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Heats of Reaction from Self-Consistent Field Energies of Closed-Shell Molecules

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Abstract: Self-consistent field energies and wave functions have been computed for 26 closed-shell molecules including many medium-sized nonlinear organic molecules. A basic set of gaussian functions comparable to a best-atom double-ζ set of Slater orbitals has been used. Standard heats of reaction have been computed for a large number of hydrogenation and related reactions under the assumption that the sum of E_{corr} (the electronic correlation energy) and $E_{\mathrm{HF}} - E_{\mathrm{DZ}}$ (the difference of the electronic energy in the Hartree–Fock and our double-ζ basis) does not change in a reaction having closed-shell reactants and products. For 16 hydrogen-transfer reactions, the mean value of the theoretical minus the experimental heat is -0.6 kcal/mole, and the root mean square value of this difference is 6.5 kcal/mole. For molecules whose ground state is well represented by a single valence-bond structure, empirical heats of reaction estimated from bond energies agree as well with experiment as the theoretical values. For molecules expected to resonate between more than one valence-bond structure and for cyclic molecules expected to exhibit strain, the theoretical heats of reaction are in much better agreement with experiment. Although the change of correlation energy is apparently small in the reactions studied, an attempt is made to examine the structure of correlation energy change. Atomic orbital populations and pair correlation energies are employed to estimate the change of intraatomic correlation energy in these chemical reactions. After incorporation of this estimate of the intraatomic correlation energy change into the theoretical heats of reaction, the difference between the theoretical and experimental heats of complete hydrogenation is attributed mainly to changes of interatomic correlation energy and in lesser part to the decreasing adequacy of our double-ζ basis with increasing unsaturation. The difference is found to decrease rapidly with increasing length of the bond to which hydrogen is added. An empirical correction which we suggest relates interatomic correlation energy to bond length is given for bonded first-row atoms. This correction is combined with calculated values for the intraatomic correlation energy to give improved estimates of reaction heats.

I. Introduction

Chemical equilibrium is of central interest to chemists. Thermodynamics[1] provides the means to predict the position of chemical equilibrium from thermal measurements alone. For a gas-phase reaction

$$\Delta F^\circ = -RT \ln K_a \tag{1}$$

Here K_a is the equilibrium constant in terms of activities and equals K_p for ideal gases. The standard change of free energy, ΔF°, is given by

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2}$$

The standard enthalpy change, ΔH°, is the heat absorbed when the reaction is carried out at constant temperature and pressure. The third law of thermodynamics permits measurements of heat capacity for the reactants and products to provide values of the standard entropy change, ΔS°.

Chemists often wish to predict chemical equilibria in systems for which experimental thermal information is not available. Quantum statistical mechanics makes it possible to compute ΔS° if moments of inertia and vibrational frequencies are available for reactant and product gas molecules. This structural and vibrational information is often obtained by the analysis of infrared and Raman spectra. The change of enthalpy, ΔH°,

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(1) F. D. Rossini, "Chemical Thermodynamics," John Wiley & Sons, Inc., New York, N. Y., 1950.

is related to the change of energy, $\Delta E°$, by

$$\Delta H° = \Delta E° + \Delta(PV) \quad (3)$$

Generally speaking $\Delta E°$ has only been available from experimental sources, spectroscopic or thermal measurements. The recent advances in computing near-Hartree–Fock wave functions for molecules give hope that $\Delta E°$ may soon be computable from theory.[2] For reactions of common stable molecules, theoretical estimates of $\Delta E°$ must be accurate to ± 10 kcal/mole to begin to be of value to chemists. This reflects the fact that a large amount of thermal information is available, and various means of correlating these data to molecular structure make it possible to give an empirical basis for predicting enthalpy changes to that accuracy for most common molecules.[3]

