CH365 Chemical Engineering Thermodynamics

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

Professor Andrew Biaglow

Summary of Constant-V and Constant-P Processes

$Q = \Delta H$

$$dU = dQ + dW$$ p. 40, top equation

$$dW = -PdV$$ 1.3, p. 10

$$dU = dQ - PdV$$ 2.7

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

dV=0 $\qquad\qquad\qquad\qquad$ 2.8 $\qquad\qquad\qquad$ 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

$$\boxed{H \equiv U + PV}$$

eq. 2.11, Lesson 5

"has units of"

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

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

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 vaporized at 100 °C and 101.33 kPa, with T and P constant. The specific volumes of liquid water and water vapor at these conditions are 0.00104 and 1.673 m^3 kg^{-1}. For this change, heat in the amount of 2,256.9 kJ is added to the water.

system: 1kg of water

$$\Delta H = Q = +2,256.9 \text{ kJ}$$ (constant P, eq. 2.12, slide 2)

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

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

1 kN·m = 1 kJ

$$= 169.4 \text{ kJ}$$

Check:
steam table, p.699
U=2087.5 kJ kg^{-1}

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

Heat Capacity

Slide 5

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

$$dQ = dU \qquad \text{eq. 2.8, slide 2}$$

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

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

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

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

U, T, and V are state functions
∴ C_V is also a state function

Constant P

$$dQ = dH \qquad \text{eq. 2.11, slide 2}$$

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

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

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

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

H, T, and P are state functions
∴ 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.

Example 2.7 - Background

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

- In problem 2.6, the black entries were given, and we completed the rows and columns (red entries) using summations across the rows and columns and the concept of state functions.
- Example 2.7 is similar, but with two steps instead of four, and the process does not return to its initial state (not cyclic).

Example 2.7

Air at 1 bar and 298.15 K (25 °C) 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 m^3 mol^{-1}.

Example 2.7, part (a)

Example 2.7, part (b)

Questions?