

# Properties from Helmholtz

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## Helmholtz free energy

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

$$F(T, V, \mathbf{N}) \quad (1)$$

It can be shown that this function contains all thermodynamic information about the system. We say that the *thermodynamic state* is uniquely determined by  $T, V, \mathbf{N}$  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  $T, p$ , and  $\mathbf{N}$ , where  $p$  is the pressure. (Note that transport properties such as viscosity and thermal conductivity are not thermodynamic properties and **cannot** be derived from  $F$ , but require separate models.)

In the following, we shall consider systems consisting of a single species. Then it is useful to consider molar properties  $f = F/N$  and  $v = V/N$  and we can express (1) as:

$$f(T, v) \quad (2)$$

## Thermodynamic properties from Helmholtz free energy

Denote the partial derivatives of  $f$  by the shorthand notation

$$f_T \equiv \frac{\partial f}{\partial T}, \quad f_v \equiv \frac{\partial f}{\partial v} \quad (3)$$

Higher derivatives follow the same pattern, e.g.

$$f_{TTv} \equiv \frac{\partial^3 f}{\partial T^2 \partial v} \quad (4)$$

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

$$f_{Tv} = f_{vT} \quad (5)$$

and

$$f_{TTv} = f_{TvT} = f_{vvT} \quad (6)$$

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

All these derivatives assume that the independent variables are  $(T, v)$ . We may also differentiate with respect to other variables, such as pressure and enthalpy  $(p, h)$ . The partial derivative of  $z$  using  $(x, y)$  as independent variables we denote by  $\left(\frac{\partial z}{\partial x}\right)_y$  and  $\left(\frac{\partial z}{\partial y}\right)_x$ . 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 $f(T, v)$ :

Property	Symbol	Expression
Entropy	$s$	$s = -f_T$
Pressure	$p$	$p = -f_v$
Internal energy	$u$	$u = f + Ts = f - Tf_T$
Enthalpy	$h$	$h = u + pv = f - Tf_T - vf_v$
Heat capacity at constant volume	$c_v$	$c_v = -Tf_{TT}$
Heat capacity at constant pressure	$c_p$	$c_p = c_v + T\frac{f_{Tv}^2}{f_{vv}}$
Speed of sound	$c$	$c^2 = \frac{v^2}{M_w} \left( f_{vv} - \frac{f_{Tv}^2}{f_{TT}} \right)$
Joule-Thompson coefficient	$\mu_{JT}$	$\mu_{JT} \equiv \left( \frac{\partial T}{\partial p} \right)_h = -\frac{T\frac{f_{Tv}}{f_{vv}} + v}{c_p}$
Coefficient of thermal expansion	$\alpha$	$\alpha \equiv \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = -\frac{1}{v} \frac{f_{Tv}}{f_{vv}}$
Isothermal compressibility	$\beta_T$	$\beta_T = \frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T = -\frac{1}{vf_{vv}}$
Adiabatic compressibility	$\beta_s$	$\beta_s = \frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_s = \beta_T - \frac{Tv\alpha^2}{c_p}$

The expressions above are all found in (Callen 1985) or derived from expressions found there.

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  $f$ .

## Solving problems using independent variables other than $T$ and $v$

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

This may require partial derivatives keeping other variables constant than  $T$  and/or  $v$ . We derive expressions for the partial derivatives  $\left(\frac{\partial T}{\partial v}\right)_s$  and  $\left(\frac{\partial p}{\partial v}\right)_s$  as examples. Other derivatives may require other techniques. See (Callen 1985) for more examples.

