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Determination of Saltiness from the Laws of Thermodynamics—Estimating the Gas Constant from Psychophysical Experiments

Kenneth H. Norwich

Department of Physiology and Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Canada

Correspondence to be sent to: K.H. Norwich, Institute of Biomaterials and Biomedical Engineering, University of Toronto, 4 Taddle Creek Road, Toronto, Ontario, Canada M5S 3G9. e-mail: k.norwich@utoronto.ca

Abstract

One can relate the saltiness of a solution of a given substance to the concentration of the solution by means of one of the well-known psychophysical laws. One can also compare the saltiness of solutions of different solutes which have the same concentration, since different substances are intrinsically more salty or less salty. We develop here an equation that relates saltiness both to the concentration of the substance (psychophysical) and to a distinguishing physical property of the salt (intrinsic). For a fixed standard molar entropy of the salt being tasted, the equation simplifies to Fechner's law. When one allows for the intrinsic 'noise' in the chemoreceptor, the equation generalizes to include Stevens's law, with corresponding decrease in the threshold for taste. This threshold reduction exemplifies the principle of stochastic resonance. The theory is validated with reference to experimental data.

Introduction

Sensory organs, the organelles of gustation not excepted, are adept at detecting changes in the sensory environment. Sustained sensory signals, particularly those regarding taste, tend to become muted due to processes of adaptation. Since 'change' implies an element of uncertainty, the process of sensing can be represented by an uncertainty or entropy function with some success (Norwich, 1977, 1993). However, the entropy function employed in these earlier works was a generic function, whose parameters had to be evaluated from the data. We attempt here to represent the taste of salinity in terms of the standard thermodynamic entropy of the substance being tasted. The chemical senses, especially the sense of taste of saltiness, seem particularly suitable for this trial, because of the relative simplicity of the chemical stimulus compared, for example, with visual or auditory stimuli. The endeavor to represent the intensity of taste solely in terms of physical and chemical quantities, which we undertake here, is compelling from a number of points of view. It can potentially cast some light on the fundamental concept of sensation—what it means to sense the environment—and it permits, in principle, 'modeling' the sensory activity with minimal use of adjustable parameters: most parameters should emerge from the associated physics and chemistry. A mathematical function developed in this way, based largely on quantities that are exterior to biology, either succeeds in its nascent state or it does not succeed; there can be very little adjustment of parameters. We shall develop such a model and confirm its accuracy to a degree using existing experimental data.

We are concerned here with saltiness. The particular physical quantity that we suggest as a measure of the sensation of saltiness is the partial molar entropy of the tastant solution. It should be stressed that, although physical entropy is regarded as a measure of uncertainty or molecular disorder, it is, none the less, measured in the laboratory by very tangible means: calorimeters, thermometers, etc. The units of entropy are joule.degree^{-1}.mole^{-1}. The reason for selecting saltiness for a first effort is because we shall need some standard values of entropy to evaluate our theoretical equation, and some of these values have been measured and are readily obtained for strong electrolytes such as sodium and potassium chloride, which convey a salty taste.

The equations we require for our 'law of sensation' are well known in physical chemistry, and we shall just state them without derivation in the body of the paper. However, in order to give the reader a feel for these equations, we provide a brief derivation, in the Appendix, beginning from the first two laws of thermodynamics. The Appendix leads us from rudiments to equation (1).

Methods

Development of theory

We consider a solution of a strong electrolyte, such as sodium chloride, which dissociates into two monovalent ions (1:1 electrolyte):

$$\mathrm{AB} \rightarrow \mathrm{A}^+ + \mathrm{B}^-$$

Then the partial molal entropies of the cation and anion respectively are given by (Appendix)

$$S_+ = S^0{}_+ - R\ln a_+ \tag{1}$$

$$S_- = S^0{}_- - R\ln a_-$$

where $S^0{}_+$ and $S^0{}_-$ are hypothetical standard partial molar entropies, a_+ and a_- are activities, and R is the gas constant. Adding these equations,

$$S_+ + S_- = (S^0{}_+ + S^0{}_-) - R\ln(a_+a_-)$$

Setting

$$a = \sqrt{(a_+a_-)} \tag{2}$$

$$S = S_+ + S_- \tag{3}$$

$$S^0 = S^0{}_+ + S^0{}_-$$

we obtain

$$-S = -S^0 + 2R\ln a \tag{4}$$

In practice, S^0 may be hard to evaluate.

