

3.3 The Ideal Gas

* The terms $\frac{B}{V}$, $\frac{C}{V^2}$, etc, of the virial expansion arise on account of molecular interactions

* If there is no such interaction, the virial coefficient B, C, \dots would be zero and

$$Z = 1 \quad \text{or} \quad PV = RT \quad \bar{V} = \frac{v}{n}$$

* Molecular interactions do in fact exist and influence the observed behavior of real gases.

* As P is reduced at constant T , V increases and the contributions of the terms $\frac{B}{V}$, $\frac{C}{V^2}$, $\frac{D}{V^3}$, decrease.

* As $P \rightarrow 0$, Z approaches unity because V becomes infinite

* So, As $P \rightarrow 0$, $Z = 1$, $PV = RT$

* From the phase rule, $U_{\text{real gas}}(T, P) = U = f(T, P)$

* Pressure dependency results from forces between the molecules.

* In the absence of molecular interactions, $U = f(T)$

* These considerations of the behavior of a hypothetical gas in which no intermolecular forces exist and of a real gas in the limit as P approaches zero lead to the definition of an ideal gas as one whose macroscopic behavior is characterized by:

$$PV = RT$$

$$U = U(T)$$

Implied Property Relations for an ideal gas

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

$$H = U + PV$$

$$H = U(T) + RT \quad \text{or} \quad H = H(T)$$

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

$$\therefore C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R$$

$$* \quad dU = C_V dT$$

$$\therefore \Delta U = \int C_V dT$$

&

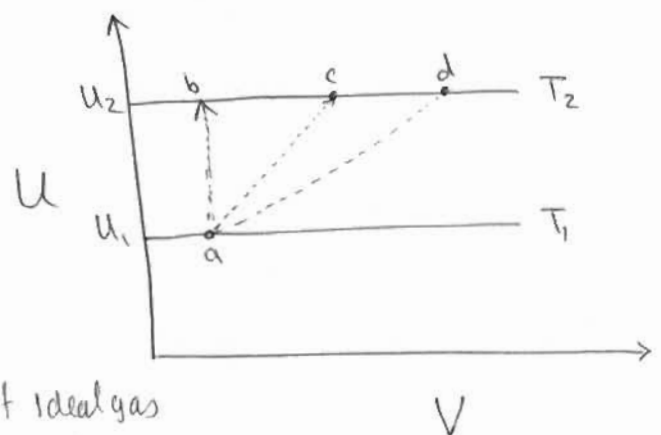
$$dH = C_P dT$$

$$\Delta H = \int C_P dT$$

* Since both U & C_V of ideal gas are function of temperature only, $\Delta U_{\text{ideal gas}} = \int C_V dT$ always regardless of the kind of process causing the change.

Note

ΔU is not always $= Q$
because $Q = f(T, \text{path of the process})$



* Same is applied for ΔH of ideal gas

Equations for Process Calculation for ideal Gases

- Process calculations provide work and heat quantities

* For mechanically reversible closed-system process,

$$dW = -Pdv$$

for ideal gas in closed system process

$$dQ + dW = C_v dT$$

$$\therefore dQ = C_v dT + PdV$$

This equation contains the variables P, V, T , only two of which are independent.

$$\text{Since } P = \frac{RT}{V}$$

$$\therefore dQ = C_v dT + RT \frac{dV}{V}$$

$$dW = -RT \frac{dV}{V}$$

$$\text{or } V = \frac{RT}{P}$$

$$dQ = C_p dT - RT \frac{dP}{P}$$

$$dW = -RdT + RT \frac{dP}{P}$$

$$\text{or } T = \frac{PV}{R}$$

$$dQ = \frac{C_v}{R} V dP + \frac{C_p}{R} P dV$$

$$dW = -P dV$$

Isothermal Process

Since

$$\Delta U = \int c_v dT \quad \& \quad \Delta H = \int c_p dT$$

$$\therefore \Delta U = 0$$

$$\Delta H = 0$$

$$\therefore Q = RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_2}{P_1} \quad \text{Constant } T$$

