

COMPENSATION LAWS

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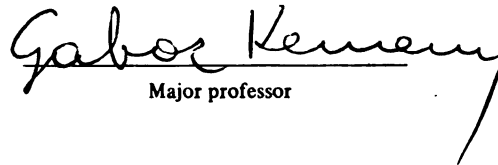
COMPENSATION LAWS

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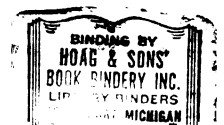
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ABSTRACT

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By

Indur M. Goklany

This thesis concerns itself mainly with linear enthalpy-entropy relationships which give rise to compensation laws.

In Chapter II, we show that experimentally determined conductivities in biological and organic molecules can be as high as 10 to 12 orders of magnitude larger than can be expected from normal solid state physics. We postulate that there is a change in the frequency spectrum of lattice vibrations due to distortions in the lattice (i.e., conformational changes in biological parlance) when charge carriers are created. We show that this can increase the number of states available into which charge carriers may be excited, leading to a large increase in conductivity. This increase in conductivity is due to an entropic increase, and is achieved at the expense of increasing the activation energy by the amount of enthalpy required to create the conformational changes. We then show on the basis of an Einstein oscillator model, that the entropy and enthalpy terms are linearly related, giving rise to a compensation law for conductivity in biological materials.

In Chapter III, we deal with the compensation law in single solute-single solvent systems. Since the late 1930's it has been known that the entropy of solution could be proportional to the enthalpy of

solution in such systems. However, the interpretation of the compensation law has been obscure, partly because there has never been a statistical model that has given rise to a compensation law. Accordingly we set up a model that leads to the compensation law. In this model we postulate that the presence of a solute molecule influences the partition function of neighboring solvent molecules identically. We then calculate the enthalpy and the entropy of solution from Henry's Law and obtain a compensation law for them. We also note that the compensation temperature (T_c) and the experimental temperature (T) cannot be identically equal. If they were identical we arrive at the paradox that the compensation law would not be observable. The compensation law for the enthalpies and entropies of transferring a given solute from H_2O to D_2O is also examined.

In Chapter IV, we examine how the compensation law fits into the structure of statistical mechanics. We note that the total change in entropy on solution differs from the change in entropy as calculated by the compensation law by the mixing entropy. This is the physical basis for not expecting T_c identically equal to T . Also, we note that T_c can be defined as the ratio of the difference in entropy to the difference in enthalpy for different sets of ensembles. This is akin to the definition of the experimental temperature defined for an ensemble. We derive the form the density of states should exhibit for a compensation law to obtain, and show that the models of Chapter II and III satisfy this derived relationship.

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Indur M. Goklany

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CHAPTER I

THE COMPENSATION LAW

There are numerous phenomena in physics, chemistry and biology^{1,2} which can be represented by a relationship of the type

$$K = K'_0 \exp [-\Delta G/(kT)] \quad (1)$$

where K could be the solubility if we are concerned with solution chemistry, it could be the conductivity in semiconductor theory or it could be the rate in the theory of absolute reaction rates, etc. ΔG is a change in Gibbs free energy, this being the free energy required for a solute molecule to go into solution (in solubility) or it could be the energy required to activate a charge carrier (in semiconductor theory) or it may be the free energy of the activated state with reference to the free energy of the reactants (in absolute reaction rate theory); k is Boltzmann's constant and T is the absolute temperature at which the experiments are carried out; K'_0 is a factor, generally algebraic, which depends on the process in question.

The free energy can be written as²

$$\Delta G = \Delta H - T \Delta S \quad (2)$$

where ΔH and ΔS are the changes in enthalpy and entropy, respectively. Substituting Eq. (2) into Eq. (1) we get

$$K = K'_0 \exp [-\Delta H/(kT)] \quad (3)$$

where

$$K_0 = K'_0 \exp [\Delta S/k] \quad . \quad (4)$$

K_0 will be referred to as the pre-exponential factor. In many instances a plot of $\ln K$ vs T^{-1} gives a straight line. This is an Arrhenius plot. This implies that ΔH and ΔS are independent of T . From Eq. (3) we see, therefore, that the slope on a Arrhenius plot will be $-\Delta H/k$. Hence, it is possible to calculate ΔH . To calculate ΔS we have to use Eqs. (1) and (2) with the known value of ΔH .

There is no known thermodynamic or statistical mechanical relationship between ΔH and ΔS or ΔH and $\ln K_0$ yet in a number of situations a linear relationship seems to exist between these terms³⁻¹¹, such that as ΔH increases so does ΔS (or $\ln K_0$). We can see by an examination of Eq. (2) that a linear $\Delta H - \Delta S$ relationship can lead to a situation where changes in ΔG are much smaller than changes in either ΔH or ΔS since the ΔH and $-T \Delta S$ terms compensate for each other. For this reason, linear $\Delta H - \Delta S$ relationships are often said to lead to compensation laws. Similarly linear $\Delta H - \ln K_0$ relationships also compensate in ΔG .

The slope on a $\Delta H - \Delta S$ or $\Delta H - \ln K_0$ plot has units of temperature and for linear plots is known as the compensation temperature T_c .

Surprisingly, though it's been known since the 1930's that compensation laws exist, there has been quite a bit of skepticism among the general scientific community to accept compensation laws as genuine physical phenomena¹²⁻¹⁴. Skepticism revolves around two basic objections. The first reason for skepticism is that the measured quantity is ΔG or K . ΔH is calculated from the slope of the K vs T^{-1} curves whereas ΔS is calculated from Eq. (2). There is no independent method

of measuring ΔS directly. Hence, it has been asserted that an error in the calculation of ΔH will automatically result in a compensating error in ΔS . In this interpretation the compensation, therefore, is regarded as a compensation of errors. However, recently Exner¹⁴⁻¹⁶ has developed stringent statistical tests to be applied to data which leads to compensation laws. His results indicate that in certain cases the compensation law is a genuine physical phenomenon.

The second objection arises from the fact that no one has given a statistical mechanical or model calculation that leads to a compensation law. In the absence of such a theory it is not possible to say why and how a compensation law arises and the interpretation, if any, of T_c is unknown^{3,4,7,13,17}. Recently¹⁷ there has been a derivation of a compensation law for solubility. We will examine this in detail. Our analysis, however, indicates that compensation in solutions comes from a source different from the one outlined in Ref. 17 (Chapters III and IV).

It is the intention of this thesis to devise model systems that lead to compensation laws. To the extent that this can be done we shall have successfully been able to refute the second objection outlined above and gained some understanding of how and why compensation laws occur and perhaps obtain an interpretation of the constant of proportionality T_c .

Models will be set up specifically for the case of conductivity in biological substances (Chapter II) and for solubility (Chapter III). The reason for choosing the conductivity is that it was in this context that we were introduced to the compensation law. Conductivity in some biological substances also exhibits the extremely interesting (and unexplained) feature of having an enormously large pre-exponential factor.

We hope to be able to explain this, too. One reason for choosing to examine the compensation law in solubility was that this was, as far as we know, the simplest compensation law in chemistry.

CHAPTER II

CONFORMONS AND ELECTRICAL CONDUCTIVITY IN BIOLOGICAL MATERIALS

2.1 INTRODUCTION

Any theory of the electrical conductivity of organic and biological semiconductors has to contend with two major problems: In many of these substances 1) the conductivity is many orders of magnitude higher than predicted by conventional semiconductor theory for the observed high activation energies and 2) the pre-exponential factor itself is an exponential function of the activation energy, leading to the compensation law.

Since the mobility of these substances is known to be quite low, a high density of activated charge carriers is the only possible way to explain high conductivities. Mechanisms familiar from solid state physics do not provide for the requisite charge carrier density. We have, therefore, assumed that the effective density of states for activated charge carriers is greatly increased by the interaction of the activated carriers with other degrees of freedom of the molecules. This provides for an activation entropy which, under appropriate circumstances, is proportional to the activation energy, leading to the compensation law¹⁹.

A recent communication by Volkenstein²⁰ introduced similar ideas, but for different purposes, specifically excluding semiconductivity from his range of applications. He considered the interaction of an electron with a biological macromolecule. Such an interaction may lead to the

transconformation of the macromolecule. The electron plus the conformational change he called the conformon.

Volkenstein's mechanism and ours are very similar from the point of view of statistical mechanics. In both cases there is a relationship between an activation energy or enthalpy and activation entropy. The entropy can take on substantial values because energy can be distributed over many degrees of freedom. We allow these degrees of freedom to spread over one or more molecules if necessary. Although the applications may be different it seems reasonable to retain Volkenstein's term and we will call the activated carrier plus the accompanying changes carrying energy and entropy the conformon.

Objections have been raised against the experimental background on which this theory rests because 1) the activation energy appears to be too high and 2) the charge carriers may be not electrons and holes, but ions. The experimental background, however, is quite solid. The electronic nature of the charge carriers and the high activation energies have been well documented in several instances. Even if the charge carriers are ionic the same experimental facts, i.e., high conductivity and the compensation law, still must be explained. Our present theory is formulated for electrons and holes, but it would be easy to reformulate it to apply to ions or protons. The concept of the conformon is a generalization of the small polaron concept. A small polaron is formed if an electron is trapped by its own polarization field²¹. The small polaron can move by thermally activated hopping or by tunnelling^{22,23}. It was suggested by Kemeny and Rosenberg²⁴ that small polaron tunnelling can account for some of the semiconductive properties of biological substances. The explanations so obtained were neither complete nor free

from objections (see Section 2.6). In the present paper we hope to overcome both types of limitations using a new mechanism. This mechanism could be called conformon hopping and it does not involve tunneling. The small polaron concept does not involve entropy changes while the conformon concept does. Herein lies the generalization.

2.2 ELECTRICAL CONDUCTIVITY AND CONFORMATION

If one examines the data on biological semiconductors^{10,25-27} one is struck by the values quoted for σ_0 which often lie above 10^{10} and can be as large as 10^{22} mho-cm⁻¹. By usual semiconductor theory the conductivity σ is given as

$$\sigma = \sigma_0 \exp(-\beta E/2) \quad (1)$$

where

$$\sigma_0 = Ne\mu \quad , \quad (2)$$

and E is the gap energy, or alternatively the negative slope in a $\ln \sigma$ vs $1/2kT$ plot, N , e and μ being the total density of charge carriers, the electronic charge and the mobility, respectively. The largest mobility found to date is of the order of 10^5 cm²(v-sec)⁻¹ in lnSb. N is given by

$$N = N_A Dn/M \quad (3)$$

where N_A , M , D and n are Avogadro's number, the molecular weight, the density and the number of charge carriers available for excitation per molecule of substance. Taking $N = N_A$, which is likely an overestimate, we get the maximum possible value of σ_0 as 10^{10} mho-cm⁻¹ which implies that in some cases the experimental values of σ_0 are larger than this by as much as ten or twelve orders of magnitude (this

point was repeatedly stressed by Prof. H. Kallmann: private communication by Prof. B. Rosenberg). This is in spite of the fact that we have here used a mobility of $10^5 \text{ cm}^2(\text{V-sec})^{-1}$ whereas for most organic or biological semiconductors it should be taken as 10 or even as low as 10^{-5} (Ref. 28).

The observed large value of σ_0 , therefore, must be associated with a large density of activated charge carriers. Unfortunately we know of no feature in solid state physics that enables us to increase the number of activated charge carriers by several orders of magnitude. Thus, we were led to search for an explanation outside the domain of solid state physics. We postulated that changes in conformation and/or coordination in the molecular system are responsible for increasing the effective number of excited electronic states¹⁹.

The creation of charge carriers in intrinsic semiconductors occurs in pairs, i.e., an electron and a hole are created simultaneously. These carriers move far from each other in the conduction process and thus one positively and one negatively charged macromolecule is present for each electron-hole pair. We shall assume that one or both of these molecular ions can exist in various conformations and/or coordinations. Due to the large statistical weight associated with the electron-hole pair, i.e., the large entropy of the activated state, the number of activated charge carriers is very large. This will account for the high conductivity, provided the above mechanism does not decrease the mobility. It may be pointed out that even if the electron and hole were separated far enough within the same molecule, the same argument could be applied for an increase in the entropy.

A lowering of the mobility could be caused in two ways. A molecule has to change its conformation and/or coordination both when the electron (or hole) reaches it and when it passes on. The conformational change may require either activation or tunnelling through some barriers. If both these processes are difficult the mobility will decrease, perhaps offsetting the gain in activated states. We will see later on that conformational activation will not raise any problems in this respect.