In order to complete the derivation, we must allow for the absolute threshold for the taste of saltiness. Modern methods for evaluating thresholds employ quite sophisticated statistical techniques. However, for the approximate model presented here, we shall introduce the threshold by adding the constant $2S^0$ to both sides of equation (4). We thus obtain

$$2S^0 - S = S^0 + 2R\ln a \tag{5}$$

For reasons discussed below, the constant on the right-hand side of the equation is best termed a ‘quasi-threshold’. The activity, a, is related to the mole fraction, X, of the electrolyte by the relationship

$$a = \gamma \mathrm{X} \tag{6}$$

where γ is the activity coefficient, which governs the deviation of the solution from ideality. For our current approximation, we shall take $\gamma = 1$, its value for an ideal solution. Thus our approximate equation for 1:1 salts can be written

$$2S^0 - S = S^0 + 2R\ln X \tag{7}$$

with X taken as a measure of concentration of the salt solution.

Comparison with Fechner’s law

Equation (7) can now be compared with Fechner’s law, which is usually written in the form

$$\psi = \alpha + \lambda\ln C \tag{8}$$

where ψ is a measure of saltiness, C is the concentration of the tasted substance, and α and λ are constants that are >0. For concentrations that are small, we can approximate equation (8) by

$$\psi = \alpha + \beta\ln X \tag{9}$$

where X is the mole fraction of the tested substance. Comparing equations (7) and (9), we see that $2S^0 - S$ may be taken equal to saltiness, ψ, with $\alpha = S^0$ and $\beta = 2R$. In other words,

$$\text{saltiness} = 2S^0 - S \tag{10}$$

and saltiness is expressed by the disorder of ions in solution, which, in turn, is measured by the logarithm of the concentration of the ions.

We can now proceed to validate the theoretical equation (7) using data that have already been published by von Skramlik (von Skramlik, 1926) and cited by Pfaffmann *et al.* (Pfaffmann *et al.*, 1971). These results are now summarized by the equation

$$\psi \approx S^0 + 2R\ln X \tag{11}$$

Results

Validation of the theory based on the data of von Skramlik

Von Skramlik (von Skramlik, 1926) compared the saltiness of five salts to the saltiness of sodium chloride. The five salts were NH_4Cl, KCl, $CaCl_2$, LiCl and $MgCl_2$. In Tables 1 and 2 are given the values of the ratio (M NaCl/M salt), the molar concentrations of sodium chloride required to match the saltiness of a comparison salt. Implicit in these data is the assumption that altering the molar concentration of a salt will not alter the value of the above comparison ratio.

Von Skramlik made similar comparisons of sodium chloride to iodides, bromides, sulfates, nitrates and bicarbonates of NH_4, K, Ca, Li and Mg. However, we shall restrict our discussion to chlorides.

It is now a simple matter to adapt our generalized form of Fechner’s law for analysis of the von Skramlik experiments.

Table 1 Mean values of ratios for equal saltiness (molarity NaCl)/(molarity salt) (Pfaffmann *et al*., 1971)

Salt	Ratio	Standard molar entropy
NH_4Cl	2.83	94.5
KCl	1.36	82.6
NaCl	1.00	72.4
LiCl	0.41[a]	59.3
$CaCl_2$	1.23	113.8
$MgCl_2$	0.29	89.5

[a] Value corrected using data from Table 2.

