

Enthalpy Change of an Ideal Gas

Enthalpy Change with Pressure

Using the definition of Enthalpy:

$$h = u + pv \quad (1)$$

With the ideal gas equation of state:

$$pv = RT \quad (2)$$

Gives:

$$h = u + RT \quad (3)$$

Since u is a function of temperature only (demonstrated experimentally by Joule in 1843, or shown using classical thermodynamics) and R is constant, it follows that ideal gas enthalpy is independent of pressure

Enthalpy Change with Temperature

Using the definition of C_p :

$$C_p = \left(\frac{\partial h}{\partial T} \right)_p \quad (4)$$

and noting that h of an ideal gas is independent of pressure gives:

$$dh = C_{p_o} dT \quad (5)$$

Integrating,

$$h_2 - h_1 = \int_1^2 C_{p_o} dT \quad (6)$$

where T is temperature (K), p is pressure (Pa), h is enthalpy (J/kg) and C_p is constant pressure heat capacity (J/kg K). Note that the 'o' on C_p indicates ideal gas 'zero pressure' value.

Calculating Enthalpy

In order to use these relations in situations involving a temperature change, we must determine how the specific heat varies with temperature. The choices available are as follows:

1. Take heat capacities to be constant – this is a fair approximation for monatomic gases, as their enthalpy and internal energy are primarily determined by translational and rotational modes of motion which are linearly dependent on temperature; but is less appropriate for polyatomic molecules for which vibrational and rotational modes (of non-axis-symmetric molecules), which depend more strongly on temperature are significant.
2. Use a correlation to describe the variation of heat capacity with temperature. Empirical correlations are available for most gases of interest over most operating ranges of interest, and reasonably accurate semi-empirical estimation techniques available in most other cases. See ‘*Materials Section*’.
3. Use statistical mechanics to determine the value of $\int_1^2 C_{p_o} dT$ from a reference temperature to any other temperature, thus bypassing the need for C_p data. According to [1] this is the most accurate method, though it depends on the quality of the data available for specific applications.

Enthalpy Reference Point

There is no law dictating the appropriate reference state for enthalpy calculations. Some tabulations, by analogy to entropy data, use 0K. However this is not always convenient as the appropriate choice of enthalpy reference point can greatly simplify calculations involving chemical reactions. To illustrate consider a mixture of CO₂, CO, H₂O and H₂. If one were to take 0K as the reference point of each species, that is $h = \int_{0K}^T C_{p_o} dT$, then as long as there were no chemical reactions one could readily calculate the thermally induced enthalpy changes by summing the change in each components enthalpy. But if the water gas shift reaction were to take place and the composition were to change then one would require additional information (the enthalpy of reaction) to link thermodynamically unrelated reference points. However if the enthalpy of all species were instead measured relative to the same reference state – elements at 0.1MPa and 298.15K, the enthalpy of each species would include the enthalpy of reaction. This is the method adopted by JANAF. Data can be found in *Thermodynamic Data*.

Reference:

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