It is necessary to present here some theoretical developments of a general nature before returning to the specific properties of the substances in question.

2.3 ELECTRONS AND HOLES IN SEMICONDUCTORS WITH CONFORMATIONAL CHANGES

Let us consider an ordinary intrinsic semiconductor first with N molecules. Each molecule has one conduction and one valence state and one electron on the average. Thus the system has a total of $2N$ states and N electrons. If we place the zero of energy in the middle of the gap the conduction levels are at energy ϵ , the valence levels at $-\epsilon$. The grand canonical partition function Q is given by

$$Q = [1 + q \exp(-\beta\epsilon) + q \exp(+\beta\epsilon) + q^2]^N \quad . \quad (4)$$

Here N represents the number of molecules, 1 that no electron is present, $q \exp(-\beta\epsilon)$ that one electron is in the conduction level, $q \exp(+\beta\epsilon)$ that one is in the valence level and q^2 that there is one electron in each. The expectation value for the number of electrons is²⁹:

$$n_e = q \frac{\partial}{\partial q} \ln Q = N \left[\frac{q \exp(-\beta\epsilon)}{1 + q \exp(-\beta\epsilon)} + \frac{q \exp(+\beta\epsilon)}{1 + q \exp(+\beta\epsilon)} \right] \quad . \quad (5)$$

Writing

$$q = \exp(\beta\mu) \quad , \quad (6)$$

where μ is the chemical potential and demanding

$$n_e = N \quad (7)$$

one finds

$$\mu = 0 \quad . \quad (8)$$

The above treatment becomes awkward if conformational changes are allowed. It requires that the above grand partition function be generalized by the inclusion of conformational effects. Eq. (4), however, allows unphysical states, i.e., states which do not have the correct number of electrons. In order to avoid the question of how to generalize the unphysical terms in Eq. (4) and still retain the advantages of the grand canonical formulation we introduce a new grand partition function Q' using the definition

$$Q' = [1 + q' \exp(-2\beta\epsilon)]^N \quad . \quad (9)$$

The first term on the right represents no particle present and the second one stands for one electron in the conduction level and one hole in the valence level. The first term, of course, can just as well be interpreted as one electron in the valence level and one hole in the conduction level. The number of electrons in the conduction level is then

$$n'_e = q' \frac{\partial}{\partial q} \ln Q' = \frac{N q' \exp(-2\beta\epsilon)}{1 + q' \exp(-2\beta\epsilon)} \quad . \quad (10)$$

n'_e has to be equal to the number of conduction electrons n_e calculated from Eq. (4), which is

$$n'_e = \frac{N q \exp(-\beta\epsilon)}{1 + q \exp(-\beta\epsilon)} \quad (11)$$

as can be seen from Eq. (5). Comparisons of Eqs. (10) and (11) show

that

$$q' = \exp(\beta\epsilon) \quad . \quad (12)$$

If the electron in question is in the valence state certain molecular conformations are possible and if it is in the conduction state some other conformations are allowed. A conformational partition function is necessary for both. Thus the complete partition function is

$$Q'' = [Q_v + Q_c q' \exp(-2\beta\epsilon)]^N \quad , \quad (13)$$

where Q_c and Q_v stands for the conformational partition functions of the respective levels. The number of electrons in the conduction levels is

$$n_c'' = N \frac{Q_c q' \exp(-2\beta\epsilon)}{Q_v + Q_c q' \exp(-2\beta\epsilon)} \quad (14)$$

For $Q_c = Q_v$ this reduces to Eq. (10) as required. If the fraction of excited electrons is not too large then

$$n_c'' = N \frac{Q_c}{Q_v} \exp(-\beta\epsilon) \quad , \quad (15)$$

where Eq. (12) has been utilized. If we introduce the conformational free energy difference between the two electron states by

$$\frac{Q_c}{Q_v} = \exp(-\beta\Delta F) \quad (16)$$

and the corresponding conformational enthalpies and entropies by

$$\Delta F = \Delta H - T\Delta S \quad , \quad (17)$$

then

$$n_c'' = N \exp\left(-\frac{\epsilon + \Delta H}{kT} + \frac{\Delta S}{k}\right) \quad . \quad (18)$$

Thus the number of activated electrons (and of holes, which is the same) is given not by the electronic activation energy alone, which would be $2e$, but must also include the conformational enthalpy. Also the conformational entropy must be considered. The experimentally measured activation energy for semiconduction includes the effect of ΔH automatically, but it may include thermal effects on the mobility also, and therefore cannot simply be read off from Eq. (18). A large value of ΔS would increase n_c and thus the conductivity. This, of course, was the purpose of the whole exercise.

2.4 CONFORMONS IN BIOLOGICAL MOLECULES

We require now some sort of a model which provides for a great rise in entropy in the presence of an activated charge carrier. Since not enough is known at this time concerning the nature of the forces in the systems under consideration one can only assert that such an idea is quite acceptable in related contexts. Volkenstein²⁰ suggested that in certain cases the free energy of an electronic transition is lowered considerably by conformational changes accompanying such a transition. We invoke this concept for conductivity. The energy available for conformational changes in the conductivity problem is comparable to the energy in other situations. The activation energy is generally $2eV$ or higher, sometimes as high as $4eV$ ³⁰. It seems possible, therefore, that the process of activation could involve setting the molecules "free" if there were sufficient gain in entropy to warrant it.

When a dielectric (e.g., water) is mixed in with the solid, the dielectric screens the effect of the charge. Thus the disruptive effect of the charge on the structure would have a shorter range. Hence as more dielectric is introduced, the disorganization due to charges is

reduced. Thus the increase in entropy is less in the presence of a dielectric.

Incidentally, the dielectric also has another effect. The charge polarizes the dielectric, which in turn produces a field that traps the charge itself. The decrease of energy due to the charge-dielectric interaction is the polaron binding energy W_p .

So far we have stated that an entropy factor is essential to explain the high values of σ_o and also we have postulated a general model by which the entropy could increase. We now attempt to estimate the increase in entropy.

Let us consider a more specific model in which the molecule is rigidly bound in the solid prior to the arrival (or creation) of the charge carrier. The partition function (Q_v) is unity and it has no entropy associated with it. After introduction of the charge carrier in this molecule, the molecule becomes "free" in a 3-dimensional infinite square well since we have given it enough energy to overcome the attractive forces. Q_c is given by²⁹

$$Q_c = (2\pi m k T a^2 / h^2)^{3/2} \quad (19)$$

where m , k and h are the mass of the molecule, Boltzmann's constant and Planck's constant, and a the width of the well. Since the entropy in the rigid conformation was zero, the increase in entropy is given by the entropy as calculated from Q_c . Using the standard recipe for finding the entropy from a partition function we get

$$\Delta S = k \ln Q_c + 3k/2 \quad (20)$$

Taking the molecular weight as 400, which is close to that of oxidized

cholesterol, $T=300^\circ\text{K}$ and $a=5\overset{\circ}{\text{\AA}}$ we get

$$\Delta S/k = 15.31 \quad . \quad (21)$$

This gives us an enhancement of σ_o by $\exp(15.31)$ or $10^{6.65}$. However, calculations of σ_o for oxidized cholesterol show that the experimental value is about $10^{11.9}$ above the calculated value (see Table I in Section 2.7 below). Hence we have to either increase the width of the potential well or we have to have an extra "free" molecule. If we have only one "free" molecule we need $a \approx 282\overset{\circ}{\text{\AA}}$ to give the right result which is absurdly large. However, two "free" molecules (one each due to the electron and the hole) could give the correct entropy factor taking $a=2.9\overset{\circ}{\text{\AA}}$ for each molecule

2.5 OSCILLATOR MODEL OF ACTIVATION ENERGY AND ENTROPY OF CONFORMONS

Let us consider a different picture of what may be going on in a biological semiconductor. Part of the activation energy can be conceived as being distributed among a number of harmonic oscillators which correspond to degrees of freedom of the biological molecules and the dielectric molecules. Let there be m such "molecular" oscillators, and d "dielectric" oscillators. We shall for sake of simplicity assume that each of the m oscillators is identical with each quantum having energy ϵ_m . Similarly the d dielectric oscillators have each quantum of energy equal to ϵ_d .

If energy

$$E = n_m \epsilon_m + n_d \epsilon_d \quad (22)$$

has to be distributed among these $m+d$ modes with n_m and n_d being the respective number of quanta, then the number of ways of distributing E is given by

$$W = \frac{(n_m + m - 1)!}{n_m! (m - 1)!} \frac{(n_d + d - 1)!}{n_d! (d - 1)!} \quad . \quad (23)$$

Fowler³¹ has worked out a similar problem. We shall assume, for simplicity, that ϵ_m and ϵ_d have no common divisor. Using the method of Lagrange Multipliers, with Eq. (22) as the auxiliary condition, we find the maximum of $\ln W$. This yields

$$\ln W_{\max} = (\bar{n}_m \epsilon_m + \bar{n}_d \epsilon_d) + (m - 1) \ln \left[\frac{\exp(\lambda \epsilon_m)}{\exp(\lambda \epsilon_m) - 1} \right] + (d - 1) \ln \left[\frac{\exp(\lambda \epsilon_d)}{\exp(\lambda \epsilon_d) - 1} \right], \quad (24)$$

where λ is the Lagrange Multiplier, $\bar{n}_m$ and $\bar{n}_d$ denote the most probable number of quanta in the m and d oscillators, respectively. λ has to satisfy the two equations

$$\lambda \epsilon_m = \ln \left[\frac{\bar{n}_m + m - 1}{\bar{n}_m} \right] \quad (25)$$

and

$$\lambda \epsilon_d = \ln \left[\frac{\bar{n}_d + d - 1}{\bar{n}_d} \right] \quad . \quad (26)$$

It should be added that we need Stirling's approximation to evaluate Eq. (24).

Equating $\ln W_{\max}$ to S/k and substituting Eq. (22) into Eq. (24) we obtain

$$S/k = \lambda E + (m - 1) \ln \left[\frac{\exp(\lambda \epsilon_m)}{\exp(\lambda \epsilon_m) - 1} \right] + (d - 1) \ln \left[\frac{\exp(\lambda \epsilon_d)}{\exp(\lambda \epsilon_d) - 1} \right] \quad . \quad (27)$$

Using Eq. (22), (25) and (26) we get

$$E = \frac{(m - 1) \epsilon_m}{\exp(\lambda \epsilon_m) - 1} + \frac{(d - 1) \epsilon_d}{\exp(\lambda \epsilon_d) - 1} \quad . \quad (28)$$

So far we have taken no approximations (barring Stirling's approximation). We will now assume that the number of quanta in the d oscillators is low. This implies that the second term in Eq. (28) can be neglected. Eq. (28) can therefore be written as

$$E = \frac{(m-1)\epsilon_m}{\exp(\lambda\epsilon_m)-1} \quad . \quad (29)$$

This assumption is valid if the energy $\epsilon_d \gg \epsilon_m$ or $d \ll m$. We expect $\epsilon_d \gg \epsilon_m$ because the mass of the dielectric molecules (generally water) is much less than that of the molecules, furthermore the interaction of the charge with the dielectric is expected to be strong leading to a large spring constant. Under these conditions we could neglect the last term in Eq. (27). Combining the resulting equation with Eq. (29) we get

$$S/k = \bar{n}_m \ln[1 + \frac{m-1}{\bar{n}_m}] + (m-1) \ln[1 + \frac{\bar{n}_m}{m-1}] \quad , \quad (30)$$

where

$$\bar{n}_m = E/\epsilon_m \quad . \quad (31)$$

Substituting Eq. (31) into Eq. (30) gives us

$$S/k = E/\epsilon_m \ln[1 + \frac{(m-1)\epsilon_m}{E}] + (m-1) \ln[1 + \frac{E}{(m-1)\epsilon_m}] \quad . \quad (32)$$

We will show below that the dependence of the entropy on m , as given by Eq. (30), or on E , as given by Eq. (32), can lead to a compensation rule.

