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SOME COMMON MISINTERPRETATIONS OF MEASURABLE THERMODYNAMIC FUNCTIONS

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SUMMARY

The widely used phrase "the Gibbs free energy of transfer" (of a solute from one solvent to another) is shown usually to be a misnomer and nearly always to be uninterpretable. The widely used interpretation of positive entropy changes as measures of increase of "mixed–upness" is shown to be false except in the very special cases of perfect–gas mixing and of purely geometrical models of solid mixtures.

INTRODUCTION

I shall explore two quite unconnected worries that I have about widely accepted "interpretations" or "rationalizations" of measurable thermodynamic functions. The first is about the so–called "transfer quantities" like the "Gibbs free energy of transfer" and the second about the physical interpretations popularly ascribed to entropy changes.

TRANSFER QUANTITIES

When is it possible to give the meaning implied by its name to the "Gibbs free energy difference for the transfer of a solute S from one solvent A to another solvent B"? Whatever it be called, when can such a difference be measured other than by brutally taking the difference between disparate quantities? When it can not be measured except in that way, is such a difference ever intellectually less barren than the difference between, say, the mass of a piece of chalk and the mass of a piece of cheese? When is such a quantity capable of any physical interpretation or rationalization? Those are the questions that I shall try to answer.

It is always possible, at least in principle, to measure the change of chemical potential:

$$\Delta\mu_{\mathrm{S}} = \mu_{\mathrm{S}}(\mathrm{sln,B},T,p,m_{\mathrm{S}}^{\mathrm{B}}) - \mu_{\mathrm{S}}(\mathrm{sln,A},T,p,m_{\mathrm{S}}^{\mathrm{A}}), \qquad (1)$$

for the transfer of the solute S from the solvent A at the molality $m_{\mathrm{S}}^{\mathrm{A}}$ to the solvent B at the molality $m_{\mathrm{S}}^{\mathrm{B}}$, both at the temperature T and the pressure p. In principle one can always separate the two solutions by a membrane permeable only to the solute S and adjust the pressures p_{A} and p_{B} on the two solutions so as to produce osmotic equilibrium. Then

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$$\Delta\mu_{\mathrm{S}} = \int_{p_{\mathrm{B}}}^{p} V_{\mathrm{S}}(T,p,m_{\mathrm{S}}^{\mathrm{B}})\mathrm{d}p - \int_{p_{\mathrm{A}}}^{p} V_{\mathrm{S}}(T,p,m_{\mathrm{S}}^{\mathrm{A}})\mathrm{d}p, \tag{2}$$

where $V_{\mathrm{S}}(T,p,m_{\mathrm{S}}^{\mathrm{X}})$ is the partial molar volume of the solute S in a solution of temperature T, pressure p, and molality $m_{\mathrm{S}}^{\mathrm{X}}$ in the solvent X.

Sadly, the quantity $\Delta\mu_{\mathrm{S}}$ is usually called "the molar free energy of transfer". It is nearly always no such thing, though it could be called "the change of chemical potential of the solute S on transfer". It is only for a reaction like

$$\mathrm{AgCl(s)} + \tfrac{1}{2}\mathrm{H_2(g)} = \mathrm{Ag(s)} + \mathrm{HCl}(\mathrm{sln},\mathrm{X},m_{\mathrm{HCl}}^{\mathrm{X}}), \tag{3}$$

for which the molar change of Gibbs free energy $\Delta_{\mathrm{r}}G_{\mathrm{m}}(\mathrm{X})$ can always be measured, for example by means of the galvanic cell:

$$\mathrm{Pt} \mid \mathrm{H_2(g)} \mid \mathrm{HCl}(\mathrm{sln},\mathrm{X},m_{\mathrm{HCl}}^{\mathrm{X}}) \mid \mathrm{AgCl(s)} \mid \mathrm{Ag} \mid \mathrm{Pt}, \tag{4}$$

that the difference:

$$\Delta_{\mathrm{r}}G_{\mathrm{m}}(\mathrm{B},m_{\mathrm{HCl}}^{\mathrm{B}}) - \Delta_{\mathrm{r}}G_{\mathrm{m}}(\mathrm{A},m_{\mathrm{HCl}}^{\mathrm{A}}), \tag{5}$$

between two values of the molar Gibbs free energy of reaction, one for the solvent A when the molality of HCl is $m_{\mathrm{HCl}}^{\mathrm{A}}$ and the other for the solvent B when the molality of HCl is $m_{\mathrm{HCl}}^{\mathrm{B}}$, happens also (because all the other reactants and products are pure substances) to be equal to the change of chemical potential of the solute on transfer:

$$\mu_{\mathrm{HCl}}(\mathrm{sln},\mathrm{B},T,p,m_{\mathrm{HCl}}^{\mathrm{B}}) - \mu_{\mathrm{HCl}}(\mathrm{sln},\mathrm{A},T,p,m_{\mathrm{HCl}}^{\mathrm{A}}). \tag{6}$$

Thus, we can always measure a chemical–potential difference like that of equation (1), and thence the corresponding difference between partial molar enthalpies or partial molar entropies, for the transfer of a solute from one solvent to another, but we should not call these "the molar free energy of transfer" or "the molar enthalpy of transfer" or "the molar entropy of transfer" unless, as is occasionally so, that is what they also are, and we should be quite sure that we have a parameter–free theory with which to interpret or rationalize such a chemical–potential difference of transfer.

