Enthalpy

Enthalpy is defined as
$$H = U + PV$$
where U, P, and V are all state functions, and therefore, H is a state function.

In general, for a change from A to B,
$$dH = dU + PdV + VdP$$
If P is constant (i.e. isobaric process), $P = P_{ext} = $ constant, then
$$dH = dU + PdV = \Delta U - W = q_P$$
dH is also a function of T only for an ideal gas.
$$dH = C_P dT$$
This is the general case for the infinitesimal change, but suppose
$$dH = dU + d(nRT) = dU + nRdT$$
Substituting $dH = C_P dT$ and $dU = C_V dT$ into the equation
$$C_P dT = C_V dT + nRdT$$
$$C_P = C_V + nR$$
$$C_P - C_V = nR$$
$$\bar{C}_P - \bar{C}_V = R$$

Consider the following reaction at constant pressure:
$$2\,\text{Na}_{(s)} + 2\,\text{H}_2\text{O}_{(l)} \rightarrow 2\,\text{NaOH}_{(aq)} + \text{H}_{2(g)} \qquad -PdV = -24.5 \text{ L atm}, \Delta U = -370.0 \text{ kJ}$$

The volume of H_2 generated at 1 atm is 24.5 L. So there is a small difference between ΔU to ΔH.

- ΔH is slightly less negative than ΔU since the system did the expansion work when H_2 was generated (so some of the internal energy released is to do work.)

- In general, the difference between ΔU and ΔH for reactions, involving gases is $\Delta(PV) = \Delta nRT$ (constant T).

- However, in reaction only involving the condensed states, the changes inn volume are minimal so
$$\Delta U \cong \Delta H$$

Example 1. *Calculate ΔH and ΔU for the transformation of 1.00 mol of an ideal gas from $27.0° C$ and 1.00 atm to $327° C$ and 17.0 atm if*
$$C_{P,m} = 20.9 + 0.042\frac{T}{K}$$
in the units of J/K mol. For an ideal gas, calculate ΔH.

Solution 1. Using the equation
$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

We have
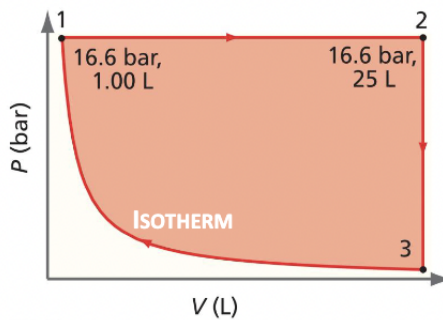$$\Delta H = \int_{T_1}^{T_2} C_{P,m} \times ndT = \int_{300}^{600} 20.9 + 0.042T dT = \left[20.9T + \frac{0.042}{2}T^2 \right]_{300}^{600}$$
$$= 11.9 \text{ kJ}$$

ΔU is calculated by using
$$\Delta U = \Delta H - \Delta(PV) = \Delta H - nR\Delta T = 11900 - (8.314)(300) = 9.45 \times 10^3 \text{ J}$$

Example 2 (*). *Calculate q, W, ΔU and ΔH for each segment and for the cycle assuming that the heat capacity is independent of temperature:*

$$C_{V,m} = 20.79 \ J/mol \ K \qquad n = 2.50 \ mol \qquad T = T_1 = T_3$$

Solution 2. Let $\vec{A} = \begin{pmatrix} 1.00 \ \text{L} \\ 16.6 \ \text{bar} \end{pmatrix}$ to $\vec{B} = \begin{pmatrix} 25.0 \ \text{L} \\ 16.6 \ \text{bar} \end{pmatrix}$, then at constant pressure:

$$\Delta U_{AB} = nC_V \Delta T = C_{V,m} \left(\frac{P_2 V_2}{R} - \frac{P_1 V_1}{R} \right)$$

and so

$$\Delta U_{AB} = \frac{20.79}{0.08314} (16.6 \times 25.0 - 16.6 \times 1.00) = 99.6 \ \text{kJ}$$

Then

$$W_{AB} = -P\Delta V = -(16.6)(24.0) \times 100 \times \frac{1}{1000} = -39.8 \ \text{kJ}$$

also,

$$q_{AB} = 99.6 - (-39.8) = 139.4 \ \text{kJ}$$

Finally,

$$\Delta H_{AB} = q_P = 139.4 \ \text{kJ}$$

Next, for the second step, let $\vec{A} = \begin{pmatrix} 1.00 \ \text{L} \\ 16.6 \ \text{bar} \end{pmatrix}$ and $\vec{C} = \begin{pmatrix} 25.0 \ \text{L} \\ P_3 \end{pmatrix}$, then since the volume is constant,

