3.61 Å). Thus, the I_d transition state for the 20-e$^-$ system has more bond breaking than the associative transition state for the 19-e$^-$ system.

Conclusion

The ab initio results on the substitution reactions of 17-e$^-$ and 18-e$^-$ octahedral hexacarbonyl transition-metal complexes indicates a pseudo-C_{2v} transition state. No intermediate in the reactions is observed. For the substitution reaction of a 17-e$^-$ metal complex, the simple two-center three-electron bond picture is not so obvious in our calculations. It is better to view both entering and leaving ligands on equal footing. From Figure 3, the occupation of one electron in the d_{yz} orbital in the 19-e$^-$ system suggests a three-center five-electron bond in the transition state for a substitution reaction of a 17-e$^-$ transition-metal complex.

The most important factor in the experimental observation of a significant difference in the substitution reaction rates of 18-e$^-$ and 17-e$^-$ metal complexes is the significant difference in the valence-electron charge distributions of the corresponding transition states. The analysis of the Laplacian of the valence electron density in the calculated transition states indicates that the single electron difference between 19-e$^-$ and 20-e$^-$ systems leads to a significant difference in the valence-electron charge concentrations. The angle between the two charge concentrations toward the entering and leaving ligands for the 20-e$^-$ system is much smaller than that for the 19-e$^-$ system. More open coordination sites for the 19-e$^-$ system allow an effective bonding of the central metal atom to the entering/leaving ligands simultaneously in the transition state. Therefore, the transition state is much more stable for the substitution reactions of 17-e$^-$ transition-metal complexes.

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On Pearson's HSAB Principle

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Some 35 examples of the exchange reaction AB + CD = AC + BD (type 1), for which Pearson's HSAB (hard–soft acid–base) principle was originally devised, are examined in terms of the experimental or calculated hardness (η) values of the various species involved. The calculation of the η values has been done at the MNDO level by using $\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2$, where ϵ is energy, LUMO indicates the lowest unoccupied molecular orbital, and HOMO is the highest occupied molecular orbital. In the case of some 75 molecules it is found that the η values calculated at the MNDO level match quite well with the experimental η values. The examples of the exchange reaction are so chosen that the experimental hardnesses of at least three of the four species involved in a particular example are known. From the present study it is concluded that an exchange reaction proceeds in a direction so as to produce the hardest possible species and the average value of the hardnesses of the products is greater than that of the reactants in a reaction of type 1. The results are explained in terms of the chemical reactivity of the four molecules involved in a particular example. Of the 35 examples studied there are only 5 exceptions.

Introduction

In 1963 Pearson[1] introduced the hard–soft acid–base (HSAB) principle which states that "hard acids prefer to coordinate to hard bases and soft acids to soft bases".[2] This apparently simple statement has been used successfully by Pearson to rationalize a variety of chemical information.[3] But the concept of hardness or softness (inverse of hardness) remained qualitative till 1983. The qualitative definition of hardness uses the idea of polarizability; a less polarizable species is hard and a more easily polarized one, soft. For ions of similar charge the ratio of charge and radius can be used for assessing their relative polarizability. However no numbers could be assigned to a particular species before 1983. The quantitative definition[4] given by eq 1 relates hardness η of

$$\eta = (\mathrm{IP} - \mathrm{EA})/2 \tag{1}$$

any chemical species to its ionization potential IP and electron affinity EA. Incidentally, the average of IP and EA gives the electronegativity (χ) of a neutral species (eq 2). By applying

$$\chi = (\mathrm{IP} + \mathrm{EA})/2 \tag{2}$$

Koopmans' theorem, Pearson has shown[5] that for closed-shell species 2η is equal to the gap between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital (eq 3). In eq 3, ϵ represents energy. Since in a

$$\eta = (\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}})/2 \tag{3}$$

chemical reaction, as first shown by Fukui,[6] of all the molecular orbitals of the reactants the HOMO and LUMO participate most actively, η is expected to be a index of chemical reactivity. This has been felt by a number of workers.[7,8] In any case, that the thermodynamic stability of a chemical species increases with the increase in the HOMO–LUMO gap is now well recognized.[9-13] Though hardness has been quantified to the extent possible, a complete theoretical proof for the statement of the HSAB principle is still not available. Very recently Parr and co-workers have provided only a partial proof.[14] Earlier Nalewajski[15] tried to justify the essence of the statement qualitatively using a modified form of the definition of electronegativity given by Iczkowski and

