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# WHY SOLIDS AND PURE LIQUIDS ARE NOT PART OF EQUILIBRIUM EXPRESSION

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**Abstract.** The article deals with the expression of equilibrium constant of a reaction that might include a solid or a pure liquid as a reactant or a product. The typical textbook explanation for excluding terms relating to solids and pure liquid is that their concentrations are constant and so need not be included. This need would not arise if the equilibrium constant were written in terms of activities rather than concentrations or pressures, but the concept of activities is not covered that early in a typical undergraduate syllabus. In this article the concept of Gibbs energy is used to explain why the equilibrium constant is written as it is.

*Keywords:* equilibrium constant; heterogeneous equilibrium; Gibbs energy

The expression for the equilibrium constant of reactions involving solids and pure liquids in terms of concentrations poses some conceptual difficulty to beginning students of college chemistry. After being taught the rules of writing the equilibrium expression for reactions involving gases and solutions, the students are told that these rules are not valid if a solid or a pure liquid is part of the equilibrium system. Only concentrations of components in solutions and gases are included and the corresponding terms of solids and pure liquids are excluded.

Of course this difficulty does not arise if the equilibrium constant is written in terms of activities, as it ought to be, instead of concentrations as is usually done in a beginning course (Klotz & Rosenberg, 2008). Activity of a pure solid is unity and its exclusion does not change the numerical value of the equilibrium constant. Activities and activity coefficients, however, are not usually covered in a typical undergraduate syllabus till much later.

Thus the equilibrium constant for the reaction:

$$CaCO_3\ (s) \leftrightharpoons CaO\ (s) + CO_2\ (g)$$

is written as: $K_c = [CO_2]$; or alternatively, in terms of partial pressure, $K_p = P\ (CO_2)$. In terms of activities, the expression for $K_c$ would be:

$$K_c = a\ (CO_2)\ a(CaO)\ /\ a\ (CaCO_3)$$

where, for example, $a\ (CO_2)$ represents the activity of $CO_2$.

The activities of the solids being unity, the expression becomes:

$$K_c = a\ (CO_2)$$

which can be approximated in terms of concentration or pressure as above.

In the absence of background knowledge of activities and activity coefficients, this exclusion of solids and pure liquids is normally explained in textbooks by stating that the concentrations of solids and pure liquids are constant so they need not be included in the expression for equilibrium. This explanation is unsatisfactory in addition to not being strictly correct.

Another approach, more rigorous but still not involving activities, is presented here. This requires that students be familiar with the following concepts: (i) for a reaction system to be at equilibrium, its total Gibbs energy, $G$, should be a minimum at a particular temperature and pressure; (ii) if $n$ moles of an ideal gas go from a pressure $P_1$ to $P_2$ at a constant temperature, $T$, the change, $\Delta G$, in the Gibbs energy of the gas is: $\Delta G = n\ RT\ \ln(P_2/P_1)$; (iii) for pure substances, the Gibbs energy, being an extensive property, increases linearly with an increase in the number of moles, $n$. So, $dG/dn = G/n$.

These concepts are covered early on in most beginning chemistry books. Typical examples are given in references (Chang, 1997; Brown et al., 1997).

For simplicity of treatment, we consider an equilibrium system with one solid and one gas, such as $CO_2(s) \leftrightharpoons CO_2(g)$

The equilibrium constant, $K_p$, for this reaction is:

$$K_p = P\ (CO_2)$$

As will be shown below, ultimately the reason for the exclusion of solids or pure liquids from the equilibrium expression is that their Gibbs energy per mole does not change, irrespective of what else is present in what state in the system.

When the system is at equilibrium, its Gibbs energy has a minimum value at a certain $T$ and $P$ and hence an infinitesimal random change in the number of moles of $CO_2(g)$ (hence $CO_2(s)$) cannot decrease it, and $dG$ remains zero.

Consequently, the random infinitesimal change of the number of moles does not persist and the system continues to be at equilibrium.

For the above-mentioned solid-gas carbon dioxide system the total Gibbs energy can be written as:

$$G = G_s + G_g,$$

where s and g refer to solid and gas, respectively. If the system is at equilibrium, the following relation holds.

$$\mathrm{d}G/\mathrm{d}n_g = (\mathrm{d}G_s/\mathrm{d}n_g + \mathrm{d}G_g/\mathrm{d}n_g) = 0 \qquad (1)$$

If, on the other hand, an increase in the amount of $CO_2$(g) leads to a decrease in $G$ for the system, the reaction as written above, goes to the right spontaneously. In this case,

$$\mathrm{d}G/\mathrm{d}n_g = (\mathrm{d}G_s/\mathrm{d}n_g + \mathrm{d}G_g/\mathrm{d}n_g) < 0$$

In these equations, for the sake of simplicity, total differential rather than partial differentials is indicated, but it is understood that $T$ and $P$ are kept constant.