Salts with monovalent cations (1:1 salts)

We now evaluate von Skramlik's ratio, (M NaCl/M salt), using equation (7). Since the two substances, NaCl and the comparison (1:1) salt, tasted equally salty, we can equate the right-hand side of equation (7), written for NaCl, with the corresponding quantity written for a comparison salt. That is

$$S^0_{\mathrm{NaCl}} + 2R\ln X_{\mathrm{NaCl}} = S^0_{\mathrm{salt}} + 2R\ln X_{\mathrm{salt}} \qquad (12)$$

The latter equation can be written in the form

$$\ln(X_{\mathrm{NaCl}}/X_{\mathrm{salt}}) = -[1/(2R)]S^0_{\mathrm{NaCl}} + [1/(2R)]S^0_{\mathrm{salt}} \qquad (13)$$

For concentrations that are not too great, we can take the ratio of mole fractions on the left-hand side of this equation as a good approximation of the von Skramlik ratio introduced in the previous section. The quantities, S^0, can be evaluated with reference to equation (4). When $a = X = 1$, then $S = S^0$. That is, when the mole fraction of the salt is equal to unity, the molar entropy is equal to the standard molar entropy at the reference temperature of 25°C. But when the mole fraction is equal to unity, the molar entropy might be taken to be that of the pure (liquid) form of the salt [hypothetically, as discussed by Smith (Smith, 1967)].

This 'fused liquid salt' may or may not exist in reality; however, we can approximate S^0 by the molar entropy of the pure crystalline solid at 25°C. S^0 for the crystalline solid will be less than S^0 for the hypothetical fused salt because of the extra degrees of freedom possessed by the liquid form. However, because of the identical crystal structures of LiCl, NaCl, KCl and NH_4Cl, the differences between S^0 for the fused salt and S^0 for the crystalline solid can be expected to remain approximately constant. Because of this constant difference, we shall be able to use values of S^0 for the crystalline form, to estimate the value of R from biological data. Therefore, we take S^0 equal to the molar entropy of the pure crystalline salt at 25°C. For chloride salts, these entropies have been measured in joule.mole^{-1}.deg^{-1} or cal.mole^{-1}deg^{-1} and can be obtained from standard books of tables (Weast and Astle, 1981).

Table 2 Raw data from which Table 1 was obtained (von Skramlik, 1926)

	Salt molarity	NaCl molarity
NH_4Cl	0.374	1.02
NH_4Cl	0.374	0.957
NH_4Cl	0.374	1.2
KCl	0.268	0.273
KCl	0.268	0.410
KCl	0.268	0.410
LiCl	0.474	0.207
LiCl	0.474	0.240
LiCl	0.474	0.136
$CaCl_2$	0.091	0.17
$CaCl_2$	0.0228	0.017
$CaCl_2$	0.0228	0.0239
$MgCl_2$	0.098	0.03
$MgCl_2$	0.098	0.027

Values are the molarity of sodium chloride whose saltiness matches that of the salt. For example, three ratios are obtained for NH_4Cl, 1.02/0.374, 0.957/0.374 and 1.2/0.374, whose mean is equal to 2.83, the value reported in Table 1.

We can now plot the values of the von Skramlik ratio for each salt with monovalent cation (LiCl, KCl and NH_4Cl) against the standard molar entropy for that salt (Table 1). The result is shown in Figure 1. The corresponding points for the two salts with divalent cations (calcium and magnesium) have also been plotted for comparison. It may be seen that the four salts with monovalent cations are arrayed linearly along the regression line given by

$$\ln(X_{\mathrm{NaCl}}/X_{\mathrm{salt}}) = -3.8148 + 0.0511S^0_{\mathrm{salt}} \qquad (14)$$

For comparison, the theoretically derived straight line, given by equation (13), is

$$\ln(X_{\mathrm{NaCl}}/X_{\mathrm{salt}}) = -4.354 + 0.0602S^0_{\mathrm{salt}} \qquad (15)$$

since $1/(2R) = 0.0602$ when R takes on its usual value of 8.3144 joule.mole^{-1}.deg^{-1}. Conversely, one can estimate the value of the gas constant, R, from the experimentally derived regression line, $R = 1/(2 \times 0.0511) = 9.79$, which differs from the accepted value by 17.8%.

