

## The First Law of Thermodynamics

### Introduction to Thermodynamics

#### System

- open system: can transfer both matter and energy
- closed system: can transfer only energy, but not mass
- isolated system: can transfer neither matter or mass

#### Property of System

- intensive properties: independent of mass of a system
- extensive properties: depend on the size of the system

#### Function of State

$$\oint z = 0$$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

#### Equation of State

$$V = \frac{nRT}{P}$$

### Van der Waals Equation

for 1 mol gas:

real volume of gas:  $V = V_m - b$ , where  $b = 4N \times \frac{4}{3}\pi r^3$

real pressure of gas:  $P = P_m + \frac{a}{V_m^2}$

$$\Rightarrow \left(P_m + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

more generally, for  $n$  mol gas:

$$\left(P_m + \frac{n^2 a}{V^2}\right)(V_m - nb) = RT$$

## The First Law of Thermodynamics

the energy of the universe is conserved

internal energy  $dU = \delta Q + \delta W$

$$\oint dU = \oint (\delta Q + \delta W) = 0$$

## Enthalpy

$$\Delta U = Q + W$$

when  $dV = 0$ , then  $W = 0 \Rightarrow dU = \delta Q$

when  $dP = 0$ ,

$$dU = \delta Q_P - PdV$$

$$\delta Q_P = dU + PdV = d(U + PV)$$

define **enthalpy**  $H = U + PV$ , then  $H = \Delta Q$

## Heat Capacity

at constant value:

$$C_V = \frac{\delta Q_V}{dT} = \left( \frac{\partial U}{\partial T} \right)_V \Rightarrow C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

$C_{V,m}$  is capacity of 1 mol gas

at constant pressure:

$$C_P = \frac{\delta Q_P}{dT} = \left( \frac{\partial H}{\partial T} \right)_P \Rightarrow C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

$C_{P,m}$  is capacity of 1 mol gas

## Free Expansion (to vacuum)

$$dU = 0, dT = 0$$

for  $P, T$ :

$$dU = \left( \frac{\partial U}{\partial T} \right)_P dT + \left( \frac{\partial U}{\partial P} \right)_T dP = \left( \frac{\partial U}{\partial P} \right)_T dP = 0 \Rightarrow \left( \frac{\partial U}{\partial P} \right)_T = 0$$

for  $T, V$ :

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV = \left( \frac{\partial U}{\partial V} \right)_T dV = 0 \Rightarrow \left( \frac{\partial U}{\partial V} \right)_T = 0$$

therefore, internal energy only depends on  $T$ :  $U = U(T)$

under constant  $T$ :

$$\Delta H = d(U + PV) = dU + nRdT = 0$$

therefore, enthalpy only depends on  $T$ :  $H = H(T)$

$$C_P - C_V = \left( \frac{\partial H}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial(U + PV)}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V$$

under constant  $P$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \Rightarrow \left( \frac{\partial U}{\partial T} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

replace  $\left( \frac{\partial U}{\partial T} \right)_P$

$$\begin{aligned} &\Rightarrow \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P - \left( \frac{\partial U}{\partial T} \right)_V \\ &= \left( \frac{\partial V}{\partial T} \right)_P \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \end{aligned}$$

for ideal gas,  $\left( \frac{\partial U}{\partial V} \right)_T = 0$

$$\Rightarrow C_P - C_V = P \left( \frac{\partial V}{\partial T} \right)_P = nR$$

for 1 mol gas:

$$C_{p,m} - C_{v,m} = R$$

for monatomic ideal gas,  $C_{v,m} = \frac{3}{2}R$ ,  $C_{p,m} = \frac{5}{2}R$

## Typical Reversible Processes for Ideal Gas

isothermal  $\Delta U = 0$

$$Q = -W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{V_2}{V_1}$$

- isochoric  $\Delta V = 0$

$$Q_V = \Delta U = C_V \Delta T$$

- isobaric  $\Delta P = 0$

$$Q_P = \Delta Q = C_P \Delta T$$

- adiabatic  $\Delta Q = 0$

$$W = \Delta U = C_V \Delta T = -P dV$$

$$\Rightarrow - \int_{V_1}^{V_2} \frac{nR}{V} dV = \int_{T_1}^{T_2} C_V \frac{dT}{T} \Rightarrow (C_V - C_P) \ln \frac{V_2}{V_1} = C_V \ln \frac{T_2}{T_1}$$

$$\Rightarrow \left( \frac{C_P}{C_V} - 1 \right) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2} \Rightarrow (\gamma - 1) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$$

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$\Rightarrow$  Poisson equation

$$TV^{\gamma-1} = \text{constant}$$

$$PV^\gamma = \text{constant}$$

$$T^\gamma P^{1-\gamma} = \text{constant}$$

Work for adiabatic expansion/compression

$$\begin{aligned}
 W &= - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{cons}{V^\gamma} dV \\
 &= cons \cdot \left( \frac{1}{(\gamma-1)V_2^{\gamma-1}} - \frac{1}{(\gamma-1)V_1^{\gamma-1}} \right) = \frac{P_2 V_2^\gamma}{(\gamma-1)V_2^{\gamma-1}} - \frac{P_1 V_1^\gamma}{(\gamma-1)V_1^{\gamma-1}} \\
 &= \frac{P_2 V_2 - P_1 V_1}{\gamma-1} = \frac{nR(T_2 - T_1)}{\gamma-1}
 \end{aligned}$$

## Polytropic Process: General Performance of Reversible Process

define  $C_m$  the heat capacity of entire process

$$dU = C_m dT = dQ + dW = C_v dT + P dV$$

$$P dV + V dP = nR dT \Rightarrow C_m dT = C_v dT + nR dT - V dP = C_p dT - V dP$$

$$\text{define } \frac{C_{p,m} - C_m}{C_{v,m} - C_m} = n = - \frac{P dV}{V dP}$$

$$\Rightarrow n \frac{dV}{V} + \frac{dP}{P} = 0$$

$$\Rightarrow \int \left( n \frac{dV}{V} + \frac{dP}{P} \right) = \text{constant}$$

$$\Rightarrow n \ln V + \ln P = \text{constant}$$

$$\Rightarrow \boxed{PV^n = \text{constant}}$$

type of process can be determined on value of  $n$