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Table I. Data for the Experimental Hardness (η_e), the Hardness (η), the Experimental Electronegativity (χ_e), and the Electronegativity (χ_m) Calculated at the MNDO Level of Some Molecules[a]

molecule	η_e[b]	η[c]	η_e/η[d]	χ_e[b]	χ_m	χ_e/χ_m[e]
H_2	8.7	10.26	0.85	6.7	5.48	1.22
N_2	8.9	7.97	1.12	6.70	6.90	0.97
F_2	6.31[f]	8.62	0.73			
Cl_2	4.6	5.10	0.90	7.0	7.35	0.95
Br_2	4.0	4.59	0.87	6.6	7.07	0.93
I_2	3.4	4.22	0.81	6.0	6.66	0.90
HF	11.0	10.05	1.09	5.0	4.77	1.05
HCl	8.0	6.96	1.15	4.7	6.04	0.78
HI	5.3	5.76	0.92	5.3	5.45	0.97
HCN	8.0	7.64	1.05	5.7	5.78	0.99
HNO_3	5.23	5.77	0.91	5.80	6.57	0.88
CO	7.9	7.29	1.08	6.1	6.13	0.99
CS	5.75	5.52	1.04	5.86	6.03	0.97
CO_2	8.8	6.82	1.29	5.0	5.97	0.84
COS	5.36[f]	5.40	0.99			
CS_2	4.54	4.71	0.96	5.35	5.87	0.91
SO_2	5.64	4.75	1.19	6.7	7.04	0.95
H_2O	9.5	8.82	1.08	3.1	3.37	0.92
H_2S	4.9	6.11	0.80	4.2	4.53	0.93
BF_3	9.70	8.67	1.12	6.2	7.39	0.84
BCl_3	5.64	5.59	1.01	5.97	7.50	0.80
BBr_3	4.85	4.98	0.97	5.67	7.06	0.80
NH_3	8.2	7.76	1.06	2.6	3.42	0.76
SO_3	5.5	4.92	1.12	7.2	8.13	0.89
CH_4	10.3	9.13	1.13	2.5	4.74	0.53
CH_3F	9.4	8.25	1.14	3.2	4.80	0.67
CH_3Cl	7.5	6.62	1.13	3.8	5.62	0.68
CH_3I	4.7	5.96	0.83	4.9	5.16	0.95
CF_3Br	5.45[f]	5.66	0.96			
CF_3I	4.41[f]	4.92	0.90			
CCl_4	5.6	5.97	0.94	5.9	7.27	0.81
CH_3CN	7.5	7.18	1.04	4.7	5.52	0.85
CH_3NO_2	5.34	5.82	0.92	5.79	6.02	0.96
CH_3NH_2	7.2	6.87	1.05	1.9	3.00	0.63
$C(CH_3)_4$	8.3	7.76	1.07	2.2	4.20	0.52
SiH_4	6.8	6.46	1.05	4.8	6.31	0.76
$O(CH_3)_2$	8.0	7.31	1.09	2.0	3.73	0.54
$S(CH_3)_2$	6.0	5.75	1.04	2.7	4.31	0.63
$N(CH_3)_3$	6.3	6.27	1.00	1.5	3.32	0.45
PH_3	6.0	6.50	0.92	4.1	4.84	0.85
$P(CH_3)_3$	5.9	5.59	1.05	2.8	4.26	0.66
PF_3	6.7	7.38	0.91	5.7	5.76	0.99
PCl_3	4.7	4.81	0.98	5.5	7.35	0.75
PBr_3	4.2	4.28	1.02	5.6	7.16	0.78
$POCl_3$	5.00[f]	3.99	1.25			
H_2CO	5.9	5.83	1.01	5.0	5.03	0.99
CH_3CHO	5.7	5.81	0.98	4.5	5.06	0.89
CH_3COCH_3	5.6	5.71	0.98	4.1	5.05	0.81
HCO_2CH_3	6.4	6.20	1.03	4.6	5.17	0.89
$HCONH_2$	6.2	5.89	1.05	4.2	4.69	0.90
$HCON(CH_3)_2$	5.8	5.75	1.01	3.4	4.37	0.78
C_2H_4	6.2	5.75	1.08	4.4	4.43	0.99
CH_2CHCN	5.6	5.32	1.05	5.4	5.29	1.02
$CH_2C(CN)_2$	4.9	4.96	0.99	6.5	5.51	1.18
$NCCHC(CN)_2$	4.7	4.73	0.99	6.8	6.52	1.04
$(NC)_2CC(CN)_2$	4.5	4.46	1.01	7.3	6.17	1.18
benzene	5.3	4.88[g]	1.09			
biphenyl	4.3	4.14[g]	1.04			
naphthalene	4.2	4.12[g]	1.02			
anthracene	3.3	3.60[g]	0.92			
naphthacene	2.90[g]	3.27[g]	0.89			
phenanthrene	3.8	4.00[g]	0.95			
pyrene	3.57[g]	3.57[g]	1.00			
benzo[*c*]phenanthrene	3.82[g]	3.81[g]	1.00			
benz[*a*]anthracene	3.41[g]	3.64[g]	0.94			
chrysene	3.79[g]	3.77[g]	1.01			
triphenylene	3.95[g]	3.97[g]	0.99			
pyridine	5.0	4.85	1.03	4.4	4.34	1.01
C_2H_2	7.0	6.57	1.06	4.4	4.84	0.91
CH_3OH		7.50				
CH_3SH		5.92				
SiH_3F		5.96				
SiH_3I		4.54				
OHF		7.82				
OHCl		6.04				
OHI		5.51				