In particular, whereas we can measure the Gibbs free energy of solution $\Delta_{\mathrm{sol}}G(\mathrm{A})$, for example from vapour–pressure measurements, for the dissolution of an amount $n_{\mathrm{S}}^{\mathrm{A}}$ of a solute S in an amount n_{A} of a solvent A:

$$\Delta_{\mathrm{sol}}G(\mathrm{A}) = n_{\mathrm{A}}\{\mu_{\mathrm{A}}(\mathrm{sln}) - \mu_{\mathrm{A}}^{*}(\mathrm{l})\} + n_{\mathrm{S}}^{\mathrm{A}}\{\mu_{\mathrm{S}}^{\mathrm{A}}(\mathrm{sln}) - \mu_{\mathrm{S}}^{*}(\mathrm{s})\}, \tag{7}$$

where $\mu_{\mathrm{A}}^{*}(\mathrm{l})$ denotes the chemical potential of the pure liquid solvent A and $\mu_{\mathrm{S}}^{*}(\mathrm{s})$ denotes the chemical potential of the pure solid solute S, the difference between two such quantities for the two solvents A and B always contains quantities like $\mu_{\mathrm{X}}(\mathrm{sln})$ that depend on the nature of the solvent, do not cancel, and in the almost invariable[a] absence of any parameter–free theory which explicitly includes the difference between the two solvents cannot lead to any inference. It is only at infinite dilution that the solvent–dependent terms disappear:

$$\lim_{n_S^A \to 0} \{\Delta_{sol}G(A)/n_S^A\} = \mu_S^{A,\infty}(\text{sln}) - \mu_S^*(\text{s}), \tag{8}$$

where $\mu_S^{A,\infty}(\text{sln})$ denotes the limit at infinite dilution of the solute S in the solvent A of the chemical potential of the solute S.

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[a] The only exception that I can think of is the Debye–Hückel limiting law for an electrolyte which ascribes the whole of the difference between two solvents to the difference in their dielectric constants.

Even when the difference under discussion is the chemical–potential difference for transfer, like (1) or (6) or (8), in the absence of an explicit parameter–free theory such a quantity has no meaning for any pair of finite values of m_S^A and m_S^B. Suppose, for example, that m_S^A and m_S^B are arbitrarily put equal, then that simply begs the question: why not use instead mole fractions or values of some other measure of composition and put them equal instead? This intellectually barren subject was much argued by Gurney ("cratic" and "unitary" quantities) in the 1950s, and is still argued ["· · · one ought (*sic*) always to compare two solutions at identical mole fractions and not at identical molalities · · · "].

ENTROPY CHANGES

When, if ever, may a positive entropy change be interpreted, as most sadly is so popular, as an increase of "mixed–upness" or "randomness" or "disorder" or "chaos"? Each of those kinds of increase is a geometrical one implying some decrease in the spatial certainty with which a three–dimensional array of points can be labelled in two (or more) ways: A or B; occupied or unoccupied; right or wrong.

It is only in an *isolated* system, that is to say one of constant energy U, constant volume V, and constant content N (overall content, irrespective of the manner of chemical combination or of the extent of any chemical reaction or of the number of phases), that any change of entropy S is necessarily positive:

$$\delta S_{U,V,N} > 0. \tag{9}$$

Thus, water and phenol, present as two phases when they are isolated at a temperature above 340 K, are metastable, will mix, and their mixing will be accompanied by a positive entropy change and certainly by an increase of mixed–upness. Molecules that were in one or other geometrically distinct part might then be anywhere. However, water and phenol, present as one phase when they are isolated at a temperature below 340 K, are metastable, will unmix, and their unmixing will be accompanied by a positive entropy change but with a *decrease* of mixed–upness. Even for changes in isolated systems, increase of entropy, then a measure of something — anything — happening macroscopically, can not be interpreted as an increase of mixed–upness or randomness or disorder or chaos.

For systems at fixed temperature and fixed pressure, approximating much more closely to the systems that we are used to dealing with on the laboratory bench or in the real world, the entropy change when "something happens macroscopically" like a mixing or an unmixing or like the extent of a chemical reaction moving from one value to another, does not even have a fixed sign. Nor is its sign any more or less related to changes in mixed–upness. (It is the Gibbs function G that now always decreases if anything happens macroscopically, though its sign is no more closely related to any change in mixed–upness.)

It is true that the mixing of perfect gases is always accompanied by an increase of entropy, regardless of whether the system is one of fixed (U,V) or one of fixed (T,p). That is so because for a perfect gas the energy depends only on the temperature. Indeed, a substance for which $U = U(T)$ is *called* a perfect gas. But what is true of perfect gases may not be wantonly extrapolated into descriptions of real gases let alone of real liquids and solids.

It is also true for many liquid mixings at fixed (T,p) that $\Delta_{\text{mix}}S > 0$. That is so no doubt because the perfect–gas "part" of the mixing dominates. However, it is not always true (water + diethylamine, for example, has a negative entropy of mixing) and there is no way of predicting when it will be untrue. When we turn to chemical reactions, moreover, perfect–gas theory does not help us at all to predict what will even "often" be true.

Finally, it is true that for many mathematically tractable models of solid or liquid mixtures the entropy of mixing turns out to be of exactly the same form as the entropy of mixing of perfect gases and is therefore positive.

But, in no other case is there any, even plausible let alone derivable, relation between the sign of an entropy change and the change in the extent of mixed–upness or randomness or disorder or chaos.