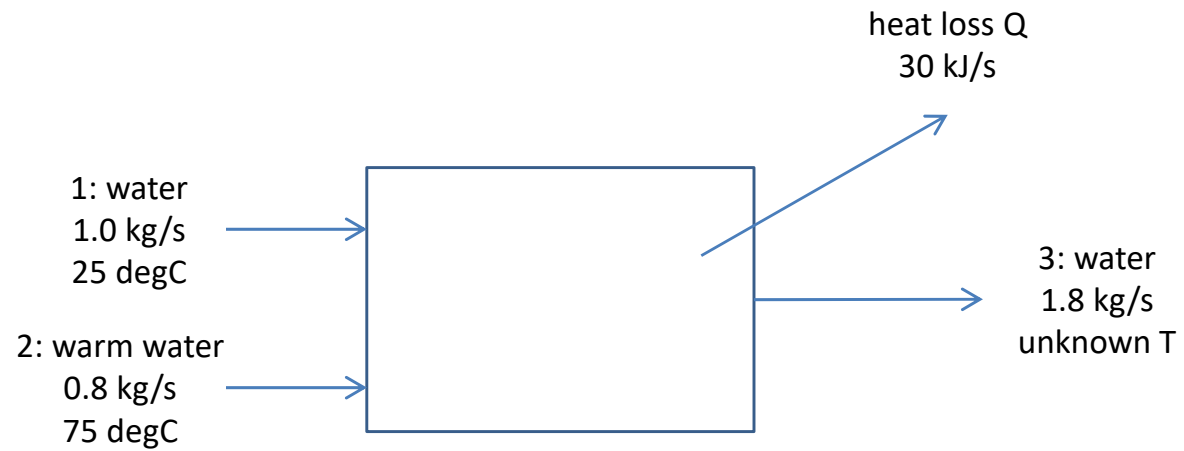$$Q_{13} = Q_{12} + Q_{23} = 12,394 - 17,352 = -4,958 \text{ J / mol}$$

$$\Delta U_{13} = \Delta U_{12} + \Delta U_{23} = 12,394 - 12,394 = 0 \text{ J / mol}$$

$$W_{13} = \Delta U_{13} - Q_{13} = 0 - (-4,958) = 4,958 \text{ J / mol}$$

Lesson 6 Problems

Problem 2.24

A stream of warm water is produced in a steady-flow mixing process by combining 1.0 kg s^{-1} of cool water at 25 degC with 0.8 kg s^{-1} of hot water at 75 degC. During mixing, heat is lost to the surroundings at the rate of 30 kJ s^{-1}. What is the temperature of the warm water stream? Assume the specific heat of water is constant at 4.18 kJ kg^{-1} K^{-1}.

heat loss Q
30 kJ/s

1: water
1.0 kg/s
25 degC

2: warm water
0.8 kg/s
75 degC

3: water
1.8 kg/s
unknown T

assume constant P so that Q=ΔH

Problem 2.40*

*Excellent review problem

One kilogram of air is heated reversibly at constant pressure from an initial state of 300 K and 1 bar until its volume triples. Calculate W, Q, ΔU, and ΔH for the process. Assume for air that $(PV/T)=83.14$ $(bar)(cm)^3(mol)^{-1}(K)^{-1}$ and $Cp=29(J)(mol)^{-1}(K)^{-1}$. Report your answers in kJ.