Table I (Continued)

molecule	η_e[b]	η[c]	η_e/η[d]	χ_e[b]	χ_m	χ_e/χ_m[e]
IF		5.82				
ICl		4.67				
IBr	6.14[h]	4.41	1.39			
HBr	6.83[h]	6.27	1.09			
HNO_2		5.59				
LiH	4.08[h]	4.87	0.84			
LiF	5.87[h]	6.11	0.96			
LiCl	4.75[h]	4.70	1.01			
LiBr		4.04				
LiI	3.20[h]	4.39	0.73			

[a] The meanings of the symbols are same as in the text. The various hardness and electronegativity values are given in electronvolts. [b] From R. G. Pearson (*Inorg. Chem.* **1988**, *27*, 734) or ref 9 unless otherwise specified. [c] This work unless otherwise mentioned. [d] Average = 1.01; standard deviation = 0.11. [e] Average = 0.86; standard deviation = 0.16. [f] From: Datta, D. *J. Phys. Chem.* **1986**, *90*, 4216. [g] From ref 18. [h] Data provided by a reviewer.

Margrave.[16] However, "hard likes hard and soft likes soft" has never been shown in terms of numbers. Herein I examine a number of examples of the exchange reaction 4, for which the

$$\mathrm{AB + CD \rightarrow AC + BD} \tag{4}$$

HSAB principle was devised originally, in terms of "numerical" hardnesses of the four species involved in a particular example.

Results and Discussion

The numerical values of the hardness (η) of various molecules involved in the present study are either experimental data or data calculated by using eq 3. These are given in Table I. For using eq 3 the energies of the HOMO and LUMO were obtained at the MNDO level[17] by using a standard MOPAC program at the optimized geometries of the species concerned. I have found that in the MNDO method, while the experimental values of IP and EA are not reproduced properly, the difference between them is reproduced quite satisfactorily. This inference is drawn on the basis of the observation that for some 75 molecules the average value of η_e/η, the ratio between the experimental hardness (η_e), calculated by eq 1 with the knowledge of experimental IP and EA, and the hardness (η) calculated by the MNDO method is found to be 1.01 with a standard deviation of 0.11; but for some 53 molecules the average value of the ratio χ_e/χ_m [χ_e = experimental χ calculated by using experimental values of IP and EA and eq 2; $\chi_m = (\epsilon_{\mathrm{HOMO}} + \epsilon_{\mathrm{LUMO}})/2$ where ϵ's are evaluated by the MNDO method] is found to be 0.86 with a standard deviation of 0.16 (see Table I). It should be mentioned here that earlier Zhou and Navangul[18] found that for some 11 aromatic hydrocarbons the MNDO method reproduces the experimental hardness data quite well (see Table I).

