G. M. Anderson
Department of Geology
University of Toronto
Toronto 5, Ontario, Canada

Standard States at Fixed and Variable Pressures

A recent contribution to THIS JOURNAL (*1*) has presented some aspects of the choice of standard state pressure in thermodynamics. The main purpose of this paper is to extend the discussion of "variable pressure standard states," placing them in a context of other types of standard states, and to point out some ways in which they are useful.

The necessity for standard states in thermodynamics arises with the introduction of the terms U and S (internal energy and entropy), which is to say (in Gibbs' treatment at least) at the very outset. The changes in these values as systems progress from one state to another play a fundamental role, but their absolute values are unknown and are of no great importance, so the necessity of having convenient arbitrary states with respect to which U and S in other states may be compared is obvious. The same of course applies to other variables of state which contain these quantities in their equations of definition. Subsequent to Gibbs and the other formulators of the classical theory, entropy acquired "absolute" values via the third law, and perhaps if in the future we learn how to measure mass with (at present) inconceivable accuracy it may prove convenient to use absolute values of U derived from its relationship with the product of mass and the square of the speed of light. Until then we must use standard states, with both the conveniences and possibilities for confusion that this entails. The conveniences arise since various standard states may be chosen for various purposes, and in terms of temperature and pressure three main categories of standard states have been used; states at fixed T and P, states at fixed P and variable T, and states at variable P and variable T.

Standard States at Fixed *P* and *T*

These states are invariably chosen for the presentation of data for a pure substance covering a range of both P and T. The standard state is normally the most stable form of that substance at some chosen P and T, which may be the P and T of the triple point, 1 atm and 0°K, 1 atm and 25°C, or any other combination. The numerical value of the tabulated function at a given P and T is then the difference in the function for the substance in the given and the standard states. There is no necessity for defining the value of the function in the standard state to be zero so that "absolute" values of the function may be given rather than "delta" values, although this is sometimes done.

Standard states with a variable P or T would be inappropriate in this type of situation, since it would result in the loss of some information. For example, for a 1-atm, variable T standard state, the values for the function at $P = 1$ atm and all temperatures would all be zero. If the user of the tabulated data wishes to use any other standard state, including ones with variable pressures or temperatures, it is a simple matter to calculate the new values of the function from the values given relative to the fixed P,T standard state.

Discussion of the role of temperature and pressure in the remaining two types of standard states will arise naturally from a discussion of the state variable which is most useful when the independent variables are T and P, that is, the Gibbs free energy, G, and the closely related variables chemical potential, μ, fugacity, f, and activity, a.

Definitions of Activity

Consider a pure substance having molar free energy G and molar volume V. Since

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

then

$$\int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} V dP \tag{1}$$

If this substance is an ideal gas, integration gives

$$G_{P_2} - G_{P_1} = RT \ln (P_2/P_1) \tag{2}$$

For dealing with real gases, the concept of fugacity was introduced which allows retention of the form of eqn. (2), thus

$$G_{P_2} - G_{P_1} = RT \ln (f_{P_2}/f_{P_1}) \tag{3}$$

Passing lightly over a considerable amount of material, we may simply note that fugacities have been defined in such a way that they retain their usefulness in gaseous solutions, and in fact they can be used for any constituent of any phase, solid, liquid, or gas, and in general

$$\mu_i'' - \mu_i' = RT \ln (f_i''/f_i') \tag{4}$$

where μ_i is the chemical potential of component i, and superscripts (′) and (″) refer to any two states at temperature T.

Equations (3) and (4) involve changes in state functions, and so once again we come to the problem of choosing one particular state as a standard state. If state (′) is designated the standard state and given a superscript °, then

$$\begin{aligned}\mu_i - \mu_i^\circ &= RT \ln (f_i/f_i^\circ) \\ &= RT \ln a_i\end{aligned} \tag{5}$$

where the activity, a_i, is defined as

$$a_i = f_i/f_i^\circ \tag{6}$$

With respect to the P and T of the standard state, we

[Reprinted from Journal of Chemical Education, Vol. 47, Page 676, October, 1970.]

first note that the form of eqn. (5) (and many analogous equations) suggests that we use a variable temperature standard state. The reason for this is that if μ_i and μ_i° refer to different temperatures, $RT \ln (f_i/f_i^\circ)$ will not give their difference, so for convenience (that is if we wish to use eqn. (5) with no extra terms), the standard state must always be at the temperature of the state of interest. Since temperature is one of the most commonly varied parameters in any series of experiments, and since it is quite inconvenient to calculate the correction term required if μ_i° and μ_i refer to different temperatures (in fact it is often impossible), the convention of the variable temperature standard state has arisen.

The pressure of the standard state is fixed when f_i° and T (or μ_i° and T) and the physical state of the system are chosen, but when this is done and if the standard state pressure is constant, then μ_i° and f_i° are independent of the pressure of the state of interest because they do not refer to that state. Looking at it another way, μ_i° is an integration constant which depends only on the value of T during integration. Its value depends on the pressure chosen for the standard state (almost universally chosen to be 1 atm) but not on the pressure of any other states which may be compared with it.