&

$$W = -RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_2}{P_1}$$

$$Q = -W$$

Isobaric Process

$$\Delta U = \int c_v dT \quad \& \quad \Delta H = \int c_p dT$$

Since

$$dQ = c_p dT = RT \frac{dP}{P}$$

$$\therefore Q = \int c_p dT \quad \text{constant } P$$

$$dW = -RdT + RT \frac{dP}{P}$$

$$W = -R(T_2 - T_1)$$

$$\& \quad \boxed{Q = \Delta H = \int c_p dT}$$

Isochoric Process constant volume

$$\Delta U = \int c_v dT \quad \& \quad \Delta H = \int c_p dT$$

$$dQ = c_v dT + RT \frac{dV}{V} \implies Q = \int c_v dT$$

$$dW = -RT \frac{dV}{V} = 0 \implies W = -\int P dV = 0$$

$$\& \quad \boxed{Q = \Delta U = \int c_v dT}$$

Adiabatic Process; Constant Heat Capacities

* No heat transfer between the system and its surroundings;
i.e. $dQ=0$

* Valid for mechanically reversible adiabatic compression or expansion of ideal gases (constant c_p & c_v)

$$\frac{dT}{T} = -\frac{R}{c_v} \frac{dV}{V}$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/c_v}$$

also, similarly

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/c_p} \quad \text{and} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{c_p/c_v}$$

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

$$TP^{(1-\gamma)/\gamma} = \text{constant}$$

$$\gamma = \frac{c_p}{c_v}$$

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

for ideal gases, the work of any adiabatic closed-system process is given by

$$dW = dU = C_V dT$$

$$\therefore W = \Delta U = C_V \Delta T \quad (\text{for constant } C_V) \quad (1)$$

Since

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$

$$\therefore C_V = \frac{R}{\gamma - 1}$$

$$\therefore W = C_V \Delta T = \frac{R \Delta T}{\gamma - 1}$$

Since $RT_1 = P_1 V_1$ & $RT_2 = P_2 V_2$

$$\therefore W = \frac{RT_2 - RT_1}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad (2)$$

Equation (1) & (2) are valid for adiabatic compression and expansion processes in a closed system, whether reversible or not, because P, V & T are state functions independent of path.

* Usually T_2 & V_2 are unknown.

$$\therefore W = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] = \frac{RT_1}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$$

Example 3.2

basis: 1 mol of air

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$\infty C_v = 20.785 \text{ J/mol}\cdot\text{K}, \quad C_p = 29.099 \text{ J/mol}\cdot\text{K}$$

$$T_i = 25^\circ\text{C}, \quad T_f = 25^\circ\text{C}$$

$$P_i = 1 \text{ bar}, \quad P_f = 5 \text{ bar}$$

$$\infty PV = RT$$

for constant T

$$\infty V_1 = \frac{RT_1}{P_1} = 0.02479 \text{ m}^3/\text{mol} = 0.02479 \text{ m}^3$$

$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479 \left(\frac{1}{5}\right) = 0.004958 \text{ m}^3$$

Since $T_1 = T_2$

$$\infty \Delta U = \Delta H = 0$$

a) Heating at constant volume followed by cooling at constant pressure

1) For heating at constant volume $P_1(1\text{bar}) \rightarrow P_2(5\text{bar})$

$$T' = T_1 \frac{P_2}{P_1} = 298.15 \left(\frac{5}{1}\right) = 1490.75 \text{ K}$$

$$Q = \Delta U = C_v \Delta T \quad (\text{constant volume}) \\ = 20.785(1490.75 - 298.15)$$

$$Q = 24,788 \text{ J}$$

2) For cooling at constant pressure ($P=5 \text{ bar}$)

$$\begin{aligned} Q &= \Delta H = C_p \Delta T \\ &= 29.1 (298.15 - 1490.75) \\ &= -34,703 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta U &= \Delta H - \Delta(PV) \\ &= \Delta H - P\Delta V \\ &= -34,703 - (5 \times 10^5 \text{ N/m}^2) (0.004958 - 0.02479) \text{ m}^3 \\ &= -24,788 \text{ J} \end{aligned}$$

∴ For the two steps together

$$Q = 24,788 - 34,703 = -9,915 \text{ J}$$

$$\Delta U = 24,788 - 24,788 = 0$$

$$W = \Delta U - Q = +9,915 \text{ J}$$

$$\Delta H = \Delta U = 0 \quad \text{since } T_1 = T_2 \Leftrightarrow P_1 V_1 = P_2 V_2$$

$\Delta PV = 0$

b) Isothermal Compression

$$\begin{aligned} Q &= -W = RT \ln \frac{P_1}{P_2} \\ &= (8.314)(298.15) \ln \frac{1}{5} \\ &= -3,990 \text{ J} \end{aligned}$$

c) Adiabatic Compression followed by Cooling at Constant Volume.