With  $T$  and  $v$  as independent variables the differential  $ds$  is:

$$ds = \frac{\partial s}{\partial T} dT + \frac{\partial s}{\partial v} dv \quad (7)$$

For an isentropic process:  $ds = 0$ . So:

$$\left(\frac{\partial T}{\partial v}\right)_s = -\frac{\frac{\partial s}{\partial v}}{\frac{\partial s}{\partial T}} \quad (8)$$

Likewise:

$$dp = \frac{\partial p}{\partial T} dT + \frac{\partial p}{\partial v} dv \quad (9)$$

With  $v$  and  $s$  as independent variables:

$$dT = \left(\frac{\partial T}{\partial v}\right)_s dv + \left(\frac{\partial T}{\partial s}\right)_v ds \quad (10)$$

Inserting for  $dT$  in (9) and setting  $ds = 0$ :

$$dp = \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial T}{\partial v}\right)_s dv + \frac{\partial p}{\partial v} dv \quad (11)$$

Using the expression for  $\left(\frac{\partial T}{\partial v}\right)_s$  from (8):

$$\left(\frac{\partial p}{\partial v}\right)_s = -\frac{\partial p}{\partial T} \frac{\frac{\partial s}{\partial v}}{\frac{\partial s}{\partial T}} + \frac{\partial p}{\partial v} \quad (12)$$

## Examples

**Example 1: Temperature  $T = T_0$  and pressure  $p = p_0$  are known.**

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

$$g(v) \equiv p(T_0, v) - p_0 = 0 \quad (13)$$

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

$$\frac{dg}{dv} = \frac{\partial p}{\partial v} = -f_{vv} \quad (14)$$

So the iteration scheme for Newton's method becomes:

$$v_{i+1} = v_i - \frac{g(v_i)}{-f_{vv}} = v_i - \frac{-f_v - p_0}{-f_{vv}} \quad (15)$$

The partial derivatives must be calculated at  $T_0$  and  $v_i$  at each iteration step. A good initial value for  $v$  may be often be the ideal gas value:

$$v_{init} = RT_0/p_0 \quad (16)$$

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  $T_0$  and pressure  $p_0$ . We wish to find the thermodynamic state after an adiabatic change (compression or expansion) pressure to  $p_1$ . In a reversible and adiabatic pressure change, entropy is conserved, so we know that the molar entropy remains at the initial value  $s_0$ . We must first solve (13) to find the initial molar volume  $v_0$  and thus  $s_0$ . Next, let  $\mathbf{x}$  denote the vector  $\begin{bmatrix} T \\ v \end{bmatrix}$ . We must now solve the two simultaneous equations:

$$\mathbf{G}(\mathbf{x}) \equiv \begin{bmatrix} s(\mathbf{x}) - s_0 \\ p(\mathbf{x}) - p_1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad (17)$$

The Jacobian of  $\mathbf{G}$  is:

$$\mathbf{J} = \begin{bmatrix} \frac{\partial s}{\partial T} & \frac{\partial s}{\partial v} \\ \frac{\partial p}{\partial T} & \frac{\partial p}{\partial v} \end{bmatrix} = \begin{bmatrix} -f_{TT} & -f_{Tv} \\ -f_{Tv} & -f_{vv} \end{bmatrix} \quad (18)$$

So Newton's method becomes

$$\mathbf{x}_{i+1} = \mathbf{x}_i - \mathbf{J}^{-1} \mathbf{G}(\mathbf{x}_i) \quad (19)$$

The ideal gas expressions  $T_1 = T_0 \left( \frac{p_1}{p_0} \right)^{\frac{\gamma-1}{\gamma}}$  and  $v_1 = v_0 \left( \frac{p_0}{p_1} \right)^{\frac{1}{\gamma}}$ , where  $\gamma = \frac{c_p}{c_v}$  may often give a good initial value for  $\mathbf{x}$ .

## Two-phase system example

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  $p_{sat}(T)$  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  $T_s$  we must solve

$$g(v) \equiv p(T_s, v) - p_{sat}(T_s) = 0 \quad (20)$$

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

For  $v_l < v < v_v$  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.