$$W_{BC} = 0$$

Then since

$$\Delta U_{BC} = nC_{V,m}(T_3 - T_2)$$

We have $T_1 = T_3$, and so

$$\Delta U_{BC} = -\Delta U_{AB} = -99.6 \ \text{kJ}$$

At constant volume,

$$q = \Delta U_{BC} = -99.6 \ \text{kJ}$$

and so

$$\Delta H_{BC} = nC_{P,m}(T_3 - T_2) = -\Delta H_{AB} = -139.4 \ \text{kJ}$$

Lastly for the last step, if $\vec{C} = \begin{pmatrix} 25 \\ P_3 \end{pmatrix}$ and $\vec{A} = \begin{pmatrix} 1.00 \\ 16.6 \end{pmatrix}$, we have that

$$\Delta U_{CA} = 0 \qquad \Delta H_{CA} = 0$$

since the temperature is kept constant. Then

$$W_{CA} = -nRT \log \left(\frac{V_1}{V_3} \right) = -(2.50)(8.314) \left(\frac{16.6 \times 1}{2.5 \times 0.08314} \right) \log \left(\frac{1}{25} \right) = 5.35 \ \text{kJ}$$

and $q_{CA} = -5.35 \ \text{kJ}$.

Assume the cylinder is thermally isolated, so there is no heat exchange during the expansion. Therefore, T drops in the expansion and $q = 0$. Then

$$dU = d(q + W) = dq + dW = -P_{ext}dV$$

If the process is reversible we can replace P_{ext} with P_{int}.

$$dW = -P_{int}dV = -PdV = -\frac{nRT}{V}dV$$

Then

$$dU = dW = -PdV = -\frac{nRT}{V}dV$$

$$\frac{dU}{nT} = -R\frac{dV}{V} \tag{or}$$

$$\frac{dU}{nT} = \frac{C_V dT}{nT} = \bar{C}_V\frac{dT}{V} = -R\frac{dV}{V} \tag{since}$$

$$\int_{T_1}^{T_2} \bar{C}_V\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V} \tag{divide both sides with nT}$$

$$\bar{C}_V \log\left(\frac{T_2}{T_2}\right) = R\log\left(\frac{V_1}{V_2}\right) \tag{Integration between initial and final states}$$

Note: This is done since we are dealing with separable differential equations.

Then since $\bar{C}_P - \bar{C}_V = R$ for an ideal gas,

$$\bar{C}_V \log\left(\frac{T_2}{T_1}\right) = (\bar{C}_P - \bar{C}_V)\log\left(\frac{V_1}{V_2}\right)$$

Divide both sides by C_V to obtain

$$\log\left(\frac{T_2}{T_1}\right) = \left(\frac{\bar{C}_P}{\bar{C}_V} - 1\right)\log\left(\frac{V_1}{V_2}\right) = (\gamma - 1)\log\left(\frac{V_1}{V_2}\right) = \log\left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

where

$$\frac{\bar{C}_P}{\bar{C}_V} = \gamma$$

For monatomic gases,

$$\bar{C}_V = \frac{3R}{2} \qquad \bar{C}_P = \bar{C}_V + R\frac{5R}{2}$$

Therefore,

$$\gamma = \frac{5}{3}$$

For diatomic gas molecules,

$$\bar{C}_V \approx \frac{5R}{2} \qquad \bar{C}_P = \bar{C}_V + R = \frac{7R}{2}$$

Therefore,

$$\gamma \approx \frac{7}{5}$$

Given that

$$\log\left(\frac{T_2}{T_1}\right) = \log\left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

Taking the exponential on both sides of the equation

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

$$\left(\frac{V_1}{V_2}\right)^{\gamma} = \frac{P_2}{P_1} \tag{since $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$}$$

or

$$P_1V_1^\gamma = P_2V_2^\gamma$$

Alternatively, divide both sides by nR (multiply by $\frac{T}{PV}$)

$$P_1V_1^\gamma \left(\frac{T_1}{P_1V_1}\right) = P_2V_2^\gamma \left(\frac{t_2}{P_2V_2}\right)$$

Then

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

Alternatively, divide both sides by $(nR)^\gamma$ (multiply by $(\frac{T}{PV})^\gamma$)

$$P_1V_1^\gamma \left(\frac{T_1}{P_1V_1}\right)^\gamma = P_2V_2^\gamma \left(\frac{T_2}{P_2V_2}\right)^\gamma$$
$$P_1^{1-\gamma}T_1^\gamma = P_2^{1-\gamma}T_2^\gamma$$

Raise both sides to to $\frac{1}{\gamma}$th power

$$T_1P_1^{\frac{1-\gamma}{\gamma}} = T_2P_2^{\frac{1-\gamma}{\gamma}}$$