Great progress has been made in recent years toward the development of convenient and inexpensive computer programs for computing SCF wave functions and energies for molecules of interest to chemists. This is exhibited in a compendium of molecular calculations assembled by Krauss.[4] Programs employing a gaussian basis set[5] have greatly reduced the computation times for electron replusion integrals. Moreover, these *ab initio* programs are applicable to nonlinear molecules. The computation of highly accurate SCF wave functions and energies for closed-shell molecules is now mainly limited by the computational resources available to chemists. The long-term outlook is that this limitation by cost will disappear with future developments in programming and computer technology. The main remaining barrier to computing accurate theoretical values of $\Delta E°$, and thus heats of reaction, is the problem of estimating the change in correlation energy.

In this work we have employed a consistent set of high quality SCF wave functions in a gaussian basis to compute heats of reaction on the assumption that correlation energy does not change at all when closed-shell reactants form closed-shell products with resulting conservation of the number of electron pairs. We then attempt to examine the structure of electronic correlation energy changes by partitioning it into intraatomic and interatomic parts. Our goal is to provide a useful method to predict heats of chemical reactions. The method should be firmly based on theory so that it may be trusted in predictions for strange and unusual molecules, as well as for the well known.

II. Basic Theory

Consider a gas-phase chemical reaction in which

$$a\mathrm{A} + b\mathrm{B} = c\mathrm{C} + d\mathrm{D} \quad (4)$$

For this reaction in which a moles of molecule A combine with b moles of B to form c moles of C and d moles of D, we define $\Delta n = (c + d) - (a + b)$. The standard heat of reaction[1] ($\Delta H_T°$) at temperature T is given by

$$\Delta H_T° = \Delta E_T° + RT\Delta n \quad (5)$$

where $\Delta E_T° = cE_T°(\mathrm{C}) + dE_T°(\mathrm{D}) - aE_T°(\mathrm{A}) - bE_T°(\mathrm{B})$. Here the total energy of a mole of A in its standard state is denoted by $E_T°(\mathrm{A})$. We assume that the total energy may be accurately written as a sum of electronic, vibrational, rotational, and translational contributions.

$$E_T° = E_{\mathrm{el}} + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}} \quad (6)$$

In addition we write the electronic part as a sum of the Hartree–Fock energy, correlation energy, and relativistic energy.

$$E_{\mathrm{el}} = E_{\mathrm{HF}} + E_{\mathrm{corr}} + E_{\mathrm{rel}} \quad (7)$$

The possibility of dividing the correlation energy of a molecule into intraatomic and interatomic parts is considered in a later section (V) of this paper.

The contributions of vibrations, rotation, and translation to the total energy may be accurately estimated.[1] At temperatures near room temperature, we take $E_{\mathrm{vib}} = {}^1/_2 h\Sigma\nu_i$. Here the sum is over all normal vibrations with observed fundamental frequencies ν_i. For E_{rot} we assume the classical value of ${}^3/_2RT$ for nonlinear molecules, RT for linear molecules, and 0 for atoms. For E_{trans} we adopt the classical value of ${}^3/_2RT$. The electronic energy is more difficult to estimate. The Hartree–Fock energy of a molecule is usually not available (at least not at modest cost) for nonlinear molecules of chemically interesting size, *i.e.*, containing three or more first-row atoms. We have employed modifications of the polyatom system of programs which compute SCF wave functions for molecules in a gaussian basis set and are capable of yielding fairly good single determinant wave functions for larger molecules at modest cost. We refer to our basis set as a double-zeta (DZ) set of gaussians. The molecular electronic energy computed in this basis is denoted by E_{DZ}. It includes the nuclear repulsion energy. We thus write

$$E_{\mathrm{HF}} = E_{\mathrm{DZ}} + (E_{\mathrm{HF}} - E_{\mathrm{DZ}}) \quad (8)$$

