# Helmholtz free energy

Consider a fluid system at thermodynamic equilibrium. Assume that we know how to express the Helmholtz free energy as a function of the temperature, volume and the array of mole numbers of all the constituent chemical species. That is, assume that we know the function:

|  |  |  |
| --- | --- | --- |
|  |  | (1) |

It can be shown that this function contains all thermodynamic information about the system. We say that the *thermodynamic state* is uniquely determined by and the relationship (1). We therefore call (1) a *fundamental thermodynamic relationship*. (Callen 1985). Other fundamental relationship exist, such as the Gibbs free energy as a function of , where is the pressure.

In the following, we shall consider systems consisting of a single species. Then it is useful to consider molar properties and and we can express (1) as:

|  |  |  |
| --- | --- | --- |
|  |  | (2) |

# Thermodynamic properties from Helmholtz free energy

Denote the partial derivatives of by the shorthand notation

|  |  |  |
| --- | --- | --- |
|  |  | (3) |

Higher derivatives follow the same pattern, e.g.

|  |  |  |
| --- | --- | --- |
|  |  | (4) |

Note that the order of differentiation has no effect, so that

|  |  |  |
| --- | --- | --- |
|  |  | (5) |

and

|  |  |  |
| --- | --- | --- |
|  |  | (6) |

For a homogenous system all thermodynamic variables can be expressed as an explicit function of the partial derivatives of . An explicit function is one that requires no iterative procedures.

All these derivatives assume that the independent variables are . We may also differentiate with respect to other variables, such as pressure and enthalpy . The partial derivative of using as independent variables we denote by . The first of these we may express as “The partial derivative of z with respect to x, keeping y constant”.

Molar properties expressed in terms of the partial derivatives of :

|  |  |  |
| --- | --- | --- |
| **Property** | **Symbol** | **Expression** |
| Entropy |  |  |
| Pressure |  |  |
| Internal energy |  |  |
| Enthalpy |  |  |
| Heat capacity at constant volume |  |  |
| Heat capacity at constant pressure |  |  |
| Speed of sound |  |  |
| Joule-Thompson coefficient |  |  |
| Coefficient of thermal expansion |  |  |
| Isothermal compressibility |  |  |
| Adiabatic compressibility |  |  |

The expressions above are all found in, or developed from, expressions in (Callen 1985).

Note that none of the properties in the table require partial derivatives of degree higher than 2. However, the efficient solution of some problems requires the derivatives of some of those properties. This may involve third derivatives of .

**Transport properties** such as viscosity and thermal conductivity are not proper thermodynamic variables. They cannot be derived from , but need separate models.

# Explicit model for Helmholtz free energy

For hydrogen (H2) Leachman and co-workers have developed a very accurate model that gives a somewhat complex, but explicit, expression for Helmholtz free energy as a function of temperature and molar volume (Leachman 2009). From this it is (relatively) straight-forward to find explicit expressions for the partial derivatives. As long as are known, all partial derivatives and thermodynamic variables may thus be calculated very quickly.

## Solving problems using independent variables other than

In many practical cases are not known. Then we must solve one or two nonlinear equations to find the corresponding values of and thus the thermodynamic state.

**Example 1: Temperature and pressure are known**.

In order to find the remaining thermodynamic variables we must solve:

|  |  |  |
| --- | --- | --- |
|  |  | (7) |

The fact that we have explicit expressions for the relevant partial derivatives of Helmholtz free energy lets us solve the problem efficiently and accurately by Newton’s method. Note that

|  |  |  |
| --- | --- | --- |
|  |  | (8) |

So the iteration scheme for Newton’s method becomes:

|  |  |  |
| --- | --- | --- |
|  |  | (9) |

The partial derivatives must be calculated at at each iteration step. A good initial value for may be often be the ideal gas value:

|  |  |  |
| --- | --- | --- |
|  |  | (10) |

In some cases other initial values may be better. This may be the case for the liquid phase or at very high pressures,

**Example 2: Isentropic (adiabatic) compression**

Let the initial state be specified by temperature and pressure . We wish to find the thermodynamic state after an adiabatic change (compression or expansion) pressure to . In a reversible and adiabatic pressure change, entropy is conserved, so we know that the molar entropy remains at the initial value . We must first solve (7) to find the initial molar volume and thus . Next, let denote the vector . We must now solve the two simultaneous equations:

|  |  |  |
| --- | --- | --- |
|  |  | (11) |

The Jacobian of is:

|  |  |  |
| --- | --- | --- |
|  |  | (12) |

So Newton’s method becomes

|  |  |  |
| --- | --- | --- |
|  |  | (13) |

The ideal gas expressions and , where may often give a good initial value for .

# Two-phase system

Hydrogen may exist in the liquid phase at temperatures between the triple point and critical temperatures (13.95K and 33.145K, respectively). Leachman and co-workers present an expression for the saturation pressure as a function of temperature. This expression is compatible with the expression for the Helmholtz free energy. To find the thermodynamic state for the saturated vapour and liquid at temperature we must solve

|  |  |  |
| --- | --- | --- |
|  |  | (14) |

In the two-phase region this equation has three or more solutions. The solution with the lowest value for represents the liquid phase and the highest value represents the vapour phase. Denote the two solutions as and . The properties can be found from the partial derivatives of and , respectively.

For the model pressure has no physical interpretation. The system is then a mixture of vapour and liquid, and the pressure is given by the saturation pressure. This is illustrated in Figure 1.

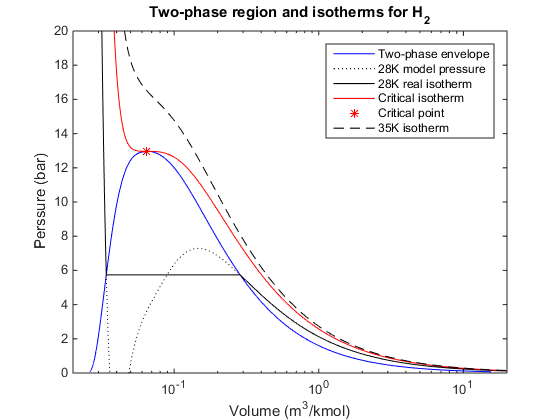


Figure 1: Two-phase, critical and supercritical isotherms

# Other partial derivatives

|  |  |  |
| --- | --- | --- |
|  |  | (15) |

For an Isentropic process: :

|  |  |  |
| --- | --- | --- |
|  |  | (15) |

So, for an isentropic process,

|  |  |  |
| --- | --- | --- |
|  |  | (17) |

So

|  |  |  |
| --- | --- | --- |
|  |  | (18) |

# Bibliography

Callen, Herbert C. *Thermodynamics and an Introduction to Thermostatistics.* John Wiley and Sons, 1985.

Leachman, J.W. & al. “Fundamental Equations of State for Parahydrogen, Normal Hydrogen, and Orthohydrogen.” *Journal of Physical and Chemical Reference Data A*, 2009: 721-784.