Now $-\mathrm{d}n_s = \mathrm{d}n_{g,}$ since, as the amount of solid decreases, that of the gas increases. Eq. (1) becomes

$$\mathrm{d}G/\mathrm{d}n_g = (-\mathrm{d}G_s/\mathrm{d}n_s + \mathrm{d}G_g/\mathrm{d}n_g) = 0 \qquad (2)$$

Let us consider two states of the system: State 1 in which the solid is mixed with the gas at any pressure $P$, and the other, state 2, in which the solid exists with the gas at equilibrium, and where the pressure of the gas is $P'$. Suppose that in state 1, a random fluctuation occurs that increases the number of moles of the gas and results in a decrease in $G$. In other words, $\mathrm{d}G/\mathrm{d}n_g < 0$, and the fluctuation will continue and the amount of the gas will continue to increase till the system reaches state 2.

In state 1,

$$\mathrm{d}G/\mathrm{dn}_g = (-\mathrm{d}G_s/\mathrm{dn}_s + \mathrm{d}G_g/\mathrm{dn}_g) < 0$$

In the state 2, G is a minimum as we have supposed, and a random fluctuation in the amount of the gas does not change it. Denoting the Gibbs energy in state 2 by $G'$, we can write:

In state 2,

$$\mathrm{d}G'/\mathrm{d}n_g = (-\mathrm{d}G'_s/\mathrm{d}n_s + \mathrm{d}G'_g/\mathrm{d}n_g) = 0 \qquad (3)$$

The solid being the same in each of the two states, its Gibbs energy per mole is identical in the two states of the system, and we have the relation:

$$\mathrm{d}G'_s/\mathrm{d}n_s = \mathrm{d}G_s/\mathrm{d}n_s \tag{4}$$

The corresponding relation in the case of the gas can be obtained as follows. Since the partial pressure of the gas is different in the two cases, the Gibbs energy also differs according to the relation:

$$G'_g = G_g + n\,RT \ln (P'/P) \tag{5}$$

This equation expresses how the Gibbs energy of an ideal gas changes if the gas goes from pressure P to P' at a constant temperature.

Differentiating Eq. (5) with respect to $n_g$, we get

$$\mathrm{dG'_g/dn_g} = dG_g/\mathrm{dn_g} + RT \ln (\mathrm{P'/P}) \tag{6}$$

Substituting Eq. (6) and Eq. (4) in Eq. (3), we obtain:

$$\mathrm{d}G'/\mathrm{d}n_g = -\mathrm{d}G_s/\mathrm{d}n_s + \mathrm{d}G_g/\mathrm{d}n_g + RT \ln (P'/P) = 0 \tag{7}$$

If $P$ is taken as pressure of the standard state (1 atm, with $CO_2$ assumed as ideal gas), the above equation becomes $-\mathrm{d}G_s/\mathrm{d}n_s + \mathrm{d}G_g/\mathrm{d}n_g = -RT \ln (P_2/1\mathrm{atm})$.

Now $\mathrm{d}G_s/\mathrm{d}n_s$ is just the Gibbs energy of the solid per mole; and similarly $\mathrm{d}G_g/\mathrm{d}n_g$ is the Gibbs energy of the gas per mole, the above expression can be written as

$-G_s/n_s + G_g/n_g = -RT \ln (P_2/1\mathrm{atm})$,

To explicitly indicate that the state 1 is the standard state, we use the symbol $G^0$ for the Gibbs energy. The equation can then be written as:

$G^0_g/n_g - G^0_s/n_s = -RT \ln (P'/1\mathrm{atm})$.

Since the two terms on the left hand side of the equation are constant, being the Gibbs energy per mole of the gas and the solid respectively, the expression on the right hand side of the equation is constant at constant temperature. If we write this constant as $K_p$, we can put the equation in the familiar form:

$$\Delta G^0 = -RT \ln K_p;$$

For the process

$$CO_2(s) \rightleftharpoons CO_2(g),$$

then

$$K_p = P\,(CO_2).$$

Thus we conclude that a solid or a pure liquid does not appear in the equilibrium constant expression. This treatment can be extended to any reaction that has a solid or a pure liquid.

It is easy to see that the reason for this is that $\mathrm{d}G'_s/\mathrm{d}n_s = \mathrm{d}G_s/\mathrm{d}n_s$. In both the states, i.e. in state 1 (the standard state) and at equilibrium, $G_s/n_s$ has the same value, so it cancels out.

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