Our expression for $\Delta E_T°$ then becomes

$$\Delta E° = \Delta(E_{\mathrm{DZ}} + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}}) + \Delta(E_{\mathrm{corr}}) + \Delta(E_{\mathrm{HF}} - E_{\mathrm{DZ}}) + \Delta(E_{\mathrm{rel}}) \quad (9)$$

The first term on the right of eq 9 contains those contributions to $\Delta E°$ for which accurate values are available from experiment or our computations. Our ability to compute heats of reaction is limited by our knowledge of the last three terms. Throughout this study we assume that $\Delta E_{\mathrm{rel}} = 0$, that the relativistic energy of an atom is independent of its state of chemical binding. We base this assumption on the work of Clementi and McLean.[6] Since the number of atoms is conserved in chemical reactions, we expect no contribution to heats of reaction from changes of relativistic energy.

Previous studies have shown that where Hartree–Fock energies are available, fairly accurate heats of reaction are computed if one assumes that $\Delta E_{\mathrm{corr}} = 0$.[2] This

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(2) L. C. Snyder, *J. Chem. Phys.*, 46, 3602 (1967).

(3) L. Pauling "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(4) M. Krauss, "Compendium of ab initio Calculations of Molecular Energies and Properties," Technical Note 438, National Bureau of Standards, Washington, D. C.

(5) I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, S. Seung, B. T. Sutcliffe, and M. P. Barnett, "The Polyatom System," Technical Notes 36 and 40, Cooperative Computing Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.; another set of programs employing gaussians has been recently documented by A. Veillard, "IBMOL: Version 4," Large Scale Scientific Computations Dept., IBM Research Laboratory, San Jose, Calif.

(6) E. Clementi and A. D. McLean, *Phys. Rev.*, 133, A419 (1964).

was found for reactions having closed-shell reactants and products: reactions with constant number of electrons paired in orbitals. The computation of heats of reaction by employing only the readily available first term of eq 9 should reveal in comparison with experimental heats the constancy of $(\Delta E_{\mathrm{corr}} + \Delta(E_{\mathrm{HF}} - E_{\mathrm{DZ}}))$. Where Hartree–Fock energies are available, it should be possible to independently check the magnitude of $\Delta(E_{\mathrm{HF}} - E_{\mathrm{DZ}})$ in several reactions.

III. Basic Data

Limited basis set Hartree–Fock–Roothaan self-consistent field calculations[7] were carried out on the ground-state electronic configurations of 26 linear and nonlinear molecules, ranging from 2 to 24 electrons, in their observed ground-state geometries. For one molecule (diaziridine, CH_4N_2), where the geometric parameters are not known, estimated bond distances and angles were used.

The basis set for each first-row atom (carbon to fluorine) was constructed out of ten s-type and five p-type (10^s5^p) gaussian primitive orbitals contracted to four s-type and two p-type (each of x, y, z) basis functions.[8] The actual exponents and coefficients, and the details of the method whereby the contracted functions were obtained from the atomic SCF calculations of Whitten[9] and Huzinaga,[10] have been described previously.[11] Similarly, four s-type gaussian primitive orbitals were contracted to two s-type basis functions to form the basis set for the hydrogen atom.[11] In the notation of Moskowitz and coworkers[8,12] this basis set is designated [42/2], the brackets denoting a contracted basis set.

In analogy to a Slater orbital basis,[13] the [42/2] basis set used here is called a double-zeta (DZ) basis for two reasons. First, it allots two basis functions to each atomic orbital, and second, test calculations on CO[11] show the gaussian DZ basis to be energetically equivalent to what is obtained in a DZ Slater orbital basis. The DZ basis is a natural step in progressing from a minimal to a Hartree–Fock calculation; it is evident from the careful work of Huo[13] that the largest single portion of radial polarization effects is obtained in doubling the atomic orbital basis from minimal to DZ. Matcha[14] has further concluded that a DZ + P (double zeta + optimized angular polarization functions) basis set essentially parallels the Hartree–Fock behavior in molecular calculations.