An example of reaction 4 is eq 5 where Li^+ is a hard (h) acid, F^- a hard base, Cs^+ a soft (s) acid, and I^- a soft base. The exothermic nature of the reaction shows that h–h and s–s inter-

$$\begin{array}{ccccccc} \mathrm{Li^+I^-} & + & \mathrm{Cs^+F^-} & = & \mathrm{Li^+F^-} & + & \mathrm{Cs^+I^-} \\ \mathrm{h\ \ s} & & \mathrm{s\ \ h} & & \mathrm{h\ \ h} & & \mathrm{s\ \ s} \end{array} \tag{5}$$
$$\Delta H^\circ = -12.1 \text{ kcal/mol}$$

actions are preferred over h–s interactions. It is interesting to note that, if Pauling's bond energy equation[19] is applied to eq 5, despite its well-known success in a variety of situations, a positive value of ΔH° is predicted.[20] This is what is now known as "Pearson–Pauling paradox".[21] It is heartening that very recently this so-called paradox has been resolved to some extent by developing a two-dimensional scale for Pauling's electronegativity.[22]

As evident from reaction 5, to apply the HSAB principle, one has to consider the heterolytic bond dissociations. When the principle says that perfect matching of hardness between the acid A^+ and the base B^- imparts an extra amount of stability to the A–B bond, it actually refers to the heterolytic dissociation of AB into A^+ and B^-. Thus it is necessary to identify the bases and the acids properly in a reaction of type 4 in order to apply the HSAB principle. Usually, the concept of electronegativity can be used for this purpose; for example, the more electronegative part of AB or CD is the anionic base. In case of comparable electronegativities of the two parts of AB or CD, depending on the reaction, any of them can act as the cationic acid or the anionic base. This aspect has been discussed by Pearson in some detail.[2,23]

The following examples of reaction 4 are now examined in terms of the numerical values of the hardness (given in electronvolts under the A–B pairs) of the various species involved. The examples are so chosen that the experimental hardnesses of at least three of the four species involved in a particular example are known. The numerals followed by an asterisk are the MNDO values (Table I).

