Reduction and Evaluation of Thermodynamics Partial Derivatives

Reduction Process: Will produce a relationship for a thermodynamic derivative that only depends on T, P, v, κ_T, β, c_P, $\left(\frac{\partial c_P}{\partial T}\right)_P$, $\left(\frac{\partial \beta}{\partial P}\right)_T$, $\left(\frac{\partial \beta}{\partial T}\right)_P$, and $\left(\frac{\partial \kappa_T}{\partial P}\right)_T$. Note that the reduction is completely general and does not depend on the substance.

Evaluation Process: Uses the reduced form for the thermodynamic partial derivative with the equations of state for the substance of interest to produce a relationship with only T, P and constants present.

Basic Definitions

Specific heat at constant pressure: $c_P = T\left(\frac{\partial s}{\partial T}\right)_P$

Thermal expansion coefficient: $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$

Isothermal compressibility: $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$

Defining Differential Equations

Internal energy: $du = Tds - Pdv$

Enthalpy: $dh = Tds + vdP$

Gibbs free energy: $dg = -sdT + vdP$

Helmholtz potential: $df = -sdT - Pdv$

Base First Order Derivatives

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_P}{T} \qquad \left(\frac{\partial s}{\partial P}\right)_T = -v\beta$$

$$\left(\frac{\partial v}{\partial T}\right)_P = v\beta \qquad \left(\frac{\partial v}{\partial P}\right)_T = -v\kappa_T$$

Base Second Order Derivatives

$$\left(\frac{\partial c_P}{\partial T}\right)_P \qquad \left(\frac{\partial \beta}{\partial P}\right)_T$$

$$\left(\frac{\partial \beta}{\partial T}\right)_P \qquad \left(\frac{\partial \kappa_T}{\partial P}\right)_T$$

Rules for Jacobian Manipulation

Notation:
$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{vmatrix}$$

If v = y, then $\frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial u}{\partial x}\right)_y$

Element interchange:
$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}$$

Chain rule:
$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(r,s)} \cdot \frac{\partial(r,s)}{\partial(x,y)}$$

Reciprocity:
$$\frac{\partial(u,v)}{\partial(x,y)} = \left[\frac{\partial(x,y)}{\partial(u,v)}\right]^{-1}$$

Steps for Reduction of First Order Thermodynamic Partial Derivative

Step 1: If the derivative consists of a thermodynamic potential or the internal energy, bring it to the numerator using Jacobian manipulations and eliminate it by use of the appropriate defining differential equation.

EXAMPLE: Given $\left(\frac{\partial g}{\partial P}\right)_v$, we use dg = -sdT + vdP to find that

$$\left(\frac{\partial g}{\partial P}\right)_v = -s\left(\frac{\partial T}{\partial P}\right)_v + v\left(\frac{\partial P}{\partial P}\right)_v = -s\left(\frac{\partial T}{\partial P}\right)_v + v.$$

Step 2: Write the derivative in Jacobian notation.

EXAMPLE: $\left(\frac{\partial T}{\partial P}\right)_v = \frac{\partial(T,v)}{\partial(P,v)}$

Step 3: Introduce P and T as the independent variables.

EXAMPLE: $\frac{\partial(T,v)}{\partial(P,v)} = \frac{\partial(T,v)}{\partial(P,T)} \div \frac{\partial(P,v)}{\partial(P,T)}$

Step 4: Transform the Jacobians back to partial derivatives using either element interchange or calculating the determinant.

EXAMPLE: $\frac{\partial(P,v)}{\partial(P,T)} = \frac{\partial(v,P)}{\partial(T,P)} = \left(\frac{\partial v}{\partial T}\right)_P$

Step 5: Using the definition of the base first order derivatives relate the partial to measurable quantities.

EXAMPLE: $\left(\frac{\partial v}{\partial T}\right)_P = v\beta$

References for further study

1. A.N. Shaw, "The derivation of thermodynamical relations for a simple system", **Philosophical Transactions of the Royal Society of London**, Ser. A., vol. 234, pp. 299-328.

2. C.W. Somerton and Ö.A. Arnas, "On the use of Jacobians to reduce thermodynamic derivatives", **International Journal of Mechanical Engineering Education**, vol. 13, pp. 9-18.