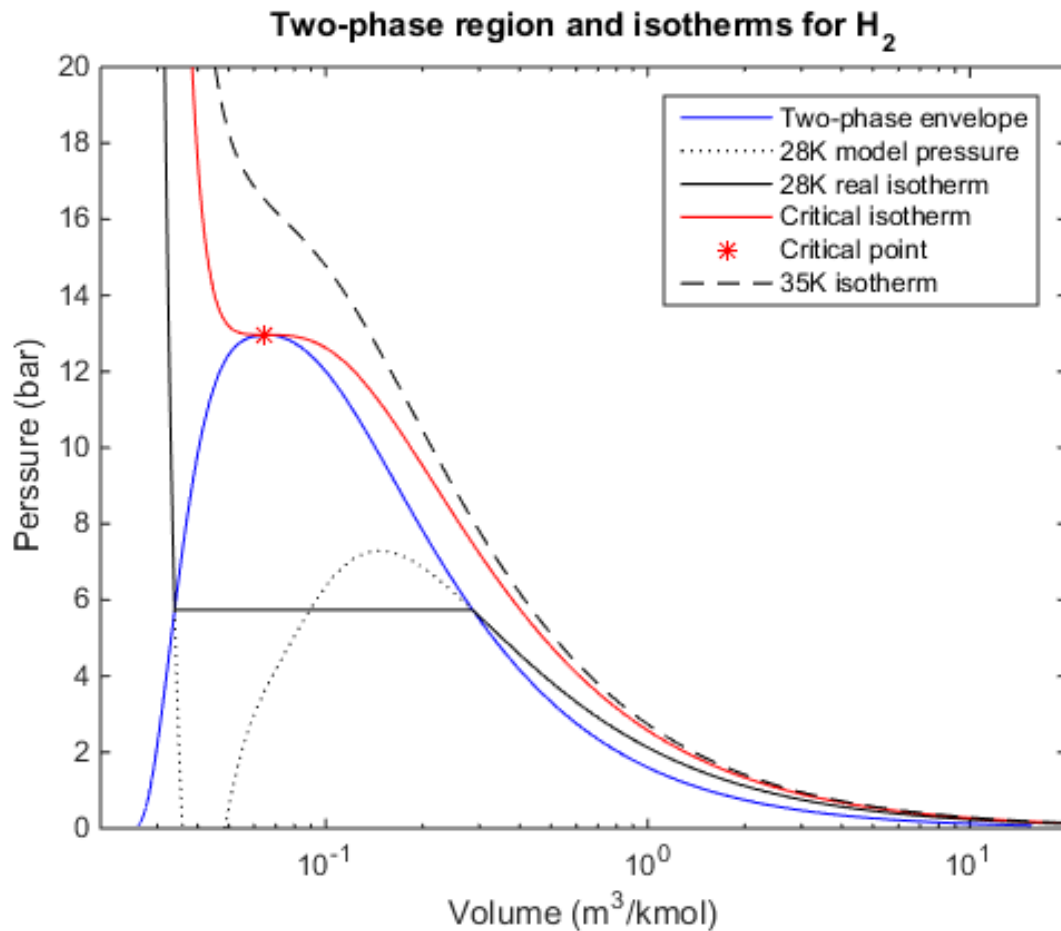


Figure 1: Two-phase, critical and supercritical isotherms

### Explicit models for Helmholtz free energy

High-accuracy models for the Helmholtz free energy as a function of temperature and molar volume have been published for several species:

- CO<sub>2</sub> : Span and Wagner (Span 1996).
- H<sub>2</sub>O: Wagner and Pruss (W. Wagner 2002).
- H<sub>2</sub>: Leachman and co-workers (Leachman 2009).

All three models have the same basic structure and can use the same calculation routine. It is (relatively) straight-forward to find explicit expressions for the partial derivatives with respect to  $T$  and  $v$ . As long as  $T$  and  $v$  are known, all partial derivatives and thermodynamic variables may thus be calculated very quickly.

### Bibliography

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