$$\begin{array}{ccccccc} \mathrm{H^+Cl^-} & + & \mathrm{Li^+H^-} & = & \mathrm{Li^+Cl^-} & + & \mathrm{H^+H^-} \\ 8.0 & & 4.08 & & 4.75 & & 8.7 \end{array} \tag{i}$$
$$\Delta H^\circ = -56.1 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{H^+Br^-} & + & \mathrm{I^+OH^-} & = & \mathrm{H^+OH^-} & + & \mathrm{I^+Br^-} \\ 6.83 & & 5.51^* & & 9.5 & & 6.14 \end{array} \tag{ii}$$
$$\Delta H^\circ = -26.4 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{Li^+H^-} & + & \mathrm{H^+I^-} & = & \mathrm{Li^+I^-} & + & \mathrm{H^+H^-} \\ 4.08 & & 5.3 & & 3.20 & & 8.7 \end{array} \tag{iii}$$
$$\Delta H^\circ = -57.5 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{HO^+F^-} & + & \mathrm{Li^+H^-} & = & \mathrm{Li^+F^-} & + & \mathrm{HO^+H^-} \\ 7.82^* & & 4.08 & & 5.87 & & 9.5 \end{array} \tag{iv}$$
$$\Delta H^\circ = -144.1 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{Li^+F^-} & + & \mathrm{H^+Br^-} & = & \mathrm{Li^+Br^-} & + & \mathrm{H^+F^-} \\ 5.87 & & 6.83 & & 4.04^* & & 11.0 \end{array} \tag{v}$$
$$\Delta H^\circ = -10.8 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{SiH_3{}^+H^-} & + & \mathrm{H^+I^-} & = & \mathrm{SiH_3{}^+I^-} & + & \mathrm{H^+H^-} \\ 6.8 & & 5.3 & & 4.54^* & & 8.7 \end{array} \tag{vi}$$
$$\Delta H^\circ = -14.4 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{SiH_3{}^+I^-} & + & \mathrm{Li^+H^-} & = & \mathrm{Li^+I^-} & + & \mathrm{SiH_3{}^+H^-} \\ 4.54^* & & 4.08 & & 3.2 & & 6.8 \end{array} \tag{vii}$$
$$\Delta H^\circ = -43.9 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{CH_3{}^+F^-} & + & \mathrm{H^+I^-} & = & \mathrm{CH_3{}^+I^-} & + & \mathrm{H^+F^-} \\ 9.4 & & 5.3 & & 4.7 & & 11.0 \end{array} \tag{viii}$$
$$\Delta H^\circ = -12.3 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{CH_3{}^+F^-} & + & \mathrm{CH_3S^-H^+} & = & \mathrm{CH_3S^-CH_3{}^+} & + & \mathrm{H^+F^-} \\ 9.4 & & 5.92^* & & 6.0 & & 11.0 \end{array} \tag{ix}$$
$$\Delta H^\circ = -12.9 \text{ kcal/mol}$$

$$\begin{array}{ccccccc} \mathrm{CH_3{}^+OH^-} & + & \mathrm{H^+I^-} & = & \mathrm{CH_3{}^+I^-} & + & \mathrm{HO^-H^+} \\ 7.50^* & & 5.3 & & 4.7 & & 9.5 \end{array} \tag{x}$$
$$\Delta H^\circ = -12.6 \text{ kcal/mol}$$

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Table II. Average Values ($\langle\eta\rangle$) of Hardness on the LHS (Left-Hand Side) and RHS (Right-Hand Side) of Examples i–xiii[a]

example	$\langle\eta\rangle_{LHS}$	$\langle\eta\rangle_{RHS}$	sign of ΔH°
i	6.04	6.72	−
ii	6.17	7.82	−
iii	4.69	5.95	−
iv	5.95	7.68	−
v	6.35	7.52	−
vi	6.05	6.62	−
vii	4.31	5.00	−
viii	7.35	7.85	−
ix	7.66	8.50	−
x	6.40	7.10	−
xi[b]	7.54	7.28	−
xii[b]	7.33	8.90	+
xiii[c]	5.72	5.11	−

[a] The η values are given in electronvolts. For identifying the reactions denoted by small Roman numerals, see text. [b] Exception; see text. [c] See text.

In the above examples where the reactions proceed thermochemically[24–26] from left to right, one of the products becomes the hardest of the four molecules involved in a particular case, as judged by the hardness values. Elsewhere it has been shown[27] that for reactions of type 4, $T\Delta S^\circ$ at 298 K lies within ±2 kcal/mol and we have also indicated[27] that, if $\Delta H^\circ \le -10$ kcal/mol, then thermochemically feasible reactions are also thermodynamically feasible. Thus it can be stated that an exchange reaction evolves in a direction so as to generate the hardest possible species. This tendency can be understood in terms of chemical reactivity. As mentioned earlier, the harder a species the better is its thermodynamic stability. Since greater thermodynamic stability usually indicates less reactivity, it follows that the higher the value of hardness the lower is the reactivity of the species concerned. As a general rule, any reaction always tries to yield species which is (are) thermodynamically as stable as possible so that the reactivity of the product(s) is (are) kept at the minimum possible level (otherwise the back-reaction is favored). This notion is in complete agreement with the present observation.