2.6 CONDUCTIVITY ON THE POLARON AND CONFORMON MODELS

Kemeny and Rosenberg^{24,32} have shown that small polaron formation occurs in biological semiconductors. The evidence for such a claim can

be based upon: (a) the fact that the experimental activation energy drops as additives of high dielectric constant are introduced into the biological material, the drop in the activation energy being proportional to the inverse of the dielectric constant³³; and (b) calculations by Kemeny and Rosenberg¹⁵ which indicate that the effective electronic mass may be as high as $100 m_e$ (m_e being the electron mass). Kemeny and Rosenberg²⁴ assumed that the polarons moved by tunnelling rather than hopping. This gave a compensation rule for the conductivity. The compensation temperature T_c was interpreted as $\theta_D/2$ where θ_D is the Debye temperature. However, at temperatures greater than $\theta_D/4$ the polaron motion is expected to be by hopping rather than tunnelling³⁴. This implies that if the data were gathered at temperatures greater than $T_c/2$, as indeed they were, polaron motion would not explain the compensation rule. Furthermore, the T_c as calculated in the theory, was a function of the additive rather than being dependent on the biological molecule only, and this is contrary to experimental results.

We will combine small polaron hopping with the harmonic oscillator model developed in the previous section to give a comprehensive explanation of biological semiconduction including the large number of activated charge carriers and the compensation rule. We shall use the results for small polaron hopping in the adiabatic approximation as described by Austin and Mott²³. Extension of the results to the non-adiabatic approximation is trivial and we shall not do it here. The results, however, should be qualitatively similar.

The mobility in the adiabatic approximation is given as²³

$$\mu = e a^2 \omega_o \beta \exp(-\beta W_p / 2) \quad (33)$$

where a is the hopping distance, ω_0 the optical vibrational frequency $\beta=1/(kT)$ and $W_p/2$ is the activation energy required for the polaron to hop. W_p is the polaron binding energy. The conductivity σ is given by

$$\sigma = n_c'' e \mu, \quad (34)$$

where n_c'' is the number of activated electrons as given by Eq. (18) and e is the electronic charge. Using Eq. (18), (33) and (34) we get

$$\sigma = N e^2 a^2 \omega_0 \beta \exp[-\beta(E+2\Delta H)/2] \exp(-\beta W_p/2) \exp(\Delta S/k). \quad (35)$$

It should be pointed out that $E=2\epsilon$ is the minimum energy required to separate the electron from the hole. ΔH is the enthalpy term that comes from the conformational changes, and ΔS the entropy corresponding to this. So that the formulae be less cumbersome, we shall assume that in the absence of dielectric there is no polaron formation (i.e., $W_p=0$). From now on quantities with a superscript 0 will mean that no dielectric has been added.

The conductivity in the absence of dielectric σ^0 is given by,

$$\sigma^0 = N e^2 a^2 \omega_0 \beta \exp[-\beta (E^0+2\Delta H^0)/2] \exp(\Delta S^0/k). \quad (36)$$

The experimentally determined activation energy (E_{exp}^0) is, therefore, given by

$$E_{\text{exp}}^0 = E^0/2 + \Delta H^0. \quad (37)$$

In the presence of dielectric the energy to separate the electron and the hole decreases by $2W_p$, that being the polaron binding energy of the electron plus the hole. Hence,

$$E = E^0 - 2W_p \quad (38)$$

and the conductivity σ is given by Eq. (35) and (38) as

$$\sigma = N e^2 a^2 \omega_o \beta \exp[-\beta (E^0 - W_p + 2\Delta H)/2] \exp(\Delta S/k) \quad . \quad (39)$$

The activation energy determined experimentally (E_{exp}) in the presence of dielectric is thus

$$E_{\text{exp}} = E^0/2 + (\Delta H - W_p/2) \quad . \quad (40)$$

Eq. (39) is the general expression for the conductivity. In the next section we shall use this in conjunction with the expressions for the entropy to derive a compensation rule.

2.7 THE COMPENSATION RULE

In Section V we derived the entropy resulting from distributing a fixed amount of energy among m molecular oscillators. In the absence of dielectric E_{exp}^0 is composed of two terms, $E^0/2$ and ΔH^0 , as can be seen from Eq. (37). Here $E^0/2$ is the energy required to separate the electron-hole pair and ΔH^0 is the energy distributed to the m^0 oscillators, where $m = m^0$ in the absence of dielectric.

In the presence of dielectric the energy distributed to the molecular oscillators is ΔH by Eq. (40). $(E^0 - W_p)/2$ is the sum of the energy required to create the electron-hole pair in the dielectric and the energy required to enable the polaron to hop. For this case we take the number of molecular oscillators as m .

The dielectric effectively screens off the effects of the charge carriers, and one could, therefore, expect the conformational changes to be of a smaller magnitude, i.e., $\Delta H < \Delta H^0$ and $\Delta S < \Delta S^0$. By the same token, as the dielectric constant is increased by adding dielectric W_p increases. It has been shown³⁵ that W_p increases linearly with the

concentration of dielectric. If we now make the assumption that the decrease in the enthalpy term, i.e., $\Delta H^0 - \Delta H$, is also linear with the amount of dielectric we can write

$$\Delta H = \Delta H^0 - W_p / f \quad (41)$$

where $1/f$ is a positive number. We will show this assumption leads to the compensation rule. Whereas this is no justification in itself it is consistent with the qualitative arguments laid out at the beginning of this paragraph.

We will now look at two specific models each of which leads to a compensation rule.

Model I. In this model we assume that as dielectric is added to the biological substance, the screening effects will reduce the number of participating molecular oscillators from m^0 to m . However, each participating oscillator has to be excited to the same level whether or not the dielectric is present, i.e., each oscillator has the same number of quanta (say r) present.

From Eq. (30) we obtain

$$\frac{\Delta S^0}{k} = rm^0 \ln \left(1 + \frac{m^0 - 1}{rm^0}\right) + (m^0 - 1) \ln \left(1 + \frac{rm^0}{m^0 - 1}\right), \quad (42)$$

and

$$\frac{\Delta S}{k} = rm \ln \left(1 + \frac{m - 1}{rm}\right) + (m - 1) \ln \left(1 + \frac{rm}{m - 1}\right), \quad (43)$$

where rm^0 and rm are the total number of quanta in the absence and presence of a dielectric, respectively. Here

$$rm^0 \epsilon_m = \Delta H^0 \quad (44)$$

and

$$rm \epsilon_m = \Delta H. \quad (45)$$

Combining Eq. (43) with (45) we get

$$\frac{\Delta S}{k} = \frac{\Delta H}{\epsilon_m} \ln \left(1 + \frac{\Delta H / (r\epsilon_m) - 1}{\Delta H / \epsilon_m} \right) + \left(\frac{\Delta H}{r\epsilon_m} - 1 \right) \ln \left(1 + \frac{\Delta H / \epsilon_m}{\Delta H / (r\epsilon_m) - 1} \right) . \quad (46)$$

From Eq. (42) and (44) the expression for $\Delta S^0/k$ is similar formally, except that all the ΔH in Eq. (46) are replaced by ΔH^0 .

The logarithmic terms in Eq. (46) are weakly dependent on $\Delta H/\epsilon_m$, hence we could write Eq. (46) as,

$$\Delta S/k = c\Delta H/\epsilon_m + b , \quad (47)$$

where

$$c = \ln \left(1 + \frac{\Delta H - r\epsilon_m}{r\Delta H} \right) + \frac{1}{r} \ln \left(1 + \frac{r\Delta H}{\Delta H - r\epsilon_m} \right) \quad (48)$$

and

$$b = - \ln \left(1 + \frac{r\Delta H}{\Delta H - r\epsilon_m} \right) \quad (49)$$

with c and b approximately constant.

Similarly,

$$\Delta S^0/k = c \Delta H^0/\epsilon_m + b . \quad (50)$$

Substituting the expressions for entropy Eq. (47) into the conductivity expression Eq. (39) and eliminating W_p with Eq. (41) we obtain

$$\sigma = N e^2 a^2 \omega_0^2 \beta \exp[-\beta (E^0 - f\Delta H^0 + (f+2)\Delta H)/2] \exp(c\Delta H/\epsilon_m) \exp(b) . \quad (51)$$

Eq. (51) can be specialized to the case where no dielectric is present by substituting ΔH^0 for ΔH .

We can reorganize Eq. (51) into the form

$$\sigma = \sigma'_0 \exp \left[E_{\exp} \left(\frac{1}{kT_c} - \frac{1}{kT} \right) \right] , \quad (52)$$

where

$$\sigma'_0 = N e^2 a^2 \omega_0 \beta \exp(b) \exp[-(E^0 - f\Delta H^0)/2kT_c] \quad , \quad (53)$$

$$E_{\text{exp}} = E^0/2 + \Delta H - W_p/2 \quad (54)$$

and

$$\frac{1}{kT_c} = \frac{2c}{(f+2)\epsilon_m} \quad . \quad (55)$$

Eq. (52) is a statement of the compensation rule. Obviously no matter what E_{exp} might be, i.e., whether the dielectric is present or not, at $T = T_c$ the conductivity is always σ'_0 which is invariant. Further, Eq. (52) is valid for the case where no dielectric is present if we redefine E_{exp} from Eq. (54) by taking $\Delta H = \Delta H^0$ and $W_p = 0$.

Using Eq. (55) we can estimate the values for T_c . ϵ_m corresponds to the energy of an optical vibrational quanta, i.e., $\epsilon_m = \hbar\omega_0$. Taking $\omega_0 = 10^{14} \text{ sec}^{-1}$ and assuming $2c/(f+2)$ to be unity we get a T_c of 720°K . This is in the right range. If we choose a larger value of $2c/(f+2)$, T_c is decreased which is reasonable in view of the experimental values.

Calculation of the mobility from Eq. (33) also gives us reasonable values. Taking a , the hopping length, as $3\text{\AA}$, $T = 300^\circ\text{K}$ and $\omega_0 = 10^{14}$, we get

$$\mu = 4 \exp(-\beta W_p/2) \text{ cm}^2 (\text{volt-sec})^{-1} \quad . \quad (56)$$

The exponential term may vary from unity to 10^{-5} (or less). This gives us values of μ between 4 and $4 \times 10^{-5} \text{ cm}^2 (\text{volt-sec})^{-1}$ which are reasonable for biological semiconductors²⁸.

In order to obtain estimates of ΔS we have calculated the conductivity assuming the substances to be conventional semiconductors, i.e.,

neglecting any entropy contribution. Whatever discrepancy there was between the values so calculated and the experimental values, was assigned as due to ΔS . The comparison of the calculated and experimental values was made at the experimentally obtained compensation temperature (T_c) of each substance. The experimental activation energies E_{exp} that we used are those for the substance with no dielectric.

The conductivity of a conventional semiconductor at T_c is

$$\sigma_{\text{conv}}^0(T_c) = Ne\mu \exp(-E_{\text{exp}}^0/kT_c) \quad (57)$$

We took $\mu = 1 \text{ cm}^2 (\text{volt-sec})^{-1}$ and $N = 10^{23}/\text{cm}^3$.

We also made approximate estimates for ΔH^0 from Eq. (50) taking c as unity and $b = 0$. We noted that all these estimates for ΔH^0 were less than the corresponding E_{exp}^0 . Finally by assuming $2c/(f+2)$ to be unity we estimated $\omega_o = \epsilon_m/n$ from Eq. (55). The results are shown in Table 1.

Table 1. Conformational Enthalpies and Entropies at T_c

	11 cis Retinal	Oxidized Cholesterol	Adenine	Uracil	Guanine	Cytosine
$(kT_c)^{-1} (\text{eV}^{-1})$	43.0*	23.6*	27.6 ⁺	27.6 ⁺	27.6 ⁺	27.6 ⁺
$E_{\text{exp}}^0 (\text{eV})$	1.7*	~2.0	2.65 ⁺	2.3 ⁺	1.75 ⁺	2.45 ⁺
$\sigma^0 (\text{conv.})$	$10^{-27.6}$	$10^{-16.3}$	$10^{-27.6}$	$10^{-23.2}$	$10^{-16.8}$	$10^{-25.2}$
$\sigma^0(T_c) = \sigma_o$	$10^{-16.7*}$	$10^{-4.4*}$	$10^{-15.4}^+$	$10^{-15.4}^+$	$10^{-15.4}^+$	$10^{-15.4}^+$
$\Delta S^0/k$	25.1	27.4	28.05	17.95	3.22	22.55
$\Delta H^0 (\text{eV})$	0.58	1.16	1.03	0.65	0.12	0.81
$\omega_o (\text{sec}^{-1})$	3.6×10^{13}	6.5×10^{13}	5.5×10^{13}	5.5×10^{13}	5.5×10^{13}	5.5×10^{13}

* Data from Ref. 30.

