

show: $\Delta H = q_p$

enthalpy, H, is defined as:

$$H = U + PV$$

"taking the derivative" [actually, should evaluate the "differential"]

$$\begin{aligned}dH &= dU + d(PV) \\ &= dU + PdV + VdP\end{aligned}\quad [1].$$

For a constant pressure process, $dP = 0$; thus [1] becomes

$$dH = dU + PdV \quad [2].$$

Work, W, is defined as:

$$\begin{aligned}W &= - F * x \\ \text{or } dW &= - F dx\end{aligned}\quad [3]$$

where F = (constant) force and x= displacement.

Pressure, P, is defined as:

$$\begin{aligned}P &= F / A \\ \text{or } F &= P A\end{aligned}\quad [4]$$

substituting [4] into [3],

$$dW = - P A dx = - P dV \quad [5]$$

substituting [5] into [2],

$$dH = dU - dW \quad [6].$$

The 1st law of thermodynamics,

$$dU = dq + dW \quad [7]$$

substituting [7] into [6],

$$dH = (dq + dW) - dW$$

$$dH = dq$$

$$\int dH = \int dq$$

hence,

$$\Delta H = q_p$$

where q_p = heat under constant pressure conditions.

aside: w, work (in the compression of a gas)

in the preceding analysis, F, force was treated as a constant. in a subsequent analysis, F will be treated as a variable, which is a function of x (or V).

$$\text{work, } W = - \int_i^f F(x) dx \quad [1]$$

where $F(x)$ = force as a function of x.

As pressure,

$$P = F / A$$

solving for F,

$$F = P A \quad [2]$$

substituting [2] into [1],

$$\begin{aligned} W &= - \int_i^f P(x) A dx \\ &= - \int_i^f P(V) dV \end{aligned} \quad [3]$$

where $P(x)$ = pressure as a function of x
 $P(V)$ = pressure as a function of V
 $dV = A dx$.

Based on the ideal gas equation,

$$PV = n R T$$

solving for P

$$P = \frac{n R T}{V} \quad [4]$$

substituting [4] into [3],

$$\begin{aligned} W &= - \int_i^f \frac{n R T}{V} dV \\ &= - n R T \int_i^f \frac{1}{V} dV \\ &= - n R T \ln \left(\frac{V_f}{V_i} \right) \\ &= n R T \ln \left(\frac{V_i}{V_f} \right). \end{aligned}$$

note: in the compression of a gas, as $V_f < V_i$, $W > 0$.

show: $\Delta G < 0$ for a spontaneous process.

The 2nd law of thermodynamics states that for a spontaneous process,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \quad [1].$$

As

$$q_{\text{system}} = - q_{\text{surrounding}}$$

and at constant pressure (see above),

$$q_{\text{system}} = \Delta H$$

thus

$$q_{\text{surrounding}} = - \Delta H.$$

Dividing by T and using the definition of ΔS ,

$$\Delta S_{\text{surrounding}} = q_{\text{surrounding}} / T = - \Delta H / T \quad [2]$$

substituting [2] into [1],

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + - \Delta H / T > 0$$

multiplying by - T,

$$- T \Delta S_{\text{universe}} = - T \Delta S_{\text{system}} + \Delta H < 0.$$

Defining the change in Gibbs Free Energy as:

$$\Delta G = - T \Delta S_{\text{universe}}$$

substituting and rearranging,

$$\Delta G = \Delta H - T \Delta S < 0 \text{ for a spontaneous process.}$$