The derivation is finished if the class of neighboring states defined by eqs 9 and 12, that is, by

$$C\beta(N - \langle N \rangle)^2 = \exp(-\beta\Delta\Omega) \tag{14}$$

can be shown to include all possible physically acceptable nearby nonequilibrium distributions that can evolve into the given original equilibrium distribution. Presumably it does, as eq 14 is a minimal requirement to produce $\langle A \rangle = \langle S \rangle$, and such assumptions are standard in traditional linear response theory. Note that constant T and μ are required because the averaging after the perturbation is removed is done with the $P_{N,i}^0$ or $f(\mathbf{r}^N, p^N)$.

Is there certainly a rule of nature that chemical systems at constant temperature and chemical potential evolve toward minimum softness or maximum hardness? A major concern with the proof just given should be whether statistical mechanics indeed applies to electrons in individual molecules in the sense employed. Evidence is accumulating that it does, at least to some reasonable accuracy,[6] but one should not, at this time, imply certainty. Nevertheless, with some confidence one may assert, with Pearson, the maximum hardness principle. If one also asserts, with Sanderson,[9] the electronegativity (chemical potential)[3] equalization principle, then one has reached two basic, broadly applicable electronic-structure principles.

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HSAB Principle

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It is generally accepted that a variety of acid–base reactions can be described by the HSAB principle:[1] "Hard likes hard and soft likes soft". It is not, however, easy to theoretically establish this principle. Here two proofs are offered of this principle with a restriction added: Among potential partners of a given electronegativity, hard likes hard and soft likes soft.

For the ground state of an N-electron system at 0 K, or for the equilibrium state at the temperature T, according to density-functional theory[2] hardness and softness are given by[3,4]

$$2\eta = \left(\frac{\partial\mu}{\partial N}\right)_{v(\mathbf{r}),T} \quad \text{and} \quad S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial\mu}\right)_{v(\mathbf{r}),T} \tag{1}$$

where μ and $v(\mathbf{r})$ are the chemical and external potentials, respectively. When two species combine to give a third, their chemical potentials are equalized. Chemical potential is the negative of electronegativity. The maximum hardness principle or minimum softness principle states that, at constant μ, $v(\mathbf{r})$, and T, systems evolve toward minimum total softness.[5,6]

First Proof.[11] When acid A and base B interact to give AB, two things happen, which can be taken as happening in succession. First there is a charge transfer producing a common chemical potential, and then there is a reshuffling of the charge distributions. In the first step there is an energy gain proportional to the square

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of the original chemical potential difference and inversely proportional to the resistance to charge transfer which is the hardness sum. The specific old formula,[3]

$$\Delta E = -\frac{(\mu_B - \mu_A)^2}{4(\eta_A + \eta_B)} = -\frac{(\Delta\mu)^2}{2}\frac{S_A S_B}{S_A + S_B} \tag{2}$$

need not be precisely valid; the essential point is the indicated dependence on softnesses. The greater $S_A S_B/(S_A + S_B)$ is, the more stabilizing is the charge transfer. For a given S_A, the larger S_B is, the better.

In the next, reshuffling step, which is at constant μ and T, the minimum-softness principle applies. The total softness is, at least roughly, $S_A + S_B$ by application of eq 1 to nonoverlapping A plus B with a total number of electrons $N_A + N_B$.[7] The preference in this step is for S_A and S_B to be as small as possible. So, for a given S_A, the smaller S_B is, the better. Thus there are two opposing tendencies, and the optimum situation will be a compromise.

Suppose S_A is fixed, let $S_B = \alpha S_A$, and consider the question of what will be the best value of S_B or α. The supremum value of $\alpha/(1 + \alpha)$, 1, corresponds to maximum initial energy gain and maximum softness, while the infimum value, 0, has these roles reversed. If nothing is known about the relative importance of the two conditions, a most natural compromise would be to take the average value, viz., $\alpha/(1 + \alpha) = {}^1/_2$. This is the HSAB principle: $\alpha = 1$. In this analysis S_A and S_B are softnesses either before or after the chemical potential equalization step; fortunately these quantities are known to be insensitive to the number of electrons.[8] The final chemical bond formation may be assumed not to much affect the partitioning $S_A + S_B$ and not to much affect the components S_A and S_B.