Some of this material has been introduced recently (Norwich, 2000).

Salts with divalent cations (2:1 salts)

The corresponding case for $CaCl_2$ and $MgCl_2$ is not quite as simple as that of the monovalent ions. We now must write one equation of the form of equation (1) for each of three ions, e.g. for Ca^{++}, Cl^-. We now obtain the equation

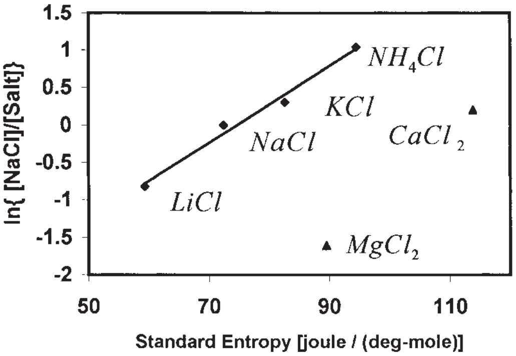

Figure 1 Prepared from the data of von Skramlik (von Skramlik, 1926). [NaCl]/[salt] is the ratio of the molarity of a solution of sodium chloride to that of a salt when the saltiness of the two solutions is equal. The natural logarithm of this ratio is plotted against the standard molar entropy of the salt at 25°C. Monovalent salts are plotted with black diamonds and are seen to lie on a straight line defined by equations (13) and (14) in the text. Divalent (2:1) salts are plotted with black triangles and are seen to fall far from the straight line.

$$\ln\frac{X^2_{\text{NaCl}}}{X^3_{\text{salt}}} = \frac{1}{R}S^0_{\text{salt}} \tag{16}$$

If the ratio on the left-hand side of this equation is plotted against S^0_{salt} for several salts, the slope of the straight line so obtained will be equal to $1/R$. Using means for $CaCl_2$ and $MgCl_2$ data from Table 2, we calculate for 2:1 salts that R = 6.53 joule.mole^{-1}.deg^{-1}, which differs from the accepted value by –21.4%. The mean of the two estimates of R is 8.16 joule.mole^{-1}.deg^{-1}, which differs from the accepted value by 1.8%.

Validation of the theory based on Stevens's data

If equation (7) were valid for very low concentrations of salt, the sensation of taste would equal zero (i.e. threshold) when

$$\ln X = -S^0/2R \tag{17}$$

The mole fraction, X, is given approximately by

$$X = M/(M + 55.6) \tag{18}$$

where M is the molarity of the salt and 55.6 = 1000/18 is the approximate molarity of water. Since $M << 55.6$, we would have

$$\text{M} = \text{quasi-threshold} = 55.6\exp(-S^0/2R) \tag{19}$$

The value of M is termed a quasi- or seeming-threshold because Fechner's law is not valid for very small concentrations. Rather we must employ Stevens's power law in this region, as shown for sodium chloride in the data in Figure 2. Inverting the latter equation,

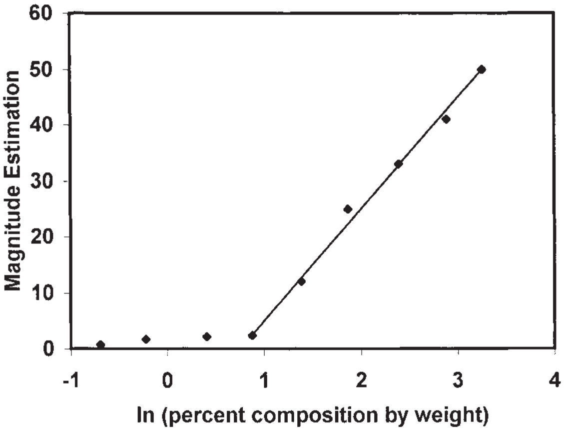

Figure 2 Data of Stevens (Stevens, 1969). Psychophysical study of the taste of solutions of sodium chloride. Magnitude estimation of the saltiness of the solution is plotted against the natural logarithm of the concentration of the solution. A least-squares regression line has been plotted for the six most concentrated solutions. The *x*-intercept of this regression line has been termed the 'quasi-threshold'. The value of the gas constant, *R*, may be estimated from this intercept [Equation (20)].

$$R = (S_0/2)/\ln(55.6/M) \tag{20}$$

which we may employ as a second psychophysical test of the theory.

