Thermochimica Acta, 12 (1975) 317–322

MAXWELL'S RELATION FOR UNIVARIANT THERMODYNAMIC SYSTEMS

T. KNUDSEN
Concrete Research Laboratory Karlstrup, DK2690 Karlslunde (Denmark)
(Received 13 March 1975)

ABSTRACT

In textbooks on thermodynamics the Maxwell relation:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

and Clapeyron's equation:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}$$

are commonly arrived at from different points of views, and considered in different contexts.

It is felt by the author, that by realizing the validity of the Maxwell relation for univariant systems, a more general way of attack can be advanced, in which Clapeyron's equation is a special case of the Maxwell relation.

INTRODUCTION

The thermodynamic systems, that we shall consider in the following, are closed systems with internal equilibrium, i.e., systems with equality in all the potentials T, P and μ.

For such systems we can write for the differential of the Helmholtz free energy A:

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V \tag{1}$$

This is an exact differential, and the Maxwell relation can be derived by differentiating A twice with respect to T and V, and by recognizing that the order of differentiation is immaterial:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{2}$$

In textbooks on thermodynamics this relation (together with the other three) is often left as it is, with relevance only to one-phase-systems having an equation of state:

$$P = \mathrm{F}(T, V) \tag{3}$$

By recognizing the validity of the Maxwell relation (2) for systems of but one degree of freedom, i.e., systems consisting of $s-1$ components distributed among s phases, this equation can be made the starting point for the derivation of such important thermodynamic equations as the Clapeyron equation, the equation for the temperature dependence of the vapour pressure of saturated solutions, the temperature dependence of the equilibrium pressure for the large group of equilibria like:

$$\mathrm{A(solid)} \rightleftarrows \mathrm{B(solid)} + \mathrm{C(gas)} \tag{4}$$

and others.

We therefore state, that the Maxwell relation (2) is indeed valid for univariant systems, i.e., systems having an equation of state:

$$P = \mathrm{F}(T) \tag{5}$$

and for these systems it should be written:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \left(\frac{\partial S}{\partial V}\right)_T \tag{6}$$

THE THERMODYNAMIC EQUATION OF STATE FOR UNIVARIANT SYSTEMS

In the following we shall derive a general equation for univariant systems, by relating the right-hand side of eqn (6) to thermodynamic functions of the single phases.

Thus let us number the $s-1$ components by the index i, and the s phases by the index j. n_j is the number of moles of phase j, and X_{ij}, S_{ij} and V_{ij} are the mole fraction, the differential molar entropy and the differential molar volume of component i in phase j. The entropy S_j and the volume V_j are defined according to:

$$\begin{aligned} S_j &= \sum_i S_{ij} \cdot X_{ij} \\ V_j &= \sum_i V_{ij} \cdot X_{ij} \end{aligned} \tag{7}$$

The entropy and the volume of the whole system can be found by:

$$\begin{aligned} S &= \sum_j S_j \cdot n_j \\ V &= \sum_j V_j \cdot n_j \end{aligned} \tag{8}$$

In order to find the partial derivative $(\partial S/\partial V)_T$ we consider a differential change of the system whereby the temperature T is kept constant.

The differentials of S and V are found by:

$$\begin{aligned} \mathrm{d}S &= \sum_j S_j \cdot \mathrm{d}n_j \\ \mathrm{d}V &= \sum_j V_j \cdot \mathrm{d}n_j \end{aligned} \tag{9}$$

as all the $\mathrm{d}S_j$'s and the $\mathrm{d}V_j$'s are equal to zero by virtue of the constancy of the temperature.

We now define a compositional matrix $\mathbf{M}$ $(s \times s)$:

$$\mathbf{M} = \left\{ \begin{matrix} X_{11} & \dots & X_{1s} \\ X_{21} & \dots & X_{2s} \\ \vdots & & \\ X_{s-1,1} & \dots & X_{s-1,s} \\ C \dots & C \dots & C \end{matrix} \right\} \tag{10}$$

where the X_{ij} is the mole fraction of component i in phase j, and C is any number different from zero.

If $\mathbf{N}$ is a column matrix $(s \times 1)$ with elements n_j, the number of moles of phase j, and $\mathbf{0}$ a column matrix of zeroes, it can easily be verified from the closeness of the system, that the following matrix-equation holds:

$$\mathbf{0} = \mathbf{M}\mathrm{d}\mathbf{N} \tag{11}$$

Such a matrix-equation only possesses a non-trivial solution, if the determinant of $\mathbf{M}$ is zero. That this is indeed so in our case, can be seen by the following.

By adding together the first $s-1$ rows of $\mathbf{M}$ we get a new row consisting of elements equal to one, and by multiplying this new row with C, we get the last row of $\mathbf{M}$. This means that the rows of $\mathbf{M}$ are not linearly independent, which again implies that:

$$|\mathbf{M}| = 0 \tag{12}$$

The non-trivial solution thus guarantied, can now be stated:

$$\left\{ \begin{matrix} \mathrm{d}n_1 \\ \mathrm{d}n_2 \\ \vdots \\ \mathrm{d}n_s \end{matrix} \right\} = C \cdot \left\{ \begin{matrix} M^{s1} \\ M^{s2} \\ \vdots \\ M^{ss} \end{matrix} \right\} \tag{13}$$

Here M^{sj} is the cofactor of element M_{sj} in $\mathbf{M}$.

We see from (13) that the system (11) can be solved except for a constant C. This uncertainty as to the absolute value of the dn_j's, which is of course to be expected, is of no importance to us, as we are out for the ratio $(\partial S/\partial V)_T$.