To quantify the argument: For a given $\Delta\mu$ and S_A, the problem is to find the most favorable S_B, or the most favorable α. From eq 2 one would want $\alpha/(1 + \alpha)$ to be as large as possible, which favors a large α value. But to minimize $S = S_A + S_B = S_A(1 + \alpha)$ one would want α to be as small as possible. Simultaneous satisfaction of the two conditions being impossible, what one must assess is the relative importance of the two conditions. Let λ be the weight of the first relative to the second. Then α is determined from

$$\frac{d}{d\alpha}\left[(1 + \alpha) - \lambda\left(\frac{\alpha}{1 + \alpha}\right)\right] = 0 \tag{3}$$

This gives $\alpha = \sqrt{\lambda} - 1$. For a fixed value of λ (λ may be hoped to be a more or less universal constant), the result is that, from among a series of B's with the same chemical potential (electronegativity), a given A will prefer one, and similarly with other A's. The HSAB principle follows precisely if one takes $\lambda = 4$, for then $\alpha = 1$ and $S_B = S_A$. An argument that λ should be close to 4 is not easy to construct.

Note that A'B + AB' → AB + A'B' is predicted to be a hardness-raising or softness-lowering process if $S_A = S_B$, $S_{A'} = S_{B'}$. The maximum hardness (minimum softness) principle is demanded by the HSAB principle.

Second Proof.[12] To obtain a second proof, rewrite eq 2 in the form

$$\Delta E = \Delta\Omega_A + \Delta\Omega_B \tag{4}$$

where

$$\Delta\Omega_A = -\frac{(\mu_B - \mu_A)^2}{4}\frac{\eta_A}{(\eta_A + \eta_B)^2}$$

$$\text{and} \quad \Delta\Omega_B = -\frac{(\mu_B - \mu_A)^2}{4}\frac{\eta_B}{(\eta_A + \eta_B)^2} \tag{5}$$

Assume that for a given $\mu_B - \mu_A$ and η_B, $\Delta\Omega_A$ is minimized with respect to η_A. There follows

(7) Nalewajski, R. F.; Korchowiec, J.; Zhou, Z. *Int. J. Quantum Chem.* **1988**, *22*, 349–366.
(8) Fuentealba, P.; Parr, R. G. *J. Chem. Phys.* In press.

$$\eta_A = \eta_B \tag{6}$$

Minimization of $\Delta\Omega_B$ with respect to η_B at fixed η_A gives the same result. The HSAB principle! Under these conditions

$$\Delta\Omega_A = \Delta\Omega_B \tag{7}$$

If this equation were assumed, it would imply eq 6.

In the molecule AB, A and B are open systems (as first pointed out by Richard Bader[9]). This means that the natural thermodynamic quantity for an atom (or other subunit) in a molecule is not the energy E but the *grand potential* $\Omega_i = E_i - (N_i - N_i^o)\mu_i$. In equilibrium at the final, equalized chemical potential μ, the grand potentials of both A and B prefer to be as negative as possible. This implies in turn that $\Delta\Omega_A$ and $\Delta\Omega_B$ in eq 5 prefer to be as negative as possible, for these $\Delta\Omega$'s are just the grand potential changes. An elementary calculation on the charge-transfer equilibration shows this; one finds $\mu = (S_A\mu_A + S_B\mu_B)/(S_A + S_B)$ and

$$\Delta\Omega_A = -\frac{1}{2}S_A(\mu - \mu_A)^2 = -\frac{(\mu_B - \mu_A)^2}{4}\frac{\eta_A}{(\eta_A + \eta_B)^2} \tag{8}$$

and similarly with $\Delta\Omega_B$, verifying eq 5.

The argument is that Ω_A and Ω_B separately like to be as negative as possible. This has the HSAB principle as a consequence, and also the equity principle of eq 7. There is a dictum in economics called the Pareto principle: Efficiency is highest when partners are both well satisfied.[10] So it appears to be in chemistry, and that is the HSAB principle.

(9) For example, Sec. III in the following: Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63–124.

(10) See, for example, pp 747–748 and especially Fig. 31–2 of the following: Samuelson, P. A.; Nordhaus, W. D. *Economics*, 13th ed.; McGraw-Hill: New York, 1989.

(11) P.K.C. and R.G.P.

(12) H.L. and R.G.P.