The gas constant, R, is equal to the product of Boltzmann's constant, k, with Avogadro's number, N_0, so we can express equation (20) in an interesting alternative format. Dividing both sides of this equation by N_0, we obtain

$$k = (S'_0/2)/\ln(55.6/M) \tag{21}$$

where $S'_0 = S_0/N_0$ is the standard entropy per molecule.

Since the quasi-threshold, M, may be read off a graph of magnitude estimate against ln (molarity) and the standard molal entropy, S_0, is found in tables, one can, quite unexpectedly, obtain a psychophysical measure of the gas constant, R. With reference to Stevens's data (Stevens, 1969), the right-most six data points fall on a straight line on a semi-log plot (Figure 2), in accordance with Fechner's law and equation (7). The least-squares regression line for these points is

$$\text{magnitude estimation} = -13.31 + 19.277\ln C$$

where concentration, C, is percentage concentration by weight of sodium chloride. For quasi-threshold, the right-hand side of this equation is set equal to zero, giving C_q = 2.0 g/100 ml, from which M = 20/58.5 = 0.342 molar. From Table 1, S_0 = 72.4 joule.mole^{-1}.deg^{-1} for sodium chloride (25°C). Substituting for M and S_0 in equation (20), we obtain

$$R \approx 7.11 \text{ joule.mole}^{-1}.\text{deg}^{-1}$$

which differs from the accepted value for R, which is 8.3144 joule.mole^{-1}.deg^{-1}, by –14.5%.

However, calculation of R from equation (20) may contain sizeable errors. First, the calculation depends on the value of M, which issues from measurements of subjective magnitude that are quite variable. Second, M may be too small due to dilution by saliva etc., which will increase the calculated value of R. Third, S^0 for the crystalline solid is less than it would be for the hypothetical fused salt, which will, again, reduce the calculated value of R.

The same kind of calculation can be made from the magnitude estimation data of Meiselman *et al*. (Meiselman *et al*., 1972) for sodium chloride. There are fewer data points available, and one can use only the upper three points, obtaining $M = 0.181$ molar and $R = 6.32$ joule.mole^{-1}.deg^{-1}. It must be appreciated that these estimates are not offered as a substitute for proper physicochemical evaluations of the gas constant; they are, rather, offered as a means of partial validation of the principle of physical entropy as a measure of taste sensation.

Validation of the theory: stochastic resonance

Stochastic resonance, in its broadest context—see, for example, Wiesenfeld and Moss (Wiesenfeld and Moss, 1995), stochastic resonance type 3—can refer to the reduction in threshold that follows the introduction of noise into a system. This phenomenon can be observed when we allow for the introduction of noise into the pathway for perception of taste.

Within the general entropy theory of sensation (Norwich, 1993), Stevens's law emerges when Fechner's law is applied to the combination of two sensory signals (convolution of two probability densities): the external taste stimulus, C, plus an internal stimulus, C_N, which may be regarded as a constant 'noise' or 'reference' signal. The procedure is much simpler here. Let us write equation (7) or (8) for the sum of the two signals:

$$\begin{aligned}\text{magnitude estimation} &= \alpha + \lambda \ln C_{\text{TOTAL}} \\ &= \alpha + \lambda \ln(C + C_N) \\ &= \alpha + \lambda \ln(1 + C/C_N) + \lambda \ln C_N.\end{aligned}$$

Defining $\ln C_N = -\alpha/\lambda$, which we recognize as the quasi-threshold, we obtain

$$\text{magnitude estimate} = \lambda \ln(1 + C/C_N) \qquad (22)$$

When $C << C_N$, the preceding expression can be represented by the first term of the Taylor series for $\ln(1 + C/C_N)$, or

$$\text{magnitude estimate} = (\lambda/C_N)C,$$

which is the Stevens law representation with the exponent of C equal to 1.

