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

$$\int_{P_1}^{P_2} \mathrm{d}G = \int_{P_1}^{P_2} V\mathrm{d}P \tag{1}$$

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 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

$$\mu_i - \mu_i^\circ = RT \ln f_i \qquad (7)$$

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

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

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

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

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

$$G_1 - G_1^* = RT \ln N_1 \qquad (10)$$

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

$$\mu_1 - G_1^\circ = RT \ln (\gamma_R N_1) \qquad (11)$$

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 homogeneous in the zeroth degree in (n_1,n_2), and by Euler's theorem (*2*) on homogeneous functions we have

$$n_1\left(\frac{\partial^2 G}{\partial n_1 \partial n_2}\right) + n_2\left(\frac{\partial^2 G}{\partial n_2^2}\right) = 0$$

Thus

$$\left(\frac{\partial^2 G}{\partial n_2^2}\right) = -n_1(-RT/n_1)/n_2$$

or

$$\frac{\partial \mu_2}{\partial n_2} = \frac{RT}{n_2} \tag{12}$$

If we let

$$n_1 = 1000/M_1$$

where M_1 is the gram formula weight of component 1 we lose no generality, and n_2 becomes the molality, m, of component 2. Thus

$$\left(\frac{\partial \mu_2}{\partial m}\right)_{T,P,n_1} = \frac{RT}{m}$$

Integrating between two arbitrarily chosen molalities, m' and m'' we have

$$\mu_2'' - \mu_2' = RT \ln (m''/m')$$

for solutions in which our previous assumptions are valid, i.e., that n_2 is small enough such that component 1 obeys Raoult's Law. Solutions of this kind are said to obey Henry's law. As n_2 gets larger, this assumption is no longer valid, and again a correction factor is applied to the concentration terms

$$\mu_2'' - \mu_2' = RT \ln \frac{(\gamma m)''}{(\gamma m)'} \tag{13}$$

where γ is the Henry's law activity coefficient.

Once again we have a difference term in a state variable $(\mu_2'' - \mu_2')$ and the necessity of choosing a standard state for common reference purposes. This time we have the restriction that the states $''$ and $'$ are at the same *T and P*, since only m was allowed to vary during integration. In a manner exactly analogous to the procedure by which we derived eqn. (7) from eqn. (5) we may now choose our standard state to be a hypothetical, ideal $(\gamma = 1)$, 1 molal solution, so that

$$(\gamma m)' = 1$$

and

$$\mu_2 - \mu_2^* = RT \ln (\gamma m) \tag{14}$$

where μ_2^* (as well as μ_2) is a function of both the temperature and the pressure on the system.

Similarly, in a manner analogous to our definition of activity in eqn. (6), we find that we have a new definition of the same term suggested by eqn. (13), that is

$$a_i = (\gamma m)_i/(\gamma m)_i^\circ \tag{15}$$

and thus in general

$$\mu_2 - \mu_2^* = RT \ln a_2 \tag{16}$$

where $(\gamma m)_i^\circ$ is the activity coefficient-molality product in any chosen standard state and $(\gamma m)_i$ is that in any other state of interest. The choice of a standard state in which $\gamma = 1$ and $m = 1$ simultaneously is dictated not only by the convenience of being then able to use eqn. (14), but having the solution ideal (obeying Henry's Law) means that most of the solute properties (partial molal enthalpy, etc.) are then the same in the standard state as in an infinitely dilute solution and hence we can obtain numerical values for them. We could also use eqn. (14) by choosing as standard state a hypothetical 2 m solution having an activity coefficient of 0.5, but we have no way of obtaining values for any solute properties in such a solution, and many other equations based on dilute solution theory would be unusable. The fact that the ideal 1 m solution has many of the properties of an infinitely dilute solution has led to the common misconception that the infinitely dilute solution is a standard state. Consideration of eqns. (13) or (15) will show that having $(\gamma m)_i^\circ$ equal or close to zero would not be practical.

The definition of activity in solution theory is usually given as

$$a = \gamma m \tag{17}$$

which of course is a special case of eqn. (15). Equation (15) seems preferable, however, not only because it makes quite explicit any choice of standard states but because of its analogy with eqn. (6). Also, it is possible to get into dimensional difficulties in equations like eqn. (14) unless the activity term is clearly seen to be dimensionless through the use of eqn. (15). Some authors circumvent this difficulty by assigning units of inverse concentration to γ, but this is clumsy and quite unnecessary.

As an example of the usefulness of being able to use uncommon standard states, suppose we have data involving stability "constants" of some aqueous complexes in solutions having an ionic strength of three. These "constants" are valid only for solutions of that ionic strength, or in other words for solutions having the same activity coefficients as the solutions in which they were measured. They are actually concentration quotients having an unknown relationship to the true thermodynamic equilibrium constant based on the ideal 1 m solution at that temperature. This relationship can be calculated by estimating all the activity coefficients involved, but this calculation is highly uncertain at best, and the general practice is to leave the data with no such correction.

These concentration quotients are more easily transformed into thermodynamic equilibrium constants by defining the standard state as a solution 1 m in the solute under consideration but with an ionic strength of 3 m at the T and P of interest. Given the usual assumption that activity coefficients in solutions of equal ionic strength are equal, this means that for each species in solution the two γ terms in eqn. (15) cancel, m in the denominator is one, and activity equals molality. An equilibrium constant thus defined is more useful than a concentration quotient in many applications. Sillén (*3*) presents a rather similar treatment of concentration quotients in constant ionic strength media, but prefers to redefine the activity coefficients such that they approach unity as the solution approaches the pure solvent which in this case is the pure ionic medium or "background salt" solution. This standard state would also be described as a 1 m solution in which the ionic strength is 3, with perhaps an added sentence or two noting the redefined meaning of γ.