+ Data from Ref. 10.

It should be noticed that the constant $2c/(f+2)$ and ϵ_m are both characteristics of the molecular substance. From Eq. (55), therefore, it is clear that T_c is a function of the intrinsic biological semiconductor. This feature also tallies with experimental results.

Model II. In this model introduction of the dielectric does not change the number of molecular oscillators. It merely changes the total energy to be distributed among the oscillators. The entropy in such a situation is given by Eq. (32) where we have to remember that m is invariant. ΔS could therefore be written as

$$\Delta S \approx \frac{c' \Delta H}{\epsilon_m} + b' \quad , \quad (58)$$

where c' and b' are slowly varying functions of ΔH analogous with Eqs. (48) and (49) in the previous model. This will also give a compensation rule for conductivity, and the final results will be similar to those depicted by Eqs. (52) through (55). In fact, numerically, it is hard to distinguish the two models.

However, we may point out that this model exhibits a very curious feature if

$$(m-1) \ll \bar{n}_m = \Delta H / \epsilon_m \quad , \quad (59)$$

i.e., each oscillator contains many quanta. In this case examination of Eq. (32) shows that

$$\Delta S/k = (m-1) \left[1 + \ln \left(1 + \frac{\Delta H / \epsilon_m}{m-1} \right) \right] \quad , \quad (60)$$

that is

$$\Delta S/k \approx \text{constant} \quad . \quad (61)$$

This means that the entropic advantage will be unchanged whether or not dielectric is present. This means that for this regime we have no compensation rule, but we could get a σ_0 much larger than expected. As far as we are aware, experimentally there is no such material, i.e., when we have a large σ_0 , we also seem to have a compensation rule. But the result, in any case, is very intriguing.

Also, when $m = 0$, from Eq. (60) we see that we get no entropic advantage. This is the situation for conventional semiconductors.

2.8 GENERAL OBSERVATIONS ON CONFORMONS

The semiconductive processes of biological substances have so far seemed to be a matter of solid state physics, a problem isolated from the physical chemistry of these substances. The solid state properties were historically related to Bloch waves, which required long range order in crystalline substances, while physical chemistry dealt with the local interactions and conformational changes of the biological molecules. This view of solid state physics is outdated, partially because small polaron formation has been increasingly incorporated into the standard ideas of solid state physics. Now that conformational change is implicated in the semiconductive properties of biological molecules the solid state physics and the physical chemistry of these substances become indistinguishable. It seems that conductivity and other trans-conformation processes only differ in the number of individual steps involved in transferring a charge from one place to another and not in the nature of the mechanisms involved.

We have shown that the large values of the pre-exponential factor in the conductivity is a consequence of the entropic advantage derived from conformational changes induced by the presence of charges. Further,

as dielectric is added to the biological substance, the activation energy drops, increasing the conductivity. Simultaneously, the entropic advantage tends to decrease thus reducing the conductivity. At a particular temperature (T_c), known as the compensation temperature, these two effects precisely cancel each other, thus leading to a compensation rule. Further, the compensation temperature is shown to be a characteristic of the biological substance as a consequence of the assumption that the number of quanta in the oscillators corresponding to the degrees of freedom of the dielectric are much fewer than the number in those oscillators corresponding to the degrees of freedom of the molecules. However, if the converse were true, i.e., if the number of quanta in the molecular oscillators was much fewer than the number in the dielectric oscillators, we could derive a compensation temperature (T_c) which is a characteristic of the dielectric.

It should be pointed out that there are a few activation phenomena that exhibit a compensation rule with a T_c characteristic of the dielectric (generally water³). We feel that these phenomena could be explained in the manner outlined above.

A point that deserves to be investigated experimentally is whether there are materials which exhibit a large σ_0 , but do not show a compensation rule.

Since we have shown that in general the number of activated charge carriers includes a free energy term we are led to ask why this term is not evident in all semiconduction. One would expect that semiconductors, in which the molecules are small and held together by covalent bonds, are not likely to be subjected to local disruption as easily as in those materials in which the molecules are held together by weak forces. We

also expect that at higher temperatures the entropic advantage due to charge creation is going to be less evident, local disruption being already present due to thermal effects.

CHAPTER III

SINGLE SOLUTE - SINGLE SOLVENT SYSTEMS

3.1 INTRODUCTION

In this chapter we will deal with compensation laws for enthalpies and entropies of solution for homologous series of non-electrolytic solutes in single solvent systems. The existence of such compensation laws has been known since the 1930's^{3,6-8,36-40}. However, as far as we are aware, there has never been a satisfactory statistical mechanical derivation for the compensation laws in such systems. We will set up models that lead to linear ΔH vs. ΔS relationships and show that though the constant of proportionality may be temperature dependent it is not, in fact, the experimental temperature. We also expect this approach to shed light as to when one can or cannot expect a compensation law to be valid.

3.2 SINGLE SOLUTE, SINGLE SOLVENT MODEL

Let us consider a solution containing n solute and N solvent molecules. Each solute molecule perturbs the energy levels of the surrounding solvent molecules. One would expect that the further a solvent molecule is from the solute molecule the less is the effect of this perturbation on its energy spectrum. Let each solute molecule perturb A solvent molecules. We, therefore, have two types of solvent molecules: those that are perturbed and those that are not. We will assume that each perturbed molecule is perturbed identically. We shall examine this assumption in the subsequent sections.

We shall now distribute the $n + N$ molecules into $M \geq N + n$ equivalent cells. Let the partition function for each of the unperturbed and perturbed solvent molecule be denoted by Q_0 and Q_1 , respectively, and let q be the partition function of each solute molecule in the solvent. If we were to calculate q , Q_0 and Q_1 we should have to restrict the spatial coordinates to the dimensions of each cell. To avoid proliferation of partition functions we shall assume that the solution is going to be dilute enough to neglect solute-solute interactions.

The canonical partition function for the system outlined above is

$$Q_c(n, N) = \frac{M!}{n! N! (M-N-n)!} Q_0^{N-An} Q_1^{An} q^n \quad (1)$$

We will now set up a grand canonical partition function Q_g where we can vary both n and N up to a maximum M . This gives

$$Q_g = \sum_{N=0}^M \sum_{n=0}^{M-N} \frac{M!}{n! N! (M-N-n)!} (\Lambda_0 Q_0)^{N-An} (\Lambda_1 Q_1)^{An} (\lambda q)^n, \quad (2)$$

where Λ_0 , Λ_1 and λ are the fugacities of the unperturbed solvent, perturbed solvent and solute molecules such that

$$\Lambda_0 = \exp(\beta\mu_0) \quad , \quad (3a)$$

$$\Lambda_1 = \exp(\beta\mu_1) \quad , \quad (3b)$$

and

$$\lambda = \exp(\beta\mu) \quad . \quad (3c)$$

Here μ_0 , μ_1 , and μ are the corresponding chemical potentials and β is $(kT)^{-1}$. We should note that in the summation for n , if $n > M/(A+1)$ then the number of perturbed solvent molecules is going to be less than An . In effect, Q_g has not been set up exactly, but if the solution is dilute enough we would expect the terms for $n > M/(A+1)$ to contribute

negligibly to the summation over n . Using the multinomial theorem we sum the right hand side in Eq. (2) to give us

$$Q_g = [1 + \Lambda_o Q_o + \lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A]^M \quad . \quad (4)$$

Using the standard methods of statistical mechanics^{12,27} we get

$$\frac{PV}{kT} = \ln Q_g = M \ln [1 + \Lambda_o Q_o + \lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A] \quad , \quad (5)$$

$$\bar{N}_o = \Lambda_o \frac{\partial(\ln Q_g)}{\partial \Lambda_o} = M [\Lambda_o Q_o - A \lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A] D^{-1} \quad , \quad (6a)$$

$$\bar{N}_1 = \Lambda_1 \frac{\partial(\ln Q_g)}{\partial \Lambda_1} = M A \lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A D^{-1} \quad , \quad (6b)$$

and

$$\bar{n} = \lambda \frac{\partial(\ln Q_g)}{\partial \lambda} = M \lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A D^{-1} \quad , \quad (6c)$$

where

$$D = 1 + \Lambda_o Q_o + \lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A \quad (6d)$$

and $\bar{N}_o$, $\bar{N}_1$ and $\bar{n}$ are the average numbers of unperturbed solvent, perturbed solvent and solute molecules, respectively. From this point on we shall drop the bar to denote averages, since we will only be dealing with averages. We should note that $N_1 = An$, since that is how we set up our grand canonical ensemble. It should be pointed out that not all cells (A) influenced by a solute molecule need necessarily be occupied by solvent molecules all the time, although it is assumed here to be so. Such a formulation would result in an average number A' of perturbed solvent molecules per solute molecule such that $A' < A$ with

A' being non-integral in general. Such a calculation has been done in Section 3.6 and shown to give results qualitatively similar in nature to those derived from the present model.

Manipulation of Eqs. (6) using the fact that $N_o + N_1 = N$ leads to

$$\Lambda_o Q_o = \frac{N}{M-N-n} \quad (7a)$$

and

$$\lambda q \left(\frac{\Lambda_1 Q_1}{\Lambda_o Q_o} \right)^A = \frac{n}{M-N-n} \quad (7b)$$

From Eqs. (3) and (7) and utilizing the fact that the chemical potentials for a solvent molecule, whether perturbed or not, are identical, i.e., $\mu_o = \mu_1$ we get

$$\frac{\mu_o}{kT} = \ln \frac{N}{M-N-n} - \ln Q_o \quad (8a)$$

and

$$\frac{\mu}{kT} = \ln \frac{n}{M-N-n} - A \ln \left(\frac{Q_1}{Q_o} \right) - \ln q \quad (8b)$$

This completes our considerations of the solution by itself. We will include a treatment of the gas phase in the next section.

3.3 ENTHALPY AND ENTROPY OF SOLUTION USING SOLUBILITY DATA

If the solute in solution is in equilibrium with its pure form then the chemical potentials in the two phases are identical. We will assume that the solute in the pure form is an ideal gas. The chemical potential of the solute in the gaseous phase is⁴¹

$$\frac{\mu^{(g)}}{kT} = \frac{\mu^{(o)}}{kT} + \ln P \quad , \quad (9)$$

where

$$\frac{\mu^{(o)}}{kT} = \ln \frac{h^3}{(2\pi m)^{3/2}} - \frac{5}{2} \ln kT \quad (10)$$

and P is the pressure of the gas phase, m is the mass of a solute molecule and h is Planck's constant. We have assumed that the solute molecule is structureless.

Equating $\mu^{(g)}$ to the chemical potential of the solute in solution μ given by Eq. (8b) we get

$$\frac{n}{N+n} = P \exp [\ln q + A \ln (Q_1/Q_0) - \ln \left(\frac{N+n}{M-N-n} \right) + \frac{\mu^{(o)}}{kT}] \quad (11)$$

The left hand side is the concentration c of the solution. We could rewrite Eq. (11) as

$$c = P \exp [-\beta \Delta G] \quad , \quad (12)$$

where

$$\Delta G = kT \ln \left(\frac{N+n}{M-N-n} \right) - \mu^{(o)} - kT \ln q - A kT \ln (Q_1/Q_0). \quad (13)$$

ΔG is generally referred to as the free energy of solution. If the volume of solution does not change much with pressure, i.e., the compressibility is very small, then for very dilute solutions we can assume the number of cells M to be fixed and also consider the volume of each cell to be invariant with pressure. Hence, the partition functions Q_0 , Q_1 and q are going to be independent of pressure. Further, for very dilute solutions, i.e., $n \ll N$, we can safely assume that

$$\ln \frac{N+n}{M-N-n} \approx \ln \frac{N}{M-N} \quad .$$

Under these circumstances $\beta \Delta G$, for a particular temperature, is going to be independent of P and c . Eq. (11) is Henry's Law⁴¹.