Next, we can see from consideration of eqn. (5) that it may often prove convenient to choose as a standard state a physical state of the substance other than its most stable state at any given P and T. For example in the case of gases, either pure or in gaseous solutions, it proves convenient to choose as the standard state the hypothetical pure ideal gas at 1 atm and temperature T, since then $f_i^\circ = 1$ at all temperatures, and

$$\mu_i - \mu_i^\circ = RT \ln f_i \tag{7}$$

For pure solids and liquids the convenient choice is the pure stable phase at 1 atm and T, since in this case although we may not know the value of f_i or f_i° we do know they are equal at 1 atm, and the activity of pure phases is 1 at 1 atm and very close to 1 at pressures not far removed from 1 atm.

Although traditional, there is nothing inherently necessary about these choices of standard states. If one wished to choose the ideal gas at T and 1000 atm rather than 1 atm, or a hypothetical gaseous state for a substance which happens to be solid or liquid, one is free to do so. For example, if a problem involves the activity of H_2O at 1000 bars over a temperature range of 25°–700°C, a convenient choice of standard state would be ideal gaseous water at T and 1 atm, regardless of the fact that below 100°C, water at 1 atm is a liquid and not a gas. Alternatively, but less wisely, one might choose as the standard state liquid water or even hypothetical ice at T and 1 atm. In this case, we must devise a scheme for calculating the fugacity of metastable water or ice at temperatures above 100°C or 0°C, respectively. The point is that there are no hard and fast rules, only good and bad judgment.

For pure ideal gaseous component 1 with a standard state T and 1 atm, eqn. (2) becomes

$$G_1 - G_1^\circ = RT \ln P$$

or

$$G_1 - G_1^\circ = RT \ln (RT/V_1)$$

where V_1 is the molar volume of component 1. Now

$$V_1 = V_T/n_1$$

where V_T is the total volume occupied by n_1 moles of component 1, so

$$G_1 - G_1^\circ = RT \ln RT + RT \ln (n_1/V_T) \tag{8}$$

To deal with gaseous solutions, we might now introduce the assumption that the same volume V_T now contains n_2 moles of component 2 as well as n_1 moles of component 1 and that this mixture also behaves as an ideal gas. That is, that

$$V_T = (n_1 + n_2)RT/P$$

Substituting for V_T in eqn. (8), we have

$$\begin{aligned} G_1 - G_1^\circ &= RT \ln RT + RT \ln \frac{n_1 P}{(n_1 + n_2)RT} \\ &= RT \ln N_1 P \end{aligned} \tag{9}$$

where $N_1 = n_1/(n_1 + n_2)$, and where G_1° still refers to the free energy of pure component 1 at T and 1 atm. Equation (9) may also be written as

$$G_1 - G_1^\circ = RT \ln P + RT \ln N_1$$

or

$$G_1 - G_1^* = RT \ln N_1 \tag{10}$$

where

$$G_1^* = G_1^\circ + RT \ln P$$

In eqn. (10), the term G_1^* representing the free energy of component 1 in the standard state is a function of temperature and the pressure of interest, whereas G_1° is a function of temperature only. Again, this does not mean that we are committed to using a variable pressure standard state, but only that if we do not we must introduce additional terms into our equation to correct for the effect of pressure on G_1^*. Incidentally, it is fairly easy to show that if eqn. (10) holds for liquid solutions, the solutions obey Raoult's law.

For real solutions, liquid or gaseous, a correction factor must be introduced if the form of eqn. (10) is to be retained, and this usually takes the form of a factor applied to the concentration term. Thus

$$\mu_1 - G_1^\circ = RT \ln (\gamma_R N_1) \tag{11}$$

where departures from ideal (or Raoult's Law) behavior are compensated for by the "rational" or "Raoult's law" activity coefficient, γ_R.

Partial differentiation of eqn. (11) with respect to the number of moles of a second component, n_2, gives

$$\begin{aligned} \left(\frac{\partial \mu_1}{\partial n_2}\right)_{T,P,n_1} &= RT \left(\frac{\partial \ln \gamma_R}{\partial n_2}\right)_{T,P,n_1} + RT \left(\frac{\partial \ln N_1}{\partial n_2}\right)_{T,P,n_1} \\ &= RT \left(\frac{\partial \ln \gamma_R}{\partial n_2}\right)_{T,P,n_1} - \frac{RT}{(n_1 + n_2)} \end{aligned}$$

Dilute solution theory demonstrates that in sufficiently dilute solutions, the solvent obeys Raoult's law, and γ_R attains a constant value of one. Thus if we consider solutions of this kind and introduce the approximation that n_2 may be neglected if the last term, then

$$\left(\frac{\partial \mu_1}{\partial n_2}\right)_{T,P,n_1} = -RT/n_1$$

Now, since the chemical potential of the solute (μ_2) is an intensive parameter it is in mathematical language