Another feature of this study is that in the above examples the average value of hardness ($\langle\eta\rangle$) on the right-hand side (RHS) is greater than that on the left-hand side (LHS) (see Table II). This shows that the exchange reactions lead to an increase in the average hardness for the products.[28,29] This purely empirical observation is reminiscent of the "maximum hardness principle" of Pearson which states that "there seems to be a general rule of nature that molecules arrange themselves so as to be as hard as possible".[2] Very recently, this principle has been proved theoretically by Parr and co-workers by using statistical mechanics under some constraints.[30]

I have examined some 25 other reactions also (Table S, supplementary material) in the present context. The same conclusions are drawn in most of the cases. However I have found that some 5 reactions out of the total 35 reactions studied behave in a manner opposite to my expectations; i.e. even though $\langle\eta\rangle_{RHS} > \langle\eta\rangle_{LHS}$ (see Table II), the reaction in these cases does not proceed from left to right, or the reaction does not tend to generate the hardest possible species. These, I believe, are exceptions. Equations xi and xii are two selected examples of such cases. In example xii I have used the calculated value of hardness for SiH_3F.

$$\begin{array}{cccc} Li^+H^- \;+ & H^+F^- \;= & Li^+F^- \;+ & H^+H^- \\ 4.08 & 11.0 & 5.87 & 8.7 \end{array} \qquad \text{(xi)}$$

$$\Delta H^\circ = -49.0 \text{ kcal/mol}$$

$$\begin{array}{cccc} H^+H^- \;+ & SiH_3{}^+F^- \;= & H^+F^- \;+ & SiH_3{}^+H^- \\ 8.7 & 5.96^* & 11.0 & 6.8 \end{array} \qquad \text{(xii)}$$

$$\Delta H^\circ = 26.2 \text{ kcal/mol}$$

Usually, $\langle\eta\rangle$ for the side where the hardest possible species is generated has been found to be greater than the $\langle\eta\rangle$ for the other side. Of the 35 reactions studied, I have found one exception to this observation

$$\begin{array}{cccc} H^+I^- \;+ & I^+Br^- \;= & I^+I^- \;+ & H^+Br^- \\ 5.3 & 6.14 & 3.4 & 6.83 \end{array} \qquad \text{(xiii)}$$

$$\Delta H^\circ = -9.6 \text{ kcal/mol}$$

Evidently example xiii proceeds in a direction so as to produce HBr, which is the hardest of the four molecules involved in the reaction, but $\langle\eta\rangle_{RHS}$ (5.11 eV) is less than $\langle\eta\rangle_{LHS}$ (5.72 eV).

Conclusions

In earlier work it has been demonstrated, with the help of a new parameter "γ" derived from the heterolytic dissociative version of Pauling's bond energy equation, that an exchange reaction tries to minimize the difference in the polarity of the two new bonds formed in the two products.[27,31] Here I have discussed Pearson's HSAB principle for the first time in a sort of quantitative manner. The important conclusions of the present work are as follows: (1) The production of the hardest possible species is the driving force for an exchange reaction. (2) In an exchange reaction the average value of the hardnesses of the products becomes greater than that of the reactants.

The implications of the above conclusions have been illustrated in terms of the chemical reactivity of the various species involved in an exchange reaction. These two conclusions are based on studies on some 35 examples of which only 5 cases were found to be the exceptions. The reasons for such exceptional behaviors are not understood now. Out of the 35 reactions studied, in only one case did my two conclusions not agree with each other.

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Supplementary Material Available: Table S, giving the experimental and calculated (at the MNDO level) hardness values of the various species and the ΔH° values of some exchange reactions (5 pages). Ordering information is given on any current masthead page.

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(24) The ΔH° values of all the reactions have been calculated from the bond dissociation energy data. Sources of data: diatomic molecules, ref 25; HOF, ref 23; other polyatomic molecules, ref 26.

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(28) It should be noted here that I do not imply that the hardness of a system containing two components is the arithmetic mean of the hardnesses of the respective components. In this context it is mentioned that Parr and co-workers[29] have dealt with the chemical potential of the mixture of two species in the gas phase. For the relation between the chemical potential and hardness, the reader is referred to the work of Pearson and Parr.[4]

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