We shall now cast Eq. (13) into a form more suitable for examining linear enthalpy-entropy relationships. If we imagine that a solute

molecule behaves as a structureless particle in a 3-dimensional box of the size of a cell then the partition function q is

$$q = \sum_{P_x, P_y, P_z} \exp \left(- \frac{P_x^2 + P_y^2 + P_z^2}{2m kT} \right) , \quad (14)$$

where momenta in the x , y and z directions are given by

$$P_x = \frac{h}{2l_x} n_x , \quad P_y = \frac{h}{2l_y} n_y , \quad P_z = \frac{h}{2l_z} n_z . \quad (15)$$

Here n_x , n_y and n_z are the quantum numbers and l_x , l_y and l_z are the dimensions of the box in the x , y and z directions. Therefore Eq. (14) can be rewritten as

$$q = \sum_{n_x, n_y, n_z} \exp \left[- \frac{h^2}{8mkT} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \right] . \quad (16)$$

If $h^2/(8ml_x^2kT)$ is much smaller than unity then we can replace the summation over n_x by an integration. Taking $l_x = 10^{-10}$ Å, $m = 10 \times$ mass of a proton and $T = 300^\circ$ K.

$$h^2/8ml_x^2kT \simeq 10^{-1} . \quad (17)$$

Hence, replacing the summation by an integration seems valid. This gives us

$$\ln q = \ln v + \frac{3}{2} \ln kT + \ln \left[\frac{(2\pi m)^{3/2}}{h^3} \right] , \quad (18)$$

where v is the volume of the cell.

Substituting Eq. (10) and (18) into (13) we get

$$\beta \Delta G = \ln \left(\frac{N}{M-N} \right) + \ln kT - \ln v - A \ln (Q_1/Q_0) . \quad (19)$$

Let us now examine what happens when the solute is a member of a homologous series, e.g., methane, ethane or n - propane, etc., and the solvent is water (for example). We expect that any water molecule that is adjacent to methane (say) will have its original energy levels shifted due to the "perturbation" we spoke of earlier. Any other water molecule adjacent to the methane molecule would have similar variations in its energy spectrum and we would expect the partition function of any perturbed water molecule to be the same. If we now substitute ethane for methane, because of the similarity in structure of these molecules, we would expect that once again adjacent water molecules would be perturbed similarly, i.e., Q_1 is the same whether methane or ethane is the solute. For that matter, Q_1 should be the same for the entire homologous series. This argument though applicable for non-electrolytic solutes would not hold for electrolytic solutes because of the complications of charged entities. From an elementary consideration of Gauss' Law we could consider that the electrostatic interaction between a charged solute and water to be approximated by that of a point charge at the center of the solute and water dipoles. The larger the size of the charge, the further is the nearest water molecule and less the electrostatic effect and, hence, perturbation of the energy spectrum of the water molecule. Therefore, we would not expect the partition function of perturbed water molecules to be the same if we replace one electrolytic solute with another if their sizes were different.

To go back to the consideration of a non-electrolytic homologous series of solutes - we would expect that as we go up the series to larger molecules it would be possible for more water molecules to be accommodated at the surface of the solute molecule, i.e., A increases.

It should be pointed out that the so-called "two state theories" of water⁴²⁻⁴⁴ in which the addition of a solute facilitates the conversion of one form of "ice" to another, or one species of water to another, fits in with our statement that each solute molecule from a homologous series affects each water molecule identically (when it is affected at all). We only add the proviso that the number of water molecules so affected depends on the size of the solute molecule. The formation of clathrates⁴⁵ could also be interpreted as being consistent with our formulation, to a certain extent. Both the clathrate theory and the two-state theories are pictorial in nature and neither are essential to our formulation. Our theory does not depend on the precise change in water structure due to the addition of non-electrolytic solutes. We are content to state that the presence of the solute affects the states of water molecules and whatever this change might be, it is represented entirely by changing the partition function from Q_0 to Q_1 .

However, the manner in which we have set up this model with equivalent cells makes it hard for us to imagine how the number of cells adjacent to a solute molecule could change if any solute molecule (whether methane or ethane) occupies only one cell. We could have set up a model in which a solute molecule could have occupied more than one cell and thereby we could have changed A , the number of solvent molecules affected by a solute molecule. Higher members of a homologous series would occupy more cells and hence, have a larger A . This would complicate the mathematics, but the principles would not be changed.

We will now compare the free energy, enthalpy and entropy of solution for a homologous series of solutes. We will denote all quantities pertaining to the i -th member of the series by a subscript i . From Eq.

(19) the free energy of solution for the i -th member is given by

$$\beta \Delta G_i = \ln \left(\frac{N}{M-N} \right) + \ln kT - \ln v_i - A_i \ln (Q_1/Q_0) \quad . \quad (20)$$

The enthalpy of solution is defined by⁴¹

$$\Delta H_i = -kT^2 \left[\frac{\partial}{\partial T} (\beta \Delta G_i) \right]_p \quad . \quad (21)$$

However, Q_1 and Q_0 in Eq. (20) are functions of T and v_i , the volume of a cell. If we assume that v_i does not change appreciably with temperature at any pressure, i.e., the coefficient of expansion of the liquid is small, then we can neglect terms that contain $\partial v_i / \partial T$ in calculating H_i . The ΔH_i so calculated does not include the contribution of the change in volume of the liquid phase. However, the major change in volume is going to occur in the gas phase and the above procedure would not result in any serious error. The enthalpy so calculated is

$$\Delta H_i = -kT + A_i (U_1 - U_0) \quad (22a)$$

where U is defined by

$$U = -kT^2 \frac{\partial}{\partial T} (-\ln Q) \quad . \quad (22b)$$

The entropy of solution is defined as

$$\Delta S_i = - \frac{\partial (\Delta G_i)}{\partial T} = \frac{\Delta H_i - \Delta G_i}{T} \quad . \quad (23)$$

From Eqs. (20), (22) and (23) we get

$$\Delta S_i = -k(1 + \ln kT) + k \ln v_i - k \ln \left(\frac{N}{M-N} \right) + A_i (S_i - S_0), \quad (24a)$$

where S is defined by

$$S = - (1 + T \frac{\partial}{\partial T}) [-k \ln Q] \quad . \quad (24b)$$

We now rewrite ΔH_i and ΔS_i in a form more suitable for examination of compensation phenomena, viz.

$$\Delta H_i = \Delta H_i^{(o)} + A_i \Delta U \quad (25)$$

and

$$\Delta S_i = \Delta S_i^{(o)} + A_i \Delta S \quad , \quad (26)$$

where

$$\Delta H_i^{(o)} = -kT \quad , \quad (27)$$

$$\Delta S_i^{(o)} = -k (1 + \ln kT) + k \ln v_i - k \ln \left(\frac{N}{M-N} \right) \quad , \quad (28)$$

$$\Delta U = U_1 - U_o \quad , \quad (29)$$

and

$$\Delta S = S_1 - S_o \quad . \quad (30)$$

Let us now compare the enthalpies and entropies of solution for $i = j$ and k . From Eqs. (25) - (30) we get

$$\Delta H_j - \Delta H_k = (A_j - A_k) \Delta U \quad (31)$$

and

$$\Delta S_j - \Delta S_k = \Delta S_j^{(o)} - \Delta S_k^{(o)} + (A_j - A_k) \Delta S \quad . \quad (32)$$

If the first two terms of Eq. (32) cancel each other out, then a plot of ΔH_i versus ΔS_i for different i , i.e., for different members of a homologous series, will result in a straight line with a slope $\Delta U/\Delta S$ of the dimension of temperature. The slope, generally referred to as the compensation temperature, is given by

$$T_c = \frac{\Delta U}{\Delta S} = \frac{T^2 \frac{\partial}{\partial T} [\ln(Q_1/Q_0)]}{(1 + T \frac{\partial}{\partial T}) [\ln(Q_1/Q_0)]}, \quad (33)$$

where we used Eqs. (22), (24), (29) and (30). From Eq. (28) the condition that the first two terms of Eq. (32) cancel, is

$$\ln(v_j/v_k) \approx 0. \quad (34)$$

If each solute molecule occupies only one cell regardless of the size of the molecule then, obviously, Eq. (34) is correct but, as we pointed out earlier this is probably too simplistic a model and that we should allow a molecule to occupy more than one cell. However, as long as v_1 is only an algebraic function of the size of the molecule the above approximation is valid.

3.4 INTERPRETATION OF T_c

T_c is the ratio of the change in enthalpy and entropy of a single solvent molecule when it is perturbed and when it is not. If a compensation phenomenon exists we do not expect $Q_1 = Q_0$ so that ΔU and ΔS are finite and non-zero.

T_c is in general dependent on the experimental temperature T , but we do not expect the two to be identical. If $T_c = T$ then the terms containing ΔU and ΔS would cancel and the free energy of solution from Eqs. (25) and (26) would be

$$\Delta G_i = \Delta H_i^{(o)} - T \Delta S_i^{(o)}. \quad (35)$$

This implies that the solubility for any solute of the homologous series would be substantially constant if the pressure and temperature of measurement were not changed.

This peculiar result of the constancy of solubility is not specific to our model. Let us examine a situation where a compensation law is valid for a process K . K may be the solubility, the rate constant or conductivity for a semiconductor. The compensation law is observed by plotting the enthalpy of the process versus its entropy for different x , where x is the parameter that has to be varied to obtain a linear enthalpy-entropy relationship. The parameter x could characterize the dielectric constant as in semiconductivity or even different members of a homologous series as presently under discussion. Let us assume that all the experiments were carried out at the same experimental temperature T . Since the compensation law is valid the enthalpy and entropy for the process K can be written as,

$$\Delta H(T, x) = \Delta H^{(o)}(T) + T_c \Delta S'(T, x) \quad (36)$$

and

$$\Delta S(T, x) = \Delta S^{(o)}(T) + \Delta S'(T, x) \quad , \quad (37)$$

where $\Delta H^{(o)}(T)$ and $\Delta S^{(o)}(T)$ are independent of x . Eqs. (36) and (37) are general enough to include the possibility of a compensation temperature T_c . The free energy for process K , therefore, is

$$\Delta G(T, x) = \Delta H^{(o)}(T) - \Delta S^{(o)}(T) + (T_c - T) \Delta S'(T, x) \quad . \quad (38)$$

If now, $T_c = T$ then the last term in the above expression vanishes, i.e.,

$$\Delta G(T, x) = \Delta H^{(o)}(T) - T \Delta S^{(o)}(T) \quad . \quad (39)$$

If T_c and T are identically equal then for any experimental temperature the right hand side, and hence $\Delta G(T, x)$, is independent of x .

The extent of process K being given by an equation of the form

$$K(T, x) \sim \exp(-\beta \Delta G(T, x)) \quad (40)$$

then implies K is also independent of x . Experimentally, however, we know that the solubility, for instance, is different for different x , i.e., size of solute, even when a compensation law holds.

Another important corollary follows if $T = T_c$. Since $K(T, x)$ is independent of x we would have only one curve to represent all x on a $\ln K(T, x)$ vs. T^{-1} plot. Therefore we would have only one enthalpy and entropy for the process K , no matter what the x , if this information were derived from the $\ln K$ vs. T^{-1} plot. Therefore, if we plot ΔH versus ΔS for different x and a fixed T , then we would not have a straight line but a single point. Hence, $\Delta S'(T, x)$ in Eqs. (36) and (37) would be zero.

We therefore assert that if ΔH and ΔS are derived from an expression like Eq. (40) then a linear ΔH versus ΔS plot will not be observable if T_c is generally identical to the experimental temperature.

Ben Naim¹⁸ has derived a compensation law for a two state model of water, with $T_c = T$. In his model, the presence of a solute molecule causes a crossover of water molecules from one component to another. The free energy, enthalpy and entropy per solute molecule are given by

$$\mu_s = \left(\frac{\partial G}{\partial N_s} \right)_{N_L, N_H} + (\mu_L - \mu_H) \left(\frac{\partial N_L}{\partial N_s} \right)_{N_w} \quad (41)$$

$$H_s = \left(\frac{\partial H}{\partial N_s} \right)_{N_L, N_H} + (H_L - H_H) \left(\frac{\partial N_L}{\partial N_s} \right)_{N_w} \quad (42)$$

and

$$S_s = \left(\frac{\partial S}{\partial N_s} \right)_{N_L, N_H} + (S_L - S_H) \left(\frac{\partial N_L}{\partial N_s} \right)_{N_w}, \quad (43)$$

where all symbols have their usual significance and the subscripts s , W , L and H refer to the solute, water and the two components of water, respectively. Since the chemical potentials of the two components of water have to be identical, i.e.,

$$\mu_L = \mu_H \quad (44)$$

he gets

$$\mu_s = \left(\frac{\partial G}{\partial N_s} \right)_{N_L, N_H} = \mu_s^* \quad (45)$$

Further, since

$$\mu_L = H_L - TS_L \quad , \quad (46)$$

and similarly for component H of water, he obtains

$$H_L - H_H = T (S_L - S_H) \quad (47)$$

Hence, the last two terms in Eqs. (42) and (43) cancel each other in the free energy with the experimental temperature masquerading as the compensation temperature. This suffers from exactly the same objections as we outlined earlier in this section.