Decakis(2,6-diethylphenyl)decastanna[5]prismane: Characterization and Molecular Structure

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The theoretical structures presented by the family of heavy-atom group IVA [*n*]prismanes, $[RM]_{2n}$, where M = Si, Ge, Sn, and Pb, R = H, and *n* = 2–6, respectively, all possess severe M–M–R and M–M–M bond-angle distortions due to the unique geometrical constraints imposed upon the M–M-bonded networks in these molecular frameworks.[1] To date, the only synthetic derivatives of this important class of compounds are represented by one [3]prismane [M = Ge, R = bis(trimethylsilyl)methyl][2] and two [4]prismanes (M = Si, R = *tert*-butyldimethylsilyl; M = Sn, R = 2,6-diethylphenyl).[3,4] Herein, we report the successful isolation

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(2) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55.
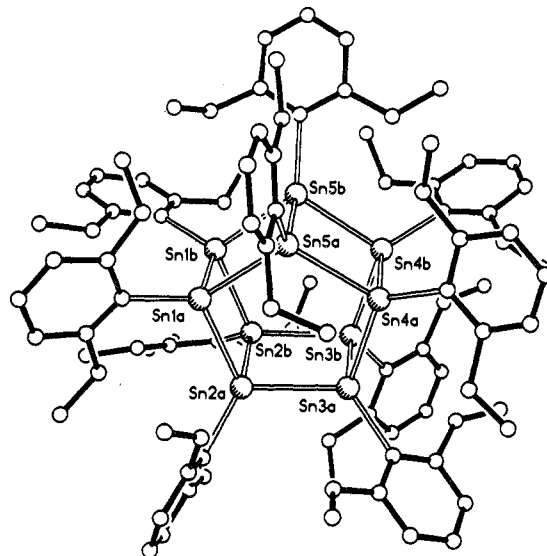

Figure 1. Molecular structure of **1**. Tin and carbon atoms are represented by large and small spheres, respectively, of arbitrarily chosen size. Hydrogen atoms have been omitted for purposes of clarity. For a complete listing of bond lengths and angles, see the supplementary material.

and characterization, including crystallographic analysis, of the titled first heavy-atom [5]prismane derivative **1** (M = Sn, R = 2,6-diethylphenyl), which is prepared through a novel process.

Preparation and Characterization. Thermolysis of a 1:1 mixture (w/w) of benzophenone and hexakis(2,6-diethylphenyl)cyclotristannane (**2**)[5] at 200 °C for 20 min provides **1** and octakis-(2,6-diethylphenyl)octastanna[4]prismane (**3**)[4] in a 2.3:1 ratio for a combined yield of 12% along with small amounts of hexakis-(2,6-diethylphenyl)distannane (**4**),[6] hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**5**)[6] (5%), recovered **2** (12%), and other tin-containing compounds (Scheme I). In contrast, substitution of naphthalene for benzophenone provides, under identical conditions, a large quantity of recovered **2** (51%), larger amounts of **4** and **5** (27%), and only traces of **1** and **3** (<2–3%). Concerning the role of benzophenone in providing higher yields of **1** and **3**, we have previously proposed[4] that perstanna[*n*]prismanes are products generated by the thermal bimolecular disproportionation of the highly reactive diorganostannylene **6**, which is in thermal equilibrium with **2**,[7] to produce the monovalent and trivalent tin species, **7** and **8**, respectively, followed by oligomerization of **7** according to Scheme I. In this mechanism, benzophenone, acting as the solvent, might serve to stabilize the stannylene monomer **6** relative to **2** through Lewis acid–base complexation,[8] thereby leading to higher concentrations of **7**, and hence to **1** and **3**.

Orange microcrystalline **1** was isolated through chromatography on silica gel using a 4:1 hexane/toluene solvent mixture as the eluant, and chemical analysis and spectroscopic data are fully consistent with the $[RSn]_{2n}$ formulation.[9,10] Due to restricted rotation about the tin–carbon bonds in **1**, the ^1H NMR spectrum is temperature-dependent with a coalescence temperature, T_c, being observed for this process at –30 °C. In contrast, the T_c value

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(9) Anal. Calcd for **1**: C, 47.68; H, 5.20. Found: C, 47.39; H, 5.00. ^1H NMR (500 MHz, toluene-d_8, 40 °C): δ (ppm) 0.84 (t, 6 H), 2.92 (q, 4 H), 6.94 (d, 2 H), and 7.08 (t, 1 H). ^{119}Sn NMR (186.5 MHz, toluene-d_8, δ reference to external Me$_4$Sn): δ (ppm) –21.3 [$^1J(^{119}Sn-^{117}Sn)$ = 693 Hz, $^2J(^{119}Sn-^{117}Sn)$ = 1224 Hz between tin atoms in different five-membered rings; $^1J(^{119}Sn-^{117}Sn)$ = 3312 Hz, $^2J(^{119}Sn-^{117}Sn)$ = 90 Hz between tin atoms within the same five-membered rings].[12] UV (hexane): λ 270 (ε 83 600), 350 nm (6100).

(10) Detailed information is supplied in the supplementary material.