So we see that both Stevens's law and Fechner's law emerge from the entropic representation of taste, Stevens's law holding more precisely for lower concentrations and Fechner's for higher concentrations. However, in the middle range, both laws hold reasonably well.

We may also see that the shift to Stevens's law from Fechner's law permits the system to decrease its threshold. When Fechner's law alone holds sway, the threshold is given by the quasi-threshold value depicted in Figure 2, which is substantially greater than zero. When noise is added to the system, the threshold diminishes to zero, as given by equation (23). In reality, there will still, of course, be a small positive threshold. The above is an example of the principle of stochastic resonance: threshold is reduced as a consequence of the addition of the noise signal.

Discussion

Entropy

Claude Shannon, who formulated the theory currently known as information theory, defined entropy as a weighted sum of the logarithms of the probabilities of the outcomes of an event. It was shown (Norwich, 1984) that if the magnitude of taste were equated to a general 'entropy' or uncertainty, governed by an unspecified probability density function, one could then derive from this single definition many of the empirically discovered sensory laws governing taste: both laws of sensation (Fechner's and Stevens's), the general function for Weber fraction, the adaptation function for taste, etc. It was suggested that the receptor might be sensitive to or uncertain about the density of particles in solution, since this quantity will fluctuate due to Brownian motion. However, the event remained unspecified—that is, it was not stipulated what the taste receptor was uncertain about—so there remained a number of parameters that had to be evaluated by fitting functions to experimental data.

In the present work, it is hypothesized that the entropy utilized by the taste receptor is the standard physical or thermodynamic entropy. Thus we were able to derive an expression for the law of taste perception largely without adjustable parameters. It was found, however, that the phenomenon of biological threshold was not evidently contained within the physical expression for entropy, and threshold was placed by conjecture.

The new derived law of taste for monovalent, strong salts is given by Equation (7), which is a form of Fechner's law defining not only the logarithmic dependence of taste on concentration of the substance tasted, but also showing how taste will vary for different salts with the same molar concentration, based on differences in the standard molar entropies, $S^0 = (S^0_+ + S^0_-)$.

Factors affecting the approximations

It is important to recognize that the final step in the derivation of Equation (1) (Appendix), replacing pressure, P, by mole fraction, X, is valid only for dilute (ideal) solutions, and may hold more closely for monovalent than for divalent ions.

One must also allow, in the interpretation of results, for the dilution of tasted solutions by saliva etc. That is, concentration of tastants that actually reach the sensory cells may be somewhat less than the values measured in the laboratory. In some cases, for example equation (13), the dilution factors will tend to cancel; in other cases not.

The hypothetical molal entropies of the fused salt would be greater than the corresponding values for crystalline substance, which could affect all calculations, but particularly will decrease the values of R calculated from equation (20).

How does a taste receptor determine the entropy?

Hitherto, we have given scant consideration to the mechanism of transduction of the taste signal. Rather, we have emphasized the results that can be observed if taste is measured simply, linearly by physical entropy. Entropy is measured in the laboratory by complex methods. It is not expected that the sensory receptor, which gives rise to the sensation of taste, will appraise entropy by laboratory techniques, and the mechanism by which it does so is a matter of speculation. Quite likely, the organism utilizes the relationship between entropy and free energy, as expressed by the Gibbs equation for constant temperature,

$$\Delta G = -T\Delta S + \Delta H$$

where G and H are the Gibbs function (free energy) and the enthalpy, respectively. That is, changes in entropy are associated with changes in free energy, that can energize the chemical reactions associated with taste. These reactions, in turn, increase the frequency of action potentials in nerve fibres in the seventh and ninth cranial nerves.

