MME 231: Lecture 07

The Laws of Thermodynamics

The Combined Statement

A. K. M. B. Rashid
Professor, Department of MME
BUET, Dhaka

Today's Topics

- Combined statement of the first and second laws of thermodynamics
- Problems

Combined Statement of the First and Second Laws

- The first law: $dU = \delta Q + \delta W + \delta W'$
- From the second law: $\delta Q_{rev} = T\,dS$
- From the work function: $\delta W_{rev} = -P\,dV$

❑ The combined statement for any reversible process:

$$dU = TdS - PdV + \delta W'$$

- **the basis of derivations of the conditions for equilibrium in thermodynamic systems.**
- **a key relationship in solving practical thermodynamic problems.**

Example 3.3

One mole of an ideal gas is kept at 10 atm pressure and 100 K temperature. The PVT relationship for an ideal gas can be expressed by the relationship PV=nRT, where the value of R, the ideal gas constant, can be taken as 0.082 litre-atm/mol-K.

Calculate the amount of mechanical work done on the system if it undergoes a reversible

(i) isothermal expansion to 1 atm,

(ii) isobaric expansion to 10 litres, and

(iii) isochoric process.

Isothermal expansion to 1 atm

The Ideal Gas Law:
$PV = n RT$

$W = -\int P\,dV$

$W_T = -\int (nRT/V)\,dV = -nRT\int (dV/V)$ (for isothermal process)

$W = -nRT \ln (V_2/V_1) = nRT \ln (V_1/V_2)$

$W = -(P_1V_1) \ln (V_2/V_1) = (P_1V_1) \ln (V_1/V_2)$

$W = -nRT \ln (P_1/P_2) = nRT \ln (P_2/P_1)$

Given Data:

n = 1 mole, P_1 = 10 atm, P_2 = 1 atm,

$T_1 = T_2$ = 100 K, R = 0.082 litre-atm/mol-K

$V_1 = nRT_1/P_1$ = (1 mol)(0.082 litre-atm/mol-K)(100 K)/(10 atm) = 0.82 litres

$V_2 = nRT_2/P_2$ = (1 mol)(0.082 litre-atm/mol-K) (100 K) / (1 atm) = 8.20 litres

$W = -nRT \ln (V_2/V_1)$
= -(1 mol) (0.082 litre-atm/mol-K) (100 K) ln (8.2 litre/0.82 litre)
= **-18.88 litre-atm**

Isobaric expansion to 10 litres

$W = -\int P\,dV = -P\int dV$ (for isobaric process, P is constant)

$W = -P (V_2 - V_1) = n R (T_1 - T_2)$

Given Data:

n = 1 mole, $P_1 = P_2$ = 10 atm, T_1 = 100 K, V_2 = 10 litres

$V_1 = nRT_1/P_1$ = (1 mol)(0.082 litre-atm/mol-K)(100 K)/(10 atm) = 0.82 litres

$W = -P (V_2 - V_1)$ = – (10 atm) (10 - 0.82 litre) = **- 91.8 litre-atm**

Isochoric process

For isochoric process, dV = 0

$W = -\int P\,dV = \mathbf{0}$

Example 3.4

An ideal gas is held in a piston-cylinder assembly undergoes a reversible adiabatic expansion for which the relationship between pressure and volume is given by PV^{γ} = constant. The initial pressure is 3 bar and the initial and final volumes are 0.1 m^3 and 0.2 m^3 respectively.

Determine :

(1) the amount of mechanical work done to the system, and

(2) the change in internal energy of the system for the process if (a) $\gamma = 1.5$, (b) $\gamma = 1.0$, and (c) $\gamma = 0$.

Work done for adiabatic process

PV^{γ} = Constant, k $\qquad P = k / V^{\gamma}$

$$W = -\int P\,dV = -\int (k/V^{\gamma})\,dV = -k\int V^{-\gamma}\,dV$$

$$W = -\frac{kV_2^{1-\gamma} - kV_1^{1-\gamma}}{1-\gamma} = \frac{kV_1^{1-\gamma} - kV_2^{1-\gamma}}{1-\gamma}$$

$$W = \frac{(P_1V_1^{\gamma})\,V_1^{1-\gamma} - (P_2V_2^{\gamma})\,V_2^{1-\gamma}}{1-\gamma} = \frac{P_1V_1 - P_2V_2}{1-\gamma}$$

$\gamma = 1.5$

Given Data:

$P_1 = 3.0$ bar, $V_1 = 0.1\ m^3$, $V_2 = 0.2\ m^3$, $\gamma = 1.5$

PV^{γ} = Constant, k

$$P_2 = P_1\ (V_1/V_2)^{\gamma} = (3.0\ \text{bar})\ (0.1\ m^3 / 0.2\ m^3)^{1.5} = 1.06\ \text{bar}$$

$$W = \left(\frac{(3.0\ \text{bar})\ (0.1\ m^3) - (1.06\ \text{bar})\ (0.2\ m^3)}{1.5 - 1}\right)\left(\frac{10^5\ N/m^2}{1\ \text{bar}}\right)\left(\frac{1\ kJ}{10^3\ N.m}\right)$$

$W = -17.6$ kJ

The process is adiabatic, thus $Q = 0$

$$\Delta U = Q + W = W = -17.6\ kJ$$

$\gamma = 1.0$

PV = constant, P = constant / V

$$\Delta U = W = -\int P\, dV = (P_1V_1)\ \ln(V_1/V_2) = -20.79\ kJ$$

$\gamma = 0$

P = Constant (Simple isobaric process)

$$\Delta U = W = -P\ (V_2 - V_1) = -30.0\ kJ$$

Table 3.1

Reversible mechanical work done on the system containing n mole of an ideal gas during various kinds of processes

Process	**Work Done On System**
Isothermal	$W = -nRT \ln(V_2/V_1) = (P_1V_1)\ln(V_1/V_2)$
Adiabatic	$W = (P_1V_1 - P_2V_2) / (1 - \gamma)$
Isobaric	$W = -P(V_2 - V_1) = nR(T_1 - T_2)$
Isochoric	$W = 0$

Next Class

Lecture 08
The Third Law of Thermodynamics

Rashid/ Ch#3