BRIEF COMMUNICATIONS

A DERIVATION OF THE CLAUSIUS-CLAPEYRON EQUATION

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A quasi-static change of the phase state of a one-component system takes place under the action of constant intensive parameters: pressure P, temperature T, and electrochemical potential μ for the two phases. The degree of change of the extensive parameters depends on the reciprocal relations for the intensive and extensive parameters. This relationship, for a simple system with constant mass (i.e., constant mole number) is expressed by the well-known Clausius-Clapeyron equation, which can be written as follows:

$$\frac{dP}{dT} = + \frac{\Delta_N S}{\Delta_N V}, \tag{1}$$

where Δ denotes the change of an extensive parameter (that which it precedes) during a total change of the phase state; the subscript indicates a parameter which remains constant during a given change of phase state (here the mole number N).

In general it is not necessary to restrict ourselves to a change of phase state occurring in a system with constant mass.

The general process of variation of phase state may be represented in a system in which none of the extensive parameters remains constant (except the mole number for which the Clausius-Clapeyron equation has been derived). This kind of very general case of change of phase state is unsuitable for direct analysis. Let us therefore consider processes (and systems) where one of the intensive parameters remains constant. Here we can refer to the case with change of phase state with constant volume, the case of change of phase state with constant entropy, and so on.

It is easy to analyze a system with constant volume. This is an open system where we permit mass to flow out from a constant volume, or mass to flow out accompanied by a change of phase state. A system with constant entropy is an open system, for which a phase change process is associated with change of volume and of mole number, the entropy remaining constant.

By using an analogy method, we may write down a full system of equations to describe these processes. From Eq. (1):

$$\frac{d\Pi}{dT} = -\Delta_N S/\Delta_N V, \tag{2}$$

$$\frac{d\mu}{d\Pi} = -\Delta_S V/\Delta_S N, \tag{3}$$

$$\frac{dT}{d\mu} = -\Delta_V N/\Delta_V S. \tag{4}$$

Here Π is the negative of the pressure (−P), corresponding to the temperature T and the electrochemical potential μ; $\Delta_N S$ is the total change of entropy at constant mole number; $\Delta_N V$ is the total change of volume at constant mole number; $\Delta_S V$ is the total change of volume at constant entropy; $\Delta_S N$ is the total change of mole number at constant entropy; $\Delta_V N$ is the total change of mole number at constant volume; $\Delta_V S$ is the total change of entropy at constant volume.

The validity of Eqs. (3) and (4) can be proved as follows: Starting from the Gibbs-Duhem relation

$$-VdP + SdT + Nd\mu = 0, \tag{5}$$

we obtain

$$\frac{d\mu}{dP} = v - s(dT/dP),$$

we determine dT/dP from the Clausius-Clapeyron equation (1)

$$\frac{dT}{dP} = (v_2 - v_1)/(s_2 - s_1)$$

and arrive at the relation

$$\frac{d\mu}{dP} = v_1 - s_1(v_2 - v_1)/(s_2 - s_1), \tag{6}$$

expressed in terms of individual extensive parameters.

We can determine the left side of (3) from the expression for the total change of volume at constant system entropy

$$\Delta_S V = N_2 v_2 - N_1 v_1 \tag{7}$$

and the total change of mole number at constant system entropy

$$(N_1 - N_2)s_2 = N_1 r/T = N_1(s_1 - s_2),$$

i.e.,

$$\Delta_S N = -N_1(s_2 - s_1)/s_2. \tag{8}$$

Substituting expressions (6), (7), and (8) into (3), we obtain

$$V_1 - N_1 s_1 (v_2 - v_1)/(s_2 - s_1) =$$
$$= s_2 (N_2 v_2 - N_1 v_1)/(s_1 - s_2),$$

whence

$$N_1 s_1 = N_2 s_2.$$

It has thus been shown that the total change of volume and of mole number occurs at constant system entropy, which confirms the validity of (3).

Relation (4), i.e.,

$$\frac{d\mu}{dT} = -\Delta_V S/\Delta_V N, \tag{9}$$

can be proved in a similar way. From (5) we have

$$\frac{d\mu}{dT} = -s_1 + v_1\, dP/dT.$$

We substitute for dP/dT from (1):

$$\frac{d\mu}{dT} = -s_1 + v_1\,[(s_2 - s_1)/(v_2 - v_1)]. \tag{10}$$

The right-hand side of (9) can be determined from the expression for the total change of entropy at constant system volume

$$\Delta_V S = N_1(s_2 - s_1) - (N_1 - N_2)\, s_2 \tag{11}$$

and the expression for the mole number at constant system volume

$$(N_1 - N_2)\, v_2 = -(V_1 - V_2),$$

$$\Delta_V N = N_1(v_1 - v_2)\, v_2. \tag{12}$$

Substituting expressions (10), (11), and (12) into (9), we obtain

$$-s_1 - v_1\,[(s_2 - s_1)/(v_2 - v_1)] =$$

$$= v_2\,[N_1(s_2 - s_1) - (N_1 - N_2)\, s_2]/N_1(v_1 - v_2),$$

whence

$$N_1 v_1 = N_2 v_2.$$

Thus it has been shown that the total change of entropy and mole number occurs at constant system volume, which confirms the validity of Eqs. (9) and (4).

By multiplying relations (2), (3), and (4), we obtain the following equations:

$$(\Delta_N S/\Delta_N V)(\Delta_V N/\Delta_V S)(\Delta_S V/\Delta_S N) =$$

$$= (-dP/dT)(d\mu/dP)(dT/d\mu) = -1.$$

The equation obtained expresses the ratio of the total changes of two of the extensive parameters of the system in terms of the remaining extensive parameters.

The parameter appearing in (3) and (4) is entropy. It should be stressed that we cannot calculate the absolute value of entropy from these equations, and that we do not need to use these relations. Since the absolute value of entropy is related to the chemical potential through the Gibbs-Duhem relation, the equations derived are in agreement with any zero reference level of entropy.

The expressions obtained make it possible to extend the Clausius-Clapeyron equation to systems with a variable mole number, the variation occurring because of leakage of material from the system, or as a result of simultaneous or subsequent chemical reaction associated with the change of phase state.

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