A Method for Deriving Expressions for the First Partial Derivatives of Thermodynamic Functions

Frank Lerman

A Method for Deriving Expressions for the First Partial Derivatives of Thermodynamic Functions

FRANK LERMAN

University of Cincinnati, Cincinnati, Ohio

(Received May 17, 1937)

By this direct method, any first partial derivative of the thermodynamic functions may be readily resolved into terms of temperature, pressure, volume, and entropy, and of six basic forms of a mathematical quantity named a vired. These six basic vireds have been expressed in terms of the better known and more easily measurable thermodynamic quantities and therefore may be used in determining any of the first partial derivatives. This method stresses the interrelationship between the partial derivatives and is a distinct departure from Bridgman's method for obtaining expressions for the first derivatives by substitution from a list of 45 arbitrarily defined quantities which have been expressed in simpler terms.

FOR the general use of equations involving partial derivatives of thermodynamic functions, the partial derivatives first need to be resolved into better known or more easily measurable terms. However, the general method for simplification usually involves a good working knowledge of differential calculus and an ingenuity of the sort needed in solving trigonometric identities.

From the ten thermodynamic functions usually selected as fundamental, there are altogether 720 partial derivatives of the form $(\partial x/\partial z)_y$, where x, y, z are any three of the ten functions.

To simplify the determination of this large number of derivatives, P. W. Bridgman[1] sets up 90 quantities of the type $(\partial x)_y$ defined so that the quotient of pairs of them form all the possible first partial derivatives. Thus the partial derivative, $(\partial x/\partial z)_y$, may be denoted as $(\partial x)_y/(\partial z)_y$. By further restricting the relationship of these quantities so that $(\partial x)_y = -(\partial y)_x$, he cuts the number required from 90 to 45. Bridgman has resolved these 45 quantities into terms of the more desirable thermodynamic functions and partial derivatives. From these quantities any of the 720 partial derivatives may be determined by substitution and use of algebra.

A method is here presented based on quantities similar to those devised by Bridgman but redefined in such a manner so as to permit the resolution of the 45 forms into a few, more basic forms. The following ten thermodynamic functions are used:

T, the temperature,

P, the pressure,

V, the volume,

S, the entropy,

dW, the increment[2] of work done by the system,

where $\qquad dW = PdV,$ $\qquad\qquad$ (1)

dQ, the increment[2] of heat absorbed by the system where $\quad dQ = TdS,$ $\qquad\qquad$ (2)

U, the internal energy of the system, where

$$dU = dQ - dW = TdS - PdV, \qquad (3)$$

H, the heat content or total heat, defined as

$$H = U + PV, \qquad (4)$$

A, the free energy of Helmholtz, defined as

$$A = U - TS, \qquad (5)$$

F, the free energy of Gibbs, defined as

$$F = U + PV - TS. \qquad (6)$$

Let us set up a quantity dx_y, where x and y are any two of the ten functions, and define it as the product of two partial derivatives, thus:

$$dx_y = -(\partial x/\partial P)_y(\partial y/\partial T)_P.[3] \qquad (7)$$

We may designate this form as the *vired*[4] of x with y constant.

---

[1] P. W. Bridgman, Phys. Rev. **3**, 273 (1914), also *A Condensed Collection of Thermodynamic Formulas* (Harvard University Press, 1925).

[2] Increments of these energy functions are used since the total functions are dependent on the path of change.

[3] Bridgman defines his quantity as $(\partial x)_y = (\partial x/\partial a)_y$ where a is an arbitrary variable.

[4] The word *vired* (pronounced vī-rĕd) has been obtained by spelling backwards, the abbreviation of "derivative."

From definition (7)[5] together with the mathematics of partial derivatives, the following relationships are proven:

$$dx_y = -dy_x \qquad (8)$$

and

$$dx_y/dz_y = (\partial x/\partial z)_y, \qquad (9)$$

where z is another thermodynamic function.

Ninety vireds may be formed from the ten functions. However, by a simple method of manipulation to be presented below, any vired may be expressed in terms of a few, more "basic" vireds.

We define a basic vired as one composed of any two of the four functions, T, P, V, and S. Any other vired may be resolved into terms of the basic vireds by application of elementary operating rules to the definitions of the functions given by (1) to (6) inclusively. These operating rules for vireds, similar to the simple rules of differentiation, are:

For vireds having a given subscript, y,

I. The vired composed of a single function is zero. Thus $dy_y = 0$.

II. The vired of a sum of variables is the sum of the vireds of the variables. Thus from (4) $dH_y = d(U+PV)_y = dU_y + d(PV)_y$.

III. The vired of a product of two variables is the sum of each variable times the vired of the other variable. Thus $d(PV)_y = PdV_y + VdP_y$.

These rules can be readily proven mathematically with the use of definition (7).

There are twelve basic vireds. Six of these have been resolved through mathematical derivation into simple terms as tabulated below.

$$dT_P = 1 = \frac{T}{C_V}dS_P,$$

$$dT_V = \left(\frac{\partial V}{\partial P}\right)_T = \frac{T}{C_P}dS_V,$$

$$dV_P = \left(\frac{\partial V}{\partial T}\right)_P = dS_T.$$

---

[5] Definition (7) for $y=P$ gives an indeterminate form $dx_P = -(\partial x/\partial P)_P (\partial P/\partial T)_P$. To solve this form it is first shown mathematically that $-(\partial x/\partial P)_y (\partial y/\partial T)_P$, the definition of the general vired dx_y, is equal to $-(\partial x/\partial P)_T (\partial y/\partial T)_P + (\partial x/\partial T)_P (\partial z/\partial P)_T$. Then for $y=P$, $dx_P = 0 + (\partial x/\partial T)_P$. Hence for further derived proofs, dx_P is taken equal to $(\partial x/\partial T)_P$.