The compensation law that we have derived comes from a slightly different source than Ben Naim's. In our formulation, recalling that Ben Naim's μ_s is our μ , we obtain from Eqs. (3) and (7)

$$\mu = kT \ln \frac{n}{M-N-n} - kT \ln q - AkT \ln (Q_1/Q_0) + A (\mu_0 - \mu_1) \quad , \quad (48)$$

where

$$A = - \left(\frac{\partial N_L}{\partial N_s} \right)_{N_W} \quad (49)$$

Hence, in Ben Naim's notation μ_s^* is identifiable with the first three

terms on the right hand side of Eq. (48) and the compensation, that we talk of, is in this μ_s^* term and not the $A(\mu_0 - \mu_1)$ term, as he has it. In fact, this term being zero, the enthalpy and entropy of solution, if derived from Henry's Law, as noted earlier, will not include terms derived from $A(\mu_0 - \mu_1)$.

If the experimental temperature is changed, Q_1 and Q_0 are going to change accordingly. This means that there is going to be a change in the occupation numbers of the states available to perturbed and unperturbed solvent molecules and in general, ΔU and ΔS as given by Eqs. (29) and (30) will change. It is therefore, not surprising that T_c (Eq. (33)) is not temperature invariant. Under very special circumstances T_c may be independent of temperature.

Comparing our treatment with that of Frank and Evans⁸, we would like to point out that they did not derive a compensation law. In their formulation the entire change in entropy was related to a change in free volume. To quote Frank⁶, "free volume is an auxiliary concept, with only such meaning as is put into it by the definition adopted". The free volume change, therefore, would also contain entropy changes due to solute-solvent interaction, i.e., the entropy changes which we represent as arising due to the change in the partition function of solvent molecules from Q_0 to Q_1 . However, the manner in which they set up their statistical mechanics gives us no prior reason to believe that ΔS is linear in ΔH . They assumed the validity of the compensation law (Barclay-Butler rule)⁶⁻⁸ and from that derived that the free volume change was exponential in ΔH . Their physical picture of non-electrolytes "freezing" the water around them is similar to our model (and the two state model) though we hesitate to go as far as stating

that the solute merely stabilizes one of the already existing "structures" of water. The latter statement is not essential to the argument we have presented.

We would like to emphasize that in deriving Henry's Law, Eq. (11), we separated out the $\ln n/(N+n)$ and $\ln P$ terms. Therefore, ΔG is not the total change in free energy of the system due to the solution process but somewhat different from it. Also, the terms ΔU and ΔS that lead to compensation have no mixing terms involved. In fact examination of Eqs. (25)-(30) show that the mixing terms are absent from enthalpies and entropies which occur in the compensation law. The fundamental significance of this point will be examined in Chapter IV.

We would not expect compensation if the number of solute molecules n is so large that the number of solvent molecules $N \ll n$. In fact, mathematically, as has already been stated, the summation to evaluate Q_g breaks down if $M \ll (A+1)n$. At about this point we would expect solute-solute interactions to play a larger role and this is one more factor that would be responsible for not having a compensation law.

Let us examine what happens if we retain the same solvent and use a different homologous series of solutes. In general for two different series of solutes, Q_1 would be different and hence, we would have in general two different compensation temperatures.

However, if the solvent is water and the series are the aliphatic hydrocarbons and the alcohols, since the difference between CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ is similar to the difference between CH_4 and C_2H_6 , it is not surprising that the T_c s for these series are almost identical^{38,39}. The starting point for both these series is different because of the difference in head groups. Hence, a plot of ΔH versus ΔS for these

series gives parallel but not identical straight lines. A rigid interpretation of the two state theories of water whereby the only effect of the solute is to change one species of water (or ice) to another, would give identical straight lines. However, a less rigid interpretation, as has been noted earlier, is consistent with but not essential to our formulation.

Since solute-solvent forces in the case of nonelectrolytes and water are essentially similar, it is not too surprising that different homologous series of nonelectrolytes give similar T_c in water.

Similarly the hydrocarbons (or alcohols) in D_2O would give rise to a compensation phenomenon. But since D_2O is not quite the same as H_2O , the strength of the deuterium bond being different from that of the H - bond, etc., we would not expect the compensation temperature for H_2O and D_2O to be identical. We will deal with the thermodynamics of transfer from H_2O to D_2O in the next section.

3.5 THERMODYNAMICS OF TRANSFER FROM H_2O TO D_2O

There is plenty of experimental evidence^{36,37} that the enthalpy and entropy of transfer of electrolytic or non-electrolytic solutes from H_2O to D_2O exhibit a linear relationship. We will only comment on the transfer of non-electrolytes.

We have seen in the previous section how it is possible to get a compensation law for a non-electrolytic homologous series in H_2O and/or D_2O . All quantities that have been defined previously will have a subscript H or D depending on whether the solvent is H_2O or D_2O . If a subscript already exists, then H or D shall be the second subscript. We will use as the reference state the vapor phase at a particular pressure and assume that the experimental temperature is the same for all cases.

The enthalpy and entropy of solution in H_2O for the i th solute of a homologous series is given by Eq. (25) and (26) as

$$\Delta H_{iH} = \Delta H_H^{(o)} + A_H \Delta U_H \quad (50)$$

and

$$\Delta S_{iH} = \Delta S_H^{(o)} + A_H \Delta S_H \quad (51)$$

where the superscript (o) once again denotes the part that does not change with the solute. Similarly for D_2O , we replace the subscript H by D.

The enthalpy of transfer is therefore

$$\Delta H_t = \Delta H_D^{(o)} - \Delta H_H^{(o)} + A_D \Delta U_D - A_H \Delta U_H \quad (52)$$

and the entropy of transfer is

$$\Delta S_t = \Delta S_D^{(o)} - \Delta S_H^{(o)} + A_D \Delta S_D - A_H \Delta S_H, \quad (53)$$

where A_H and A_D are the number of H_2O and D_2O molecules perturbed by the solute. Normally we would expect these to be identical, but we will keep our options open.

Recalling that the compensation law holds for H_2O as well as D_2O we have the two compensation temperatures T_{cH} and T_{cD} given by

$$T_{cD} = \Delta U_D / \Delta S_D \quad (54)$$

and

$$T_{cH} = \Delta U_H / \Delta S_H. \quad (55)$$

From Eqs. (52)-(55) we get

$$\Delta H_t = \Delta H_D^{(o)} - \Delta H_H^{(o)} + A_D T_{cD} \Delta S_D - A_H T_{cH} \Delta S_H. \quad (56)$$

We will now assign the prescript 1 and m for the 1th and mth solutes in a homologous series. The compensation temperatures, $\Delta H_{D(H)}^{(o)}$, $\Delta S_{D(H)}^{(o)}$, $\Delta U_{D(H)}$ and $\Delta U_{D(H)}$ will not be affected at all, but A_H and A_D will be different for the two solutes. Hence, we get

$${}_m \Delta H_D^{(o)} - {}_m \Delta H_H^{(o)} - {}_1 \Delta H_D^{(o)} + {}_1 \Delta H_H^{(o)} \approx 0, \quad (57)$$

i.e., the terms with superscript (o), the parts that do not change with the solute will be absent when the difference in the enthalpy of transfer is considered. A similar statement is valid for the terms in the entropy which are invariant of the solute.

From Eqs. (52) - (56) we get the difference in the enthalpy and entropy of transfer, for the 1th and mth solute as

$${}_m \Delta H_t - {}_1 \Delta H_t = \Delta A_D(m,1) T_{cD} \Delta S_D - \Delta A_H(m,1) T_{cH} \Delta S_H \quad (58)$$

and

$${}_m \Delta S_t - {}_1 \Delta S_t = \Delta A_D(m,1) \Delta S_D - \Delta A_H(m,1) \Delta S_H \quad (59)$$

where

$$\Delta A(m,1) = {}_m A - {}_1 A. \quad (60)$$

A plot of ΔH_t versus ΔS_t would therefore have a slope

$$T_{ct}(m,1) = \frac{\Delta A_D(m,1) T_{cD} \Delta S_D - \Delta A_H(m,1) T_{cH} \Delta S_H}{\Delta A_D(m,1) \Delta S_D - \Delta A_H(m,1) \Delta S_H}. \quad (61)$$

To have a straight plot, i.e., a compensation law, $T_{ct}(m,1)$ should be independent of m and 1. On the right hand side of Eq. (58) all the quantities are independent of m and 1 except $\Delta A_D(m,1)$ and $\Delta A_H(m,1)$. Therefore to have a constant T_{ct} , ΔA_D and ΔA_H must be linearly related by a constant independent of m or 1. Letting

$$\Delta A_D(m,1) = c \Delta A_H(m,1) \quad (62)$$

and substitute Eq. (62) into (61) we get

$$T_{ct} = T_{ct}(m,1) = \frac{c T_{cD} \Delta S_D - T_{cH} \Delta S_H}{c \Delta S_D - \Delta S_H} \quad (63)$$

Let us examine Eqs. (62) and (63) in greater detail. First of all, if the number of H_2O or D_2O molecules affected by a solute molecule is precisely the same, then $c = 1$. Further, if $T_{cD} = T_{cH}$ are identical, then $T_{ct} = T_{cH} = T_{cD}$. However T_{cD} and T_{cH} are defined by Eq. (33) as

$$T_{cD} = \frac{\Delta U_D}{\Delta S_D} = \frac{T^2 \frac{\partial}{\partial T} [\ln(Q_{1D}/Q_{oD})]}{(1+T \frac{\partial}{\partial T}) [\ln(Q_{1D}/Q_{oD})]} \quad (64)$$

similarly for T_{cH} we replace subscript D by H everywhere.

Hence, if $T_{cD} = T_{cH}$ then $Q_{1D}/Q_{oD} = Q_{1H}/Q_{oH}$ and going back to Eq. (54)-(60), (22), (24), (29) and (30) we see that

$$\Delta S_D = \Delta S_H \quad (65a)$$

$$\Delta U_D = \Delta U_H \quad (65b)$$

$$m \Delta H_t - l \Delta H_t \approx 0 \quad (65c)$$

and

$$m \Delta S_t - l \Delta S_t \approx 0 \quad (65d)$$

and we no longer have a compensation rule. Hence, the conditions $c = 1$ and $T_{cH} = T_{cD}$ do not lead to compensation phenomena. We see, on further examination, that if $c \neq 1$ and $T_{cH} = T_{cD}$ then we have compensation with T_{cT} identical to the two compensation temperatures. Also, if $c = 1$, then $T_{cH} \neq T_{cD}$ gives rise to a compensation phenomenon such

that $T_{ct} \neq T_{cD}$ or T_{cH} . However, $T_{cH} = T_{cD}$ implies $Q_{1D}/Q_{oD} = Q_{1H}/Q_{oH}$ which does not seem reasonable since H_2O and D_2O , though similar, are not quite the same, and we would expect that the partition function of an H_2O molecule to be different from that of a D_2O molecule. In fact we would expect that any finite, measureable difference in the enthalpy (entropy) of solution in D_2O and H_2O to be reflected in different partition functions, rather than in a change of c , though this possibility cannot be ruled out entirely. If we had allowed the existence of holes next to the solute molecule (see Appendix) then the number of H_2O (or D_2O) molecules affected would be dependent on the partition functions of the H_2O (or D_2O) molecules in the presence or absence of the solute molecule. Hence, c , Q_{1D}/Q_{oD} and Q_{1H}/Q_{oH} are correlated, and the compensation temperature for transfer processes would best be written as in Eq. (61), which, as we have already mentioned, may not be identical to either T_{cD} or T_{cH} .

3.6 GENERALIZATION OF THE MODEL

In the previous model (Section 2.2) we assumed that each solute molecule "perturbed" A sites and all these A sites were occupied by solvent molecules. In this model we will not require occupation of all these A sites, hence for each solute molecule we will have less than A perturbed solvent molecules. We will see that this model also leads to results similar to those derived for the previous model. The symbols used in this section are identical, and have the same significance, as in the previous model.