The transduction of the taste of sodium chloride is believed to involve the permeation of sodium ions through amiloride-sensitive sodium channels (Herness and Gilbertson, 1999; Geran and Spector, 2000; Hendricks *et al.*, 2000). An avenue for exploration, then, may be the relationship between changes in free energy produced by the sodium chloride tastant to changes in sodium permeability via amiloride-sensitive sodium channels.

The principle of molar entropy as a measure of the sensation of taste can be expected to apply more widely. For example, it might be expected to hold, *mutatis mutandis*, for other taste qualities such as sweetness, bitterness, etc. It might also find applicability in the sense of olfaction. However, as the molecules involved become more complex, the associated chemistry becomes more complicated, and published data scarcer.

The entropy principle suggests that the percept of taste originates in the receptor itself, and is modulated at higher centers.

Conclusions

By hypothesis, the negative of the molar entropy of a tastant in solution is taken as a measure of the magnitude of the taste of saltiness. It was shown that under these circumstances, the taste of saltiness becomes a linear function of the logarithm of the concentration of the tastant, in accordance with Fechner's law. To this fundamental hypothesis it was necessary to append a second condition: the line defining Fechner's law must be displaced upward in parallel displacement until the intercept of the line with the x-axis (quasi-threshold) is equal to the standard molar entropy of the salt. The result was a generalized form of Fechner's law defining not only the change in sensation with concentration, but also the difference in sensation (saltiness) between two different salts that have the same molar concentrations. The hypothesis was verified by several techniques using published data. The standard molar entropies were approximated by the entropies of the crystalline form of the salt. The theoretical equations were readily conformed to the data of von Skramlik (von Skramlik, 1926) on saltiness-matching. The more complete test utilized only 1:1 salts such as KCl. Von Skramlik's data not only conformed to the entropy hypothesis, but permitted the estimation of the value of the gas constant, R. They theory of 2:1 salts was worked out in part and 2:1 salts such as $CaCl_2$ also permitted estimation of the gas constant. The mean estimate of R was close to the accepted value. The entropy hypothesis was also confirmed using psychophysical data by plotting saltiness against the logarithm of salt concentration. The value of the quasi-threshold, which could be read from the graph, again permitted estimation of the value of R.

Adding to the pure sensory signal from the tastant is noise arising within the taste receptor itself. The result of adding this noise was to convert Fechner's law, which governed larger salt concentrations, to Stevens's power law, which was more accurate for lower salt concentrations. The quasi-threshold was replaced by a smaller, more realistic threshold, demonstrating the thesis of stochastic resonance: addition of noise to a system may, under certain conditions, lower the threshold for signal detection. Finally, the issue of signal transduction for sodium chloride was addressed.

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Glossary of symbols used in the main text

a_+, a_-	activity of a positive and negative monovalent ion, respectively
a	activity, defined by equation (2)
C, C_q, C_N	concentration of salt in solution, expressed in units of convenience, but with dimension (mass.volume^{-1})
G	Gibbs free energy (joules)
H	enthalpy (joules)
k	Boltzmann's constant
M	molarity of a solution (mole.l^{-1})
N_0	Avogadro's number
R	gas constant (8.3144 joule.deg^{-1}.mole^{-1})
S_+, S_-	partial molar entropies of positive and negative monovalent ions (joule.deg^{-1}.mole^{-1}), $S = S_+ + S_-$
S^0_+, S^0_-	standard molal entropies etc., $S^0 = S^0_+ + S^0_-$
ΔS	change in entropy associated with a chemical reaction (joule.deg^{-1})
X	mole fraction of a salt in solution
α, β, λ	constants
γ	activity coefficient = a/X
ψ	subjective magnitude of saltiness

References

Alberty, R.A. and **Silbey, R.J.** (1997) Physical Chemistry, 2nd edn. Wiley, New York.

Geran, L.C. and **Spector, A.C.** (2000) *Sodium taste detectability in rats is independent of anion size: the psychophysical characteristics of the transcellular sodium taste transduction pathway*. Behav. Neurosci., 114, 1229–1238.