Now inserting (13) into (9) we end up with:

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\sum_j M^{sj} S_j}{\sum_j M^{sj} V_j} \tag{14}$$

or by inserting into the Maxwell relation:

$$\frac{dP}{dT} = \frac{\sum_j M^{sj} S_j}{\sum_j M^{sj} V_j} \tag{15}$$

This equation, which we have called the thermodynamic equation of state for univariant systems, could of course have been arrived at from another point of view, namely by considering a change of the system by which $dT \neq 0$ and by accounting for the changes in the μ_{ij}'s.

Here it is derived from the Maxwell relation by considering a change by which $dT = 0$.

CLAPEYRON'S EQUATION

Clapeyron's equation relates to systems composed of one component in equilibrium between two phases.

The compositional matrix for such systems can be written down immediately:

$$\mathbf{M} = \begin{Bmatrix} 1 & 1 \\ 1 & 1 \end{Bmatrix} \tag{16}$$

Here we have chosen the number 1 as the elements in the last row, for convenience.

Applying now the thermodynamic equation of state for univariant systems (15) gives:

$$\frac{dP}{dT} = \frac{1 \cdot S_1 - 1 \cdot S_2}{1 \cdot V_1 - 1 \cdot V_2} = \frac{\Delta S}{\Delta V} \tag{17}$$

PRESSURE-DEPENDENCE ON TEMPERATURE FOR SATURATED SOLUTIONS

Here we shall consider a most important class of thermodynamic systems, namely saturated solutions of non-volatile solid compounds in a volatile liquid solvent (salts in water, etc.). The solubility of the volatile component in the solids is considered negligible. We number the phases according to: gas = 1, liquid = 2, solid 1 = 3, solid 2 = 4 etc., and the components: volatile comp. = 1, solid 1 = 2, solid 2 = 3 etc.

Now we can write up the compositional matrix:

$$\mathbf{M} = \begin{Bmatrix} 1 & X_{12} & 0 & 0 & \dots & 0 \\ 0 & X_{22} & 1 & 0 & \dots & 0 \\ 0 & X_{32} & 0 & 1 & \dots & 0 \\ \dots & & & & & \\ 0 & X_{s-1,2} & 0 & 0 & \dots & 1 \\ 1 & 1 & 1 & 1 & \dots & 1 \end{Bmatrix} \tag{18}$$

A little scrutiny will reveal that the M^{sj}'s can be written (except for a factor ± 1, which depends on the dimension of the matrix M):

$$M^{s1} = X_{12}, \quad M^{s2} = -1, \quad M^{s3} = X_{22}, \quad M^{s4} = X_{32}, \text{ etc.}$$

Inserting into (15) and a little rearrangement yields:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} S - \sum_{i=2}^{s-1} X_i \Delta_{\mathrm{sol},i} S}{\Delta_{\mathrm{vap}} V - \sum_{i=2}^{s-1} X_i \Delta_{\mathrm{sol},i} V} \tag{19}$$

where the X_i's are the molar ratios:

$$X_i = \frac{X_{i2}}{X_{12}}$$

SOLID–GAS EQUILIBRIA

The following kinds of equilibria are very often encountered:

$$\mathrm{A(solid)} \rightleftharpoons \mathrm{B(solid)} + \mathrm{C(gas)} \tag{20}$$

Examples are:

$$\mathrm{CaCO_3} \rightleftharpoons \mathrm{CaO} + \mathrm{CO_2}$$

$$\mathrm{NaBr \cdot 2H_2O} \rightleftharpoons \mathrm{NaBr} + \mathrm{2H_2O}$$

$$\mathrm{CuO} \rightleftharpoons \mathrm{Cu} + \tfrac{1}{2}\mathrm{O_2}$$

These systems consist of three phases and two components. It is natural to choose the two components as B and C, and consider A the 'mixture' of B and C. Doing this, it is to be emphazised, that the correct way to find the number of moles of A is by:

$$n_{\mathrm{A}} = n_{\mathrm{B}} + n_{\mathrm{C}}$$

which of course will conflict with the usual 'chemical' conception of A as a component.

Numbering the phases: gas 1, solid B = 2 and solid A = 3, and the components C = 1 and B = 2, we can write the compositional matrix:

$$\mathbf{M} = \begin{Bmatrix} 1 & 0 & X_C \\ 0 & 1 & X_B \\ 1 & 1 & 1 \end{Bmatrix} \tag{21}$$

where the mole fractions are to be found according to the conception of A as the mixture of B and C.

We now find the cofactors:

$$M^{31} = -X_C, \quad M^{32} = -X_B, \quad M^{33} = 1$$

and by inserting into (15):

$$\frac{dP}{dT} = \frac{S_{A(mix)} - X_B S_B - X_C S_C}{V_{A(mix)} - X_B V_B - X_C V_C} \tag{22}$$

or by again recognizing the stoichiometry of the reaction:

$$\frac{dP}{dT} = \frac{\Delta_{react} S}{\Delta_{react} V} \tag{23}$$

CONCLUSION

By realizing the validity of Maxwell's relation (2) for univariant systems, for which it should be written:

$$\frac{dP}{dT} = \left(\frac{\partial S}{\partial V}\right)_T$$

and by solving for the differential mass-balances for the closed systems, we arrive at an equation:

$$\frac{dP}{dT} = \frac{\sum_j M^{sj} S_j}{\sum_j M^{sj} V_j}$$

which we have called the thermodynamic equation of state for univariant systems. M^{sj} is here the cofactor of the element M_{sj} in a matrix **M** that we have called the compositional matrix. This equation has as special cases, equations often encountered in thermodynamics, but derived from different points of views and in different contexts.