1) First step $V_1 \rightarrow V_2$

$$\begin{aligned} T' &= T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} \\ &= 298.15 \left(\frac{0.02479}{0.004958} \right)^{0.4} \\ &= 567.57 \text{ K} \end{aligned}$$

Since $Q = 0$

$$\begin{aligned} W &= C_V \Delta T \\ &= (20.785)(567.57 - 298.15) \\ &= 5,600 \text{ J} \end{aligned}$$

2) For constant volume step, No work is done

$$Q = \Delta U = C_V (T_2 - T') = -5600 \text{ J}$$

$$\Delta U = \Delta H = 0$$

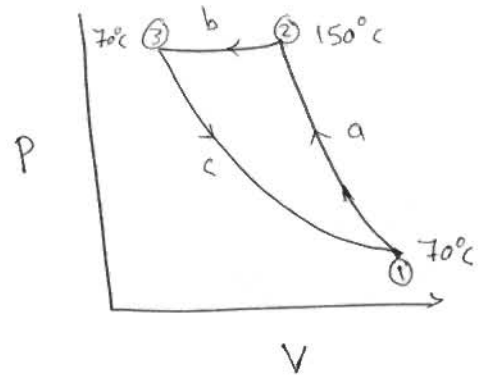
Q & W are Path dependent.

Example 3.3

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$C_V = 12.471 \text{ J/mol}\cdot\text{K} \quad C_P = 20.785 \text{ J/mol}\cdot\text{K}$$

Basis: 1 mol of gas



a) ideal gas, adiabatic compression

$$Q = 0$$

$$\begin{aligned} \Delta U = W &= C_V \Delta T \\ &= (12.471)(150 - 70) \\ &= 998 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H &= C_P \Delta T \\ &= (20.785)(150 - 70) \\ &= 1663 \text{ J} \end{aligned}$$

and P_2 will be

$$\begin{aligned} P_2 &= P_1 \left(\frac{T_2}{T_1} \right)^{\frac{\gamma}{\gamma-1}} \\ &= (1) \left(\frac{150 + 273.15}{70 + 273.15} \right)^{2.5} \end{aligned}$$

$$P_2 = 1.689 \text{ bar}$$

b) Cooling at constant Pressure

$$Q = \Delta H = C_p \Delta T$$
$$= (20.785)(70-150)$$

$$Q = -1,663 \text{ J}$$

$$\Delta U = C_v \Delta T$$
$$= (12.471)(70-150)$$

$$\Delta U = -998 \text{ J}$$

$$W = \Delta U - Q$$
$$= -998 - (-1663)$$

$$W = 665 \text{ J}$$

c) expanding isothermally

$$\Delta U = \Delta H = 0 \quad (\text{constant } T)$$

$$Q = -W = RT \ln \frac{P_3}{P_1}$$
$$= RT \ln \frac{P_2}{P_1}$$
$$= (8.314)(343.15) \ln \frac{1.689}{1}$$

$$Q = 1,495 \text{ J}$$

& For the entire cycle

$$Q = 0 - 1663 + 1495 = -168 \text{ J}$$

$$W = 998 + 665 - 1495 = 168 \text{ J}$$

$$\Delta U = 998 - 998 + 0 = 0$$

$$\Delta H = 1663 - 1663 + 0 = 0$$

it can be seen that

$$\Delta U = \Delta H = 0$$

because $T_i = T_f$

and $Q = -W$ since $\Delta U = 0$

Example 3.4

$$\text{efficiency} = 80\%$$

a) For mechanically reversible, adiabatic compression

$$W = 998 \text{ J} \quad \text{work done on the system}$$

$$\therefore W_{\text{rev}} = \frac{998}{0.8} = 1,248 \text{ J}$$

and hence, this ^{step of the} process can not be adiabatic

$$\begin{aligned} \text{Since } Q &= \Delta U - W \\ &= 998 - 1248 = -250 \text{ J} \end{aligned}$$

b) ^{for} mechanically reversible cooling

$$W = 665 \text{ J}$$

$$\therefore W_{\text{rev}} = \frac{665}{0.8} = 831 \text{ J}$$

$$\begin{aligned} Q &= \Delta U - W \\ &= -998 - 831 = -1,829 \text{ J} \end{aligned}$$

c) isothermal process

$$W = -1495 \text{ J} \quad \text{done by the system}$$

$$\therefore W_{\text{rev}} = (-1495)(0.8) = 1,196 \text{ J}$$

$$\begin{aligned} Q &= \Delta U - W \\ &= 0 + 1,196 = 1,196 \text{ J} \end{aligned}$$

For entire process

$$\Delta U = \Delta H = 0$$

$$Q = -250 - 1829 + 1196 = -883 \text{ J}$$

$$W = 1248 + 831 - 1196 = 883 \text{ J}$$