Hendricks, S.J., Stewart, R.E., Heck, G.L., DeSimone, J.A. and **Hill, D.L.** (2000) *Development of rat chorda tympani sodium responses: evidence for age-dependent changes in global amiloride-sensitive Na$^+$ channel kinetics*. J. Neurophysiol., 84, 1531–1544.

Herness, M.S. and **Gilbertson, T.A.** (1999) *Cellular mechanisms of taste transduction*. Annu. Rev. Physiol., 61, 873–900.

Meiselman, H.L., Bose, H.E. and **Nykvist, W.F.** (1972) *Magnitude production and magnitude estimation of taste intensity*. Percept. Psychophys., 12, 249–252.

Norwich, K.H. (1977) *On the information received by sensory receptors*. Bull. Math. Biol., 39, 453–461.

Norwich, K.H. (1984) *The psychophysics of taste from the entropy of the stimulus*. Percept. Psychophys., 35, 269–278.

Norwich, K.H. (1993) Information, Sensation and Perception. Academic Press, San Diego, CA.

Norwich, K.H. (2000) *Physics makes 'sense'*. Canadian Medical and Biological Engineering Society Conference, October 2000, Proceedings, pp. 92–93.

Pfaffmann, C., Bartoshuk, L.M. and **McBurney, D.H.** (1971) In Beidler, L.M. (ed.), Handbook of Sensory Physiology: Vol. IV, Chemical Senses 2: Taste. Springer, New York, pp. 85–86.

Smith, N.O. (1967) Chemical Thermodynamics: A Problems Approach. Reinhold, New York.

Stevens, S.S. (1969) *Sensory scales of taste intensity*. Percept. Psychophys., 6, 302–308.

von Skramlik, E. (1926) Handbuch der Physiologie der Niederen Sinne. Georg Thieme, Leipzig, pp. 458–460.

Weast, R.C. and **Astle, J.J.** (eds) (1981) CRC Handbook of Chemistry and Physics. CRC Press, Boca Raton, FL.

Wiesenfeld, K. and **Moss, F.** (1995) *Stochastic resonance and the benefits of noise: from ice ages to crayfish and SQUIDS*. Nature, 373, 33–36.

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Appendix: the molar entropy of an ion in solution

The following is a very brief derivation of equation (1), emphasizing physical content. The derivation is based largely on the first two laws of thermodynamics, the ideal gas law, and the existence of the Gibbs function as a state variable in thermodynamics.

The first law of thermodynamics expresses changes in the internal energy of a system, dU, as a balance between heat added to the system, d$'Q$ and P–V work done by the system, PdV:

$$\mathrm{d}U = \mathrm{d}'Q - P\mathrm{d}V$$

The second law of thermodynamics expresses the change in entropy, dS, for a reversible reaction by means of the equation

$$\mathrm{d}'Q = T\mathrm{d}S$$

The two laws can be combined in the form

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

The Gibbs function is defined by

$$G = U + PV - TS$$

Differentiating and introducing the combined first and second laws,

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T$$

i.e. G can be represented by means of a complete differential, so that

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_P \mathrm{d}T$$

Comparing the latter two equations,

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

For one mole of an ideal gas,

$$V = RT/P$$

so that

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

which may be integrated with respect to P to give G, the Gibbs free energy per mole, usually designated by μ:

$$\mu = \mu_0 + RT\ln P$$

The quantity μ_0 arises as a constant of integration. Differentiating partially with respect to T and recognizing that this derivative is equal to $-S$, as derived above,

$$-S = -S'_0 + R\ln P$$

where S and S'_0 refer to entropies per mole.

We make the transition from ideal gas to ideal solution, appealing to Henry's law, by replacing P by the mole fraction of solute, X (Smith, 1967; Alberty and Silbey; 1997),

$$S = S_0 - R\ln X$$

Setting X equal to the activity, a, we obtain equation (1).