The canonical partition function (Q_c) is given by,

$$Q_c = \sum_{\substack{N=N_1+N_o \\ N_1=A_n}} \left[\frac{M!}{n!(M-n)!} \cdot \frac{(M-A_n-n)!}{N_o!(M-A_n-n-N_o)!} \cdot \frac{(A_n)!}{N_1!(A_n-N_1)!} Q_o^{N_o} Q_1^{N_1} q^n \right] \quad (66)$$

Here A the number of sites that are influenced by each solute molecule. If a solvent molecule occupies one of these "perturbed" sites it is considered to be "perturbed". There are N_1 such molecules. That such a perturbed site need not be occupied is expressed in the last set of factors. The grand canonical partition function (Q_g) is given by

$$Q_g = \sum_{n=0}^M \frac{M!}{n! (M-n)!} (\lambda q)^n \sum_{N_o=0}^{M-An-n} \frac{(M-An-n)!}{N_o! (M-An-n-N_o)!} (\Lambda_o Q_o)^{N_o} \sum_{N_1=0}^{An} \frac{An!}{N_1! (An-N_1)!} (\Lambda_1 Q_1)^{N_1} \quad (67)$$

Here, as for the previous model, we have not taken into consideration the fact that if $n > M/(A+1)$ then $N_1 < An$, but once again since we will deal with dilute solutions this does not introduce any error in the summation of the right hand side. Using the multinomial theorem, we get

$$Q_g = [1 + \Lambda_o Q_o + \frac{\lambda q (1 + \Lambda_1 Q_1)^A}{(1 + \Lambda_o Q_o)^A}]^M \quad (68)$$

Calculating the average values of N_o , N_1 and n as in the previous model we get

$$N_o = M \Lambda_o Q_o [1 - \frac{A \lambda q (1 + \Lambda_1 Q_1)^A}{(1 + \Lambda_o Q_o)^{A+1}}] D^{-1} \quad (69a)$$

$$N_1 = A M \Lambda_1 Q_1 \lambda q \frac{(1 + \Lambda_1 Q_1)^{A-1}}{(1 + \Lambda_o Q_o)^A} D^{-1} \quad (69b)$$

and

$$n = M \lambda q \left(\frac{1 + \Lambda_1 Q_1}{1 + \Lambda_o Q_o} \right)^A D^{-1} \quad (69c)$$

where

$$D = 1 + \Lambda_o Q_o + \frac{\lambda q (1 + \Lambda_1 Q_1)^A}{(1 + \Lambda_o Q_o)^A} . \quad (69d)$$

Manipulation of Eqs. (69) gives us

$$\Lambda_o Q_o = \frac{N_o}{M - An - n - N_o} , \quad (70a)$$

$$\Lambda_1 Q_1 = \frac{N_1}{An - N_1} , \quad (70b)$$

and

$$\lambda q = \frac{n}{M - n} \left[\frac{M - n - An}{M - n - An - N_o} \right]^{A+1} \left[\frac{An - N_1}{An} \right]^A . \quad (70c)$$

From Eqs. (70) the chemical potential of the solute in solution is

$$\mu = kT \left[\ln \frac{n}{M - n} + (A+1) \ln (1 + \Lambda_o Q_o) - A \ln (1 + \Lambda_1 Q_1) - \ln q \right] . \quad (71)$$

Proceeding as in Section 3.3, we derive Henry's Law for equilibrium of the solute in solution with its vapor phase. We get

$$c = P \exp (-\beta \Delta G) , \quad (72)$$

where

$$\begin{aligned} \beta \Delta G = & -A \ln (Q_1 / Q_o) + A \ln (p_1 / p_o) + \ln \left(\frac{kT}{v} \right) \\ & + \ln \left(\frac{M - n - An}{M - n - An - N_o} \right) + \ln \left(\frac{N + n}{M - n} \right) \end{aligned} \quad (73)$$

with

$$p = \frac{\Lambda Q}{1 + \Lambda Q} , \quad (74)$$

p_1 (p_o) being the probability that a water molecule occupies a "perturbed" ("unperturbed") site. Clearly, p_1 and p_o are less than one.

For a homologous series of solutes we would not expect $\ln (Q_0 p_1 / Q_1 p_0)$ to change drastically as we vary solutes, but we would expect A to change. If these changes in $A \ln (Q_0 p_1 / Q_1 p_0)$ are much greater than the changes in the other terms in ΔG , then, once again, we have a compensation law. We would like to remark that for very dilute solutions the changes in the last two terms will be negligible if we change solutes. In any case, the changes in the last three terms of Eq. (74) are logarithmic.

CHAPTER IV

THEORETICAL FOUNDATIONS

4.1 INTRODUCTION

In Chapter III we examined single solute-single solvent systems and the conditions under which they lead to a compensation law. In the present chapter we will delve deeper into the theoretical foundations of the compensation law. We will examine the underlying physical basis for having the compensation temperature different from the experimental temperature.

We will give an exposition of the compensation law as it fits into the structure of statistical mechanics. This will lead us to a density of states relationship that has to be satisfied if the compensation law is to hold. Finally, we will prove that the models of Chapters II and III invoked to explain the compensation laws for biological conductors and for single solute-single solvent systems satisfy this density of states relationship.

4.2 THE ORIGIN OF THE DIFFERENCE BETWEEN THE TEMPERATURE AND THE COMPENSATION TEMPERATURE

In statistical mechanics the properties of a system are examined by constructing an ensemble of identical systems and averages are calculated over the ensemble. In a canonical ensemble the derivative of the entropy with respect to the energy is the reciprocal of the absolute temperature

$$\frac{dS}{dE} = \frac{1}{T} \quad . \quad (1)$$

This, in fact, is the definition of the absolute temperature scale⁴⁶. Eq. (1) is an energy-entropy relationship of a kind, but it is not a compensation law. Nevertheless, it contributes to the confusion. We will show now how this confusion comes about. This point was also touched upon in the previous chapter (page 43). We will in this chapter ignore the difference between enthalpy and energy since it is not important for our purpose.

Let us consider the equilibrium of a solute between two solvents, or between a pure solute and its solution. We may also consider the equilibrium of one substance, e.g., water, between two forms. In any one of these cases the chemical potentials of two subsystems will be equal:

$$\mu_I = \mu_{II} \quad . \quad (2)$$

We may write

$$\mu = H - TS \quad (3)$$

and thus

$$H_I - TS_I = H_{II} - TS_{II} \quad (4)$$

or

$$\frac{\Delta S}{\Delta H} = \frac{S_I - S_{II}}{H_I - H_{II}} = \frac{1}{T} \quad . \quad (5)$$

The above formula was given by Ben Naim¹⁸. This enthalpy-entropy relationship leads to the experimental temperature and not to a compensation temperature. This is to be expected because Eq. (5) is derived on a basis very similar to the derivation of Eq. (1). As shown by Landau and Lifschitz⁴⁶, Eq. (1) follows from the requirement that a closed system consisting of two subsystems, which can exchange energy with each other,

should be in equilibrium. Each one of the three systems above have two subsystems, designated by I and II, which can exchange energy with each other.

It is evident that the compensation law must have another basis. In fact the compensation law cannot be derived by the examination of a single system. It is a consequence of the examination of a set of related systems. In other words, it is not enough to consider one ensemble, but it is necessary to consider a set of ensembles. Curiously, quantities defined over a set of related ensembles resemble those defined over a single ensemble. We shall show that while ensembles lead to the conventional statistical mechanical quantities, sets of ensembles lead to closely analogous quantities related to the compensation law.

Let us consider specifically the equilibrium of a solute in solution and in the gas phase. The chemical potential of the solute in solution can be written as

$$\mu_{II} = \mu_{II}^{(o)} + RT \ln c \quad , \quad (6)$$

where c is the mole fraction concentration of the solution and $\mu_{II}^{(o)}$ is concentration-independent, the solution being considered to be ideal. The chemical potential of a solute molecule in the gaseous phase, also assumed to be ideal, is given by

$$\mu_I = B(T) + RT \ln P \quad , \quad (7)$$

where P is the pressure of the gas phase and $B(T)$ is a temperature dependent factor.

Equating the two chemical potentials we can derive Henry's law, i.e.,

$$c = P \exp [-(\mu_{II}^{(o)} - B(T))/RT] \quad . \quad (8)$$

The concentration c being an equilibrium constant, we can use the van't Hoff relationship to calculate the enthalpies and entropies of solution. Recasting Eq. (8) as

$$c = \exp [-(\mu_{II}^{(o)} - \mu_I)/RT] \quad , \quad (9)$$

the free energy of solution is

$$\Delta G^{(o)} = \mu_{II}^{(o)} - \mu_I \quad (10)$$

and the enthalpy and entropy of solution are given by

$$\Delta H^{(o)} = -RT^2 \frac{d}{dT} \left(\frac{\Delta G^{(o)}}{RT} \right) \quad (11)$$

and

$$\Delta S^{(o)} = \frac{\Delta H^{(o)} - \Delta G^{(o)}}{T} \quad , \quad (12)$$

respectively.

We will now compare $\Delta H^{(o)}$ and $\Delta S^{(o)}$ with ΔH and ΔS . To facilitate comparison we first obtain from Eqs. (3) and (6) the relationship

$$\mu_{II}^{(o)} = H_{II} - TS_{II} - RT \ln c \quad . \quad (13)$$

From Eqs. (3), (10) and (13) we have

$$\Delta G^{(o)} = H_{II} - TS_{II} - H_I + TS_I - RT \ln c \quad . \quad (14)$$

Using Eq. (5) this reduces to

$$\Delta G^{(o)} = \Delta H - T \Delta S - RT \ln c \quad . \quad (15)$$

From Eqs. (11), (12) and (15) the enthalpy and entropy of solution are, respectively,

$$\Delta H^{(o)} = \Delta H \quad (16)$$

and

$$\Delta S^{(o)} = \Delta S + R \ln c \quad (17)$$

Hence, from Eqs. (16) and (17)

$$\frac{\Delta H^{(o)}}{\Delta S^{(o)}} = \frac{\Delta H}{\Delta S + R \ln c} \quad (18)$$

Comparing $\Delta H^{(o)}/\Delta S^{(o)}$ with $\Delta H/\Delta S$, i.e., Eqs. (18) and (5), we see that, in general, $\Delta H^{(o)}/\Delta S^{(o)}$ cannot be identical to T . The difference between the two ratios being due to the $R \ln c$ term. In fact the $R \ln c$ term is comparable in magnitude to the ΔS term. As an example, for butane³⁷ at 25°C and 1 atm. pressure the concentration of solution is about 10^{-5} . The calculated $\Delta S^{(o)}$ is about 40 e.u. and the $R \ln c$ term about -23 e.u.. It is interesting to note from Eq. (17) that $\Delta S^{(o)}$ is always less than ΔS .

The $\Delta H^{(o)}$ and $\Delta S^{(o)}$ calculated above are for a single solution. To talk of a compensation law we should compare the $\Delta H^{(o)}$ and $\Delta S^{(o)}$ for a series of solutions, i.e., a set of ensembles. We will assume all the $\Delta H^{(o)}$ and $\Delta S^{(o)}$ are calculated for experiments done at the same experimental temperature T and pressure P . Obviously, a plot of $\Delta H^{(o)}$ versus $\Delta S^{(o)}$ for arbitrary solute-solvent pairs should result in no discernible pattern.

However, we do know that if we examine $\Delta H^{(o)}$ and $\Delta S^{(o)}$ for a particular set of solute-solvent pairs we get straight lines and then we have a compensation law. The slope of this line is given by

$$\frac{\Delta H_j^{(o)} - \Delta H_i^{(o)}}{\Delta S_j^{(o)} - \Delta S_i^{(o)}} = T_c \quad (19)$$

where i and j stand for the i^{th} and j^{th} ensemble. To get a perfect straight line, T_c should be independent of i and j .

Substituting Eqs. (16) and (17) into Eq. (19) we obtain

$$T_c = \frac{\Delta H_j^{(o)} - \Delta H_i^{(o)}}{\Delta S_j - \Delta S_i + R \ln (c_j/c_i)} \quad . \quad (20)$$

To bring out the difference between T and T_c more clearly, substituting Eq. (5) into Eq. (20) we get

$$T_c = \frac{(\Delta S_j - \Delta S_i) T}{(\Delta S_j - \Delta S_i) + R \ln (c_j/c_i)} \quad . \quad (21)$$

For experiments done at the same temperature and pressure, we would not in general expect $c_j = c_i$. Therefore, in general, $T_c \neq T$. However, if the experimental temperature and compensation temperature are equal then we would have $c_j = c_i$. As was noted in Section 3.4, whereas T_c may be a function of the experimental temperature, the two temperatures could not be identical for all T , since a plot of $\Delta H^{(o)}$ vs. $\Delta S^{(o)}$ for all ensembles, would give a single point and not a straight line.