In essence, all we have said so far with respect to the choice of standard states for solution theory is that if we wish to use equations like eqn. (16), the only mathematical restriction is that the standard state and the state of interest have the same temperature and pressure. Further definition of the state as to composition or other physical attributes should be entirely a matter of convenience.

Standard States at Higher Pressures

With these definitions before us (and so far we have not deviated from the conventional except in being somewhat more explicit than usual), we can now examine the definition of activities at pressures other than 1 atm. As used by Rock (*1*) the term "fixed pressure standard state" refers to a standard state which remains at one pressure (almost invariably chosen as 1 atm) regardless of the experimental pressures, whereas "variable pressure standard states" may be chosen at various pressures, presumably the experimental pressures involved in a given situation. These names are not entirely adequate to cover the range of possibilities, since there are cases where a standard state remains entirely fixed as to pressure, though not at 1 atm. This includes cases where the pressure chosen is the only experimental pressure used and cases where it is only one pressure of many used (perhaps the highest or lowest) or perhaps a pressure not used in experiments at all. Prausnitz (*4*) discusses the choice of standard state pressure for certain applications. However, this aspect of the problem of nomenclature is not important because in every instance, definitions must be explicit enough to make the usage clear.

The advantages of using the fixed pressure standard state have been outlined by Rock (*1*). Most of these advantages hold regardless of whether the pressure is fixed at 1 atm or any other pressure, but 1 atm will always have the very great advantage of being closest to most experimental data. It will be useful now to consider the use of the "variable pressure standard state."

Consider the simple solubility reaction

$$\mathrm{X(crystal)} + \mathrm{y}\cdot\mathrm{H_2O\ (supercritical\ fluid)} \rightleftharpoons X\cdot y\mathrm{H_2O\ (aqueous\ solute)}$$

at high temperatures and 5000 bars pressure. Defining our standard states as pure crystalline X, pure H_2O, and a hypothetical ideal 1 *m* solution of $X\cdot yH_2O$ at *T* and 5000 bars, the equilibrium constant

$$K = \frac{a_{\mathrm{solute}}}{a_x \cdot a^y{}_{H_2O}}$$

reduces to $K = a_{\mathrm{solute}}$, since both X and the aqueous phase are quite pure (we will assume that X is only slightly soluble). If we also have reason to believe that the solute is not appreciably ionized in solution, then its activity coefficient is close to one, and the equilibrium constant becomes equal to the concentration. In this example, use of the (log *K* versus $1/T$) relationship will give us a ΔH° value which is a very good estimate of the differential heat of solution of X in pure H_2O at whatever temperature is considered, a quantity which under these conditions is very difficult to derive in any other way.

Obviously, if solubility data are available at a number of isobars in addition to 5000 bars, then choosing the standard state as equal to the experimental pressure in all cases constitutes a good example of the use of the "variable pressure standard state." An example of this type of equilibrium is discussed in greater detail by Anderson and Burnham (*5*) and some other applications of the variable pressure standard state are discussed by Anderson (*6*).

Another advantage of a variable pressure standard state is that it eliminates the need for a *reference state* as defined by Pitzer and Brewer (*7*) and Rock (*1*). This reference state is in fact unnecessary for gases and pure solids and liquids, and unusable for solutes for which partial molar volume data is not available from 1 atm up to the pressure of interest. In work at very high pressures and temperatures this means virtually all solutes, and a high pressure standard state is the only reasonable alternative.

To summarize these remarks about variable pressure standard states, we may simply note that the reasons for using them are identical with those for using variable temperature standard states. The convenience and utility of these states greatly outweigh the apparent simplification which would result from universal use of a standard state at a fixed *P* and *T*. The simplification is only apparent because with a fixed *P*, *T* standard state the relationships between activities and the various state variables all become more complicated, and in many cases unusable.

Acknowledgment

The use of Euler's theorem in the derivation of eqn. (13) was first shown to the writer by the late Professor A. R. Gordon during a lecture course at the University of Toronto. The use of these equations in discussing standard states, and any mistakes, originate with the writer. A preliminary draft of this paper received very useful criticism from Dr. H. R. Shaw and Dr. H. J. Greenwood.

Literature Cited

(1) Rock, P. A., J. Chem. Educ. **44**, 104 (1967).
(2) Many texts give Euler's theorem and its applications in thermodynamics, for example, Reiss, H., "Methods of Thermodynamics," Blaisdell, Publishing Co., New York, **1965**.
(3) Sillén, L. G., *article in* "Equilibrium in Natural Water Systems," Advances in Chemistry Series, No. 67, American Chemical Society, Washington, D. C., **1967**, p. 45.
(4) Prausnitz, J. M., "Molecular Thermodynamics of Fluid Phase Equilibria," Prentice-Hall, Inc., New Jersey, **1969**.
(5) Anderson, G. M., and Burnham, C. W., *Amer. J. Science*, **263**, 494 (1965).
(6) Anderson, G. M., *Amer. J. Science* (in press).
(7) Lewis, G. N., and Randall, M., "Thermodynamics," (2nd ed., revised by Pitzer, K. S., and Brewer, L.), McGraw-Hill Book Co., New York, **1961**.

✦ ✦ ✦