The other six basic vireds can be obtained from this table by use of equality (8). All other vireds can be expressed in terms made up of these twelve vireds and the four functions, T, P, V, and S. It then becomes obvious when noting Eq. (9) that all of the 720 possible partial derivatives of the ten thermodynamic can be expressed in terms of T, P, V and S, together with the specific heats, C_P and C_V, and the easily measurable partial derivatives, $(\partial V/\partial P)_T$ and $(\partial V/\partial T)_P$.

For example, to obtain the partial derivative $(\partial A/\partial S)_V$ express it as the vired quotient dA_V/dS_V. From the table it can be seen that $T/C_V dS_V = (\partial V/\partial P)_T$.

Therefore
$$dS_V = \frac{C_V}{T}\left(\frac{\partial V}{\partial P}\right)_T.$$

Since

$A = U - TS$ from (5)

$dA_V = dU_V - d(TS)_V$ Rule II

$dA_V = dU_V - (TdS_V + SdT_V)$ Rule III

$= (TdS_V - PdV_V) - (TdS_V + SdT_V)$ from (3) and II

$= TdS_V - 0 - TdS_V - SdT_V$ Rule I

$= -SdT_V = -S(\partial V/\partial P)_T$ from table.

Therefore

$$\left(\frac{\partial A}{\partial S}\right)_V = \frac{dA_V}{dS_V} = \frac{-S(\partial V/\partial P)_T}{(C_V/T)(\partial V/\partial P)_T} = -\frac{ST}{C_V}.$$

The most complex vired is of the form dF_x, where x is some other function not basic. Consider for example the vired dF_U.

$dF_U = dU_U + d(PV)_U - d(TS)_U$
     from (6) and Rule II

$= 0 + PdV_U + VdP_U - TdS_U - SdT_U$ Rule III

$= -PdU_V - VdU_P + TdU_S + SdU_T$ from (8)

$= -P(TdS_V - PdV_V) - V(TdS_P - PdV_P)$
$\quad + T(TdS_S - PdV_S) + S(TdS_T - PdV_T)$
     from (3) and II

$= -PTdS_V + 0 - VTdS_P + VPdV_P + 0$
$\quad - TPdV_S + STdS_T - SPdV_T$ from Rule I.

Since $dV_S = -dS_V$ the first and fourth sig-

nificant terms cancel, $dF_U = -VTdS_P + VPdV_P + STdS_T - SPdV_T$. By substitution from the table,

$$dF_U = -VT\left(\frac{C_P}{T}\right) + VP\left(\frac{\partial V}{\partial T}\right)_P$$

$$+ST\left(\frac{\partial V}{\partial T}\right)_P + SP\left(\frac{\partial V}{\partial P}\right)_T$$

$$= -VC_P + [VP + ST]\left(\frac{\partial V}{\partial T}\right)_P + SP\left(\frac{\partial V}{\partial P}\right)_T.$$

The method presented here is mathematically exact. It emphasizes the interrelationships between the partial derivatives of the thermodynamic functions. Any partial derivative containing a function not already considered can be determined by the method providing the new function is expressible in terms of the ten functions used here.

Should it be desired to express the partial derivatives in terms other than used here, the expressions for basic vireds tabulated above need only be changed mathematically into the terms wanted.

Studies in the Autoxidation of Monolayers

I. The Mechanism of Autoxidation of Maleic Anhydride β-Elaeostearin

Geoffrey Gee and Eric K. Rideal
*Department of Colloid Science, Cambridge University, England*
(Received August 2, 1937)

The autoxidation of monolayers of maleic anhydride β-elaeostearin is examined in detail and a free radical mechanism proposed. The effect of temperature and pressure on the rate of oxidation over a very wide pH range has been investigated, and the variation of oxidation rate with pH shown to be of the form to be anticipated from the postulated mechanism. The absolute values of such constants as can be separately determined are consistent with the physical picture of the process.

IN two earlier papers[1] a general account has been given of an investigation of the reactions which occur in monolayers of maleic anhydride β-elaeostearin spread on $N/100$ H_2SO_4 or HCl. This material
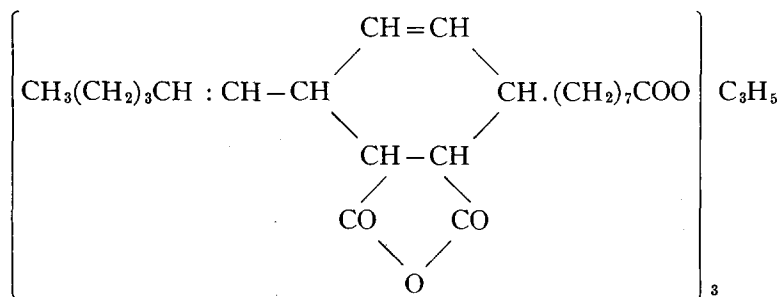
spreads readily on these substrates but the films are unstable, undergoing a spontaneous reaction which can be stopped by the addition to the substrate of 0.1 percent of hydroquinone. The sequence of reactions which occurs was identi-

[1] Proc. Roy. Soc. **A153**, 116, 129 (1935). Cf. also, ibid. **155**, 692 (1936).

fied with the normal process of "drying" of an oil, and has been shown to comprise essentially an autoxidation, followed by polymerization of the oxidation product. If the oil be denoted by X, there are two oxidation products XO_2' and XO_2 of which the former is much the more reactive, and the complete reaction can be