From Eq. (21) it is clear that the difference between the compensation and experimental temperatures arises because the entropies used to calculate both quantities differ due to the mixing entropy embodied in the $R \ln c$ term.

4.3 DENSITIES OF STATES AND THE COMPENSATION LAW

Eq. (19) shows that the compensation law involves not the total entropy ΔS , but only the part due to molecular interactions. The mixing entropy is excluded from $\Delta S^{(o)}$. We shall therefore define our systems in such a way that the mixing entropy should play no further role.

Let us consider a set of solutions. Each solution contains the same number of moles of the same solvent. The solutions differ only in the kind of solute used. The solutes are chosen from a homologous series and the same number of moles of each is dissolved in their respective solutions. (This is not an isobaric experiment.) One could now apply the machinery of statistical mechanics to each of these solutions, starting with the partition functions, as was done in Section 3.2. That is, however, not the path we want to follow. We are not interested in the behavior of the individual solutions, but only in the relationship of the solutions to each other.

The relevant thermodynamic quantities can be derived from the free energy F :

$$F = -\frac{1}{\beta} \ln Q \quad , \quad (22)$$

where Z is the partition function and $\beta = T^{-1}$. The comparison between two solutions of our set requires only the difference in the free energies. If i and j represent two such solutions we only require

$$\Delta F_{ij} = F_i - F_j = -\frac{1}{\beta} \ln (Q_i/Q_j) \quad . \quad (23)$$

The crucial point is that the combinatorial factors in Q_i and Q_j , the terms that give rise to the mixing entropy, cancel. Thus ΔF_{ij} relates strictly to the molecular properties of the solutes and the solvent. Using the standard statistical mechanical definitions of internal energy and entropy we can also write

$$\Delta E_{ij} = \Delta F_{ij} + \beta \frac{d}{d\beta} \Delta F_{ij} \quad (24)$$

and

$$\Delta S_{ij} = \beta^2 \frac{d}{d\beta} \Delta F_{ij} . \quad (25)$$

Let us now drop the subscripts and consider ΔF , ΔE and ΔS in an idealized way as possibly continuous variables. We are then talking about a set of ensembles because these quantities represent differences between ensembles. Let us now construct a theory for the set of ensembles by analogy to the theory of ensembles. In analogy with Eq. (1) we write

$$\frac{\Delta S}{\Delta E} = \frac{1}{T_c} . \quad (26)$$

This is a definition. If it is valid we have a compensation law and T_c is the compensation temperature. This is fairly obvious by comparison with the Chapter III and will also be shown below. It is also obvious that T_c is not the experimental temperature T , because the latter quantity refers to a single ensemble and T_c to a set of ensembles. This is not to say that T_c is independent of T , but the two temperatures are clearly different concepts.

In order to show that Eq. (26) represents a compensation law, and for other purposes, we shall solve this equation. Utilizing Eqs. (23) - (26) we can write

$$\frac{\beta^2 \frac{d}{d\beta} \Delta F}{(1 + \beta \frac{d}{d\beta}) \Delta F} = \beta_c . \quad (27)$$

We shall introduce ΔZ by the definition

$$\Delta F = - \frac{1}{\beta} \ln \Delta Q . \quad (28)$$

ΔZ is the ratio of two Q 's, not their difference. Substitution of Eq. (28) into Eq. (26) yields

$$\frac{d}{d\beta} \ln \ln \Delta Q = \frac{1}{\beta - \beta_c} \quad . \quad (29)$$

We shall assume that β_c is independent of β . This equation can be integrated separately for $\beta > \beta_c$ and $\beta < \beta_c$.

One obtains

$$\ln \ln \Delta Q = \begin{cases} \ln(\beta - \beta_c) + \ln \epsilon & \text{for } \beta > \beta_c \\ \ln(\beta_c - \beta) + \ln \epsilon & \text{for } \beta < \beta_c \end{cases} \quad (30)$$

where $\epsilon > 0$. This can be written as

$$\Delta Q = \begin{cases} e^{\epsilon(\beta - \beta_c)} & \text{for } \beta > \beta_c \\ e^{\epsilon(\beta_c - \beta)} & \text{for } \beta < \beta_c \end{cases} \quad (31)$$

The alternative forms in the last two equations merely mean that the ratio of two Q 's must always be taken such that the ratio should be greater than or equal to unity.

Let us now draw some conclusions from Eq. (31). We may choose two solutions from our set and then we may write

$$Q_i/Q_j = e^{\epsilon_{ij}(\beta - \beta_c)} > 1 \text{ for } \beta > \beta_c$$

and

$$Q_j/Q_i = e^{\epsilon_{ij}(\beta_c - \beta)} > 1 \text{ for } \beta < \beta_c \quad . \quad (32)$$

If we have chosen the same solution twice $Q_i = Q_j$, thus $\epsilon_{ij} = 0$. By assumption, any pair of solutions in our set has the same β_c and thus different pairs of solutions are characterized by different ϵ_{ij} pairs. Since the solutions are physically independent entities ϵ_{ij} can only depend on the structure of each solution separately. In other words the

number of independent ϵ_{ij} is equal to the number of different solutions and not to the number of pairs of such solutions. This means that

$$\epsilon_{ij} = \epsilon_j - \epsilon_i \quad . \quad (33)$$

These ϵ 's can be put into a monotonic sequence such that

$$\epsilon_j > \epsilon_i \quad , \quad (34)$$

so that $\epsilon_{ij} > 0$ is always satisfied.

To verify that the compensation law is satisfied, we can write

$$Q_j = e^{\epsilon_{ij}(\beta_c - \beta)} Q_i \quad . \quad (35)$$

Using again the standard formulae of statistical mechanics we find

$$E_j = \epsilon_{ij} + E_i \quad , \quad (36)$$

$$S_j = \beta_c \epsilon_{ij} + S_i \quad , \quad (37)$$

which lead to

$$\frac{\Delta S}{\Delta E} = \frac{1}{T_c} \quad (38)$$

as required. We emphasize again that the differences in energy and entropy are taken between two ensembles (leading to T_c) and not within the same ensemble (which would lead to T).

We can answer one more question here, namely what conclusions can one reach with regard to the density of states of each solution? We may write

$$Q_i(\beta) = \int_{-\infty}^{\infty} e^{-\beta E} R_i(E) dE \quad . \quad (39)$$

$R(E)$ will vanish below some lower bound. Since the compensation law is

not going to give any information concerning the mixing terms we may as well regard Q_i and R_i as defined without them. Substituting Eq. (39) for both i and j into Eq. (35) we obtain

$$R_i(E) = R_j(E + \epsilon_{ij}) e^{-\beta_c \epsilon_{ij}} \quad (40)$$

As expected we only get information concerning the relationship among R 's, but not of the individual R 's. Going from one solution to another in the sequence the density of states is rigidly displaced along the energy axis and its scale is changed by an exponential function of this displacement. The proportionality factor in the exponent is β_c .

Finally we point out that if the compensation temperature were the experimental temperature the entire development would be meaningless, beginning with Eq. (24).

4.4 PARTITION FUNCTION FOR INDIVIDUAL DEGREES OF FREEDOM

We will now show that one method of satisfying Eq. (40), and hence the compensation law, is to change the number of units or degrees of freedom involved in the process (for which we have compensation) as we change ensembles. Let the i^{th} ensemble have n_i degrees of freedom affected in a certain way so as to change the partition function for an affected degree of freedom from q_0 to q_1 . Let there be a total of n such degrees altogether such that $n_i < n$ for any i . Setting up the total partition function for the ensemble i we obtain

$$Q_i = Q_i^{(0)} q_0^n \left(\frac{q_1}{q_0}\right)^{n_i} \quad (41)$$

For the j^{th} ensemble we shall have a similar expression. Taking the ratios Q_j/Q_i we get

$$Q_j/Q_i = (Q_i^{(o)}/Q_j^{(o)}) \left(\frac{q_1}{q_o}\right)^{n_j - n_i} . \quad (42)$$

$Q_i^{(o)}$ and $Q_j^{(o)}$ is the combined partition function of those degrees of freedom that are not capable of being affected. We would expect $Q_i^{(o)} = Q_j^{(o)}$ and, hence

$$Q_j/Q_i = (q_1/q_o)^{n_j - n_i} . \quad (43)$$

We could write q_1 and q_o as

$$q_1 = e^{-\beta f_1} \quad (44a)$$

and

$$q_o = e^{-\beta f_o} . \quad (44b)$$

Substituting Eqs. (44) into Eq. (43) we obtain

$$q_i = q_j e^{\epsilon_{ij}(\beta - \beta_c)} , \quad (45)$$

where

$$\epsilon_{ij} = (n_j - n_i) \Delta u , \quad (46a)$$

$$\beta_c = \Delta S / \Delta u \quad (46b)$$

and

$$f_1 - f_o = \Delta f = \Delta u - \Delta S / \beta . \quad (46c)$$

Eqs. (45) and (35) are identical. Hence, a model of the kind described above will lead to a compensation law. Such a model will also automatically satisfy the requirement upon the density of states embodied in Eq. (40). Further, the compensation temperature in this model is decided by the ratio of the change in internal energy to the change in entropy for

a single participating unit, i.e., for each degree of freedom whose partition function is changed [Eq. (46b)]. This model is a generalization of the models devised in Chapter III and Model I of Section 2.7.

CHAPTER V

CONCLUSION

In the introduction we had stated that our aim was to set up model systems that could lead to compensation laws. This, besides being an end to itself, was undertaken with the intention of understanding of how and why compensation laws occur and of the physical significance of T_c . We succeeded in this undertaking by setting up models which led to compensation in conductivity of biological substances (Chapter II) and solubility of nonelectrolytic homologous series in a particular solvent (Chapter III).

For the conductivity case we postulated that creation of a charge carrier led to distortions of the lattice (or conformational changes in the system). We showed that these conformational changes would contribute an extra free energy term in the conductivity. This free energy term can be split into an entropy term and an enthalpy term. The measured activation energy would therefore consist of at least two contributions, one arising from the above-mentioned enthalpy and the second contribution coming from the energy required to create the charge carrier. A third contribution may be present arising from the mobility. The entropy term would boost the pre-exponential factor. This would explain the large pre-exponential factors found for the conductivity of biological substances.

The compensation law for conductivity in biological substances can be explained by a linear enthalpy-entropy relationship for the conformational changes. T_c , in this case, can be interpreted as a local temperature different from the temperature of the entire system (i.e., experimental temperature). Conformational changes occur because of fluctuations in the energy in the environment of charge carriers.

From the model for the compensation law in solubility, T_c can be interpreted as the ratio of the change in enthalpy to the change in entropy of a solvent molecule when it is "perturbed" by a solute molecule. T_c is therefore a characteristic of the molecular interactions in a solution before and after the solute molecule is introduced. Unfortunately, it is not possible to evaluate T_c since an a priori calculation of the partition function for a solvent molecule when it is perturbed or unperturbed is not possible.

We also showed that in general T and T_c would not be identical. Ben Naim's derivation of the compensation law would give T and T_c identical. However, we showed that the source of compensation for single solute-single solvent systems was not the same as that of Ben Naim's.

We identified why exactly T and T_c would not be identical. The origin of this difference lay in that the total change in entropy of the system was different from the change in entropy as calculated by Henry's Law because of the $R \ln c$ term.

We derived a density of states relationship which would hold if a compensation law was valid. Finally, we showed that a model in which different degrees of freedom were perturbed identically (the number of perturbed degrees of freedom depending on the change in parameter which

results in the compensation law) satisfied the compensation law. This model was general enough to include the models for the compensation law in conductivity as well as solubility.

We think that the Einstein oscillator-like model developed for the conductivity could be applied to any activated phenomenon that exhibits a compensation law. The interpretation of T_c as a local temperature would once again be valid.

We think it is necessary at all times to keep in mind that a compensation law occurs not for the enthalpy and entropy changes in a particular system, but rather when the enthalpy and entropy changes of different systems are compared. It is our feeling that if we have a set of processes, each process involving a large number of degrees of freedom (not necessarily identical degrees of freedom) then comparison between different members of the set (of processes) could lead to a compensation law. This point deserves careful attention and might make possible a general derivation for the compensation law.

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