The Thermodynamic Properties Enthalpy, Entropy & Gibbs Function

Enthalpy

The property enthalpy arises from use of the First Law of Thermodynamics when applied to certain processes.

To demonstrate its origin, consider a piston containing a fixed quantity of gas, which expands (in quasi-equilibrium) at constant pressure (set by the weight of the piston) thereby changing the state of the gas from state 1 to state 2. Taking the control volume to contain just the gas and neglecting kinetic and potential energy changes of the gas, application of the First Law gives:

$$\mathbf{Q = U_2 - U_1 + W}$$

Where Q is the amount of heat energy entering the gas, W the amount of work done by the gas expanding against the pressure exerted on the gas by the weighted piston and $\boldsymbol{U}$ is the internal energy of the gas at the end states. From Newton's Second Law ($\boldsymbol{F} = \boldsymbol{ma}$) it can be shown that the work done by the gas in expanding (displacement work) is given by:

$$W = \int_1^2 p\partial V$$

Where p is the pressure of the gas and V the volume of gas. Since the pressure is constant,

$$\boldsymbol{W = p\int_1^2 \partial V = p(V_2 - V_1)}$$

Therefore,

$$\mathbf{Q = U_2 - U_1 + p_2V_2 - p_1V_1}$$

$$\mathbf{= (U_2 + p_2V_2) - (U_1 + p_1V_1)}$$

Hence we see that, in this specific case, the heat transferred during the expansion process is given by the change in the quantity $\boldsymbol{U + pV}$ between the initial and final states. As $\boldsymbol{U}$, $\boldsymbol{p}$ and $\boldsymbol{V}$ are thermodynamic properties, their combination is also a thermodynamic property. This combination is called Enthalpy.

$$\mathbf{H = U + pV}$$

Though the result, that the change in enthalpy is equal to the change in internal energy plus the expansion work done, is restricted to this specific case of constant pressure quasi-equilibrium expansion; the property enthalpy can always be defined and therefore used if we find it convenient to group $\boldsymbol{U}$, $\boldsymbol{p}$ and $\boldsymbol{V}$ in this manner.

When values of enthalpy (as opposed to differences in enthalpy between states) are quoted they are always relative to an arbitrarily chosen reference state, thus when performing calculations it is important that a consistent reference state is used and that the thermodynamic implications of that reference state understood. See *Enthalpy Change of an Ideal Gas*

Reference:

[1] R.E. Sonntag & G.J. Van Wylen, Introduction to Thermodynamics, John Wiley & Sons, Inc, 1991.