A final aspect of interest about the gaussian orbital DZ basis is its effectiveness relative to a completely uncontracted basis. Neumann and Moskowitz[12] have found for H_2O, H_2CO, and CO that the [42/2] basis is essentially equivalent to a completely uncontracted (95/3) basis set; very little is lost in the contraction. The results of Robin, *et al.*,[15] and Schulman[8] support this conclusion. It is felt that this very favorable state of affairs is obtained because the ten s-type gaussian primitive orbitals used to form the four s-type contracted basis functions in the DZ basis were optimized in an atomic SCF calculation[10] as grouped or contracted functions directly, although with different p-type functions than those used to form the p-type contracted basis set. This latter point is not crucial, as has been pointed out by Hornback.[16] An example of poor contraction in a basis set is seen in the work of Clementi[17] on C_2H_6 and NH_3 where a larger number of primitive orbitals were used but with energetically inferior results to that reported in Table I under E_{DZ}. Hopefully, the better ground-state wave function correlates with the better total energy (although one-electron properties are known not to converge uniformly with energy),[13] and from that point of view the best total energy for a given number of primitives is desirable. Although not used here directly, for the sake of completeness we present the computed atomic energies using the DZ basis set. They are (in atomic units): H (^2S) −0.4976, C (^3P) −37.6812, N (^4S) −54.3897, O (^3P) −74.7931, F (^2P) −99.3863.

Our calculations of molecular wave functions have been made on an IBM-7090 computer and on the GE-645, which is of comparable speed. For each molecule the major computation consisted of constructing a list of integrals, evaluating the integrals, and making ten SCF iterations. For the molecules HF, NH_3, H_2O_2, C_2H_2, C_3H_6, and diazomethane, the required total computation times were respectively 1, 6, 16, 8, 106, and 43 min. We consider these times and the corresponding cost to be modest in view of the rather good basis set employed.

The ground-state geometries for the molecules studied are available in the published literature.[17–27] No attempt was made to differentiate r_0 from r_e values in the bond distances. It is expected that the flexibility of the basis set can absorb the few hundreths of an ångström difference in bond lengths involved to the point where any conclusions drawn based on the computed E_{DZ} are insensitive to the effect of these differences.

In the first three columns of Table I we have tabulated the molecules, their computed DZ energies (E_{DZ}), and the virial theorem test ($-V/2T$) for each molecular wave function. The virial is seen to be uniformly good

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Table I. Basic Data[a]

Molecule	E_{DZ}	$-V/2T$	E_{vib}	E_T	$E_{corr-intra}$	$\Delta H_f°(298°)$
H_2[b]	−1.1266	0.99935	0.0099[c]	−1.1144	−0.0409	0.0[d]
CH_4[e]	−40.1822	1.00013	0.0432[c]	−40.1362	−0.2952	−17.895[f]
NH_3[e]	−56.1714	1.00012	0.0327[c]	−56.1359	−0.3354	−11.04[f]
H_2O[g]	−76.0037	0.99942	0.0206[c]	−75.9803	−0.3645	−57.7979[f]
HF[b]	−100.0149	1.00003	0.0093[c]	−100.0033	−0.3728	−64.8[f]
C_2H_6[h]	−79.1981	1.00029	0.0721[e]	−79.1232	−0.5288	−20.236[i]
N_2H_4[j]	−111.1261	0.99996	0.0435[k]	−111.0798	−0.5994	+22.75[f]
H_2O_2[l]	−150.7373	0.99950	0.0198[m]	−150.7152	−0.6472	−32.53[f]
F_2[b]	−198.6932	1.00038	0.0020[c]	−198.6889	−0.6492	0.0[d]
C_2H_4[e]	−78.0052	1.00039	0.0491[c]	−77.9533	−0.4772	+12.496[f]
CH_2O[g]	−113.8209	1.00002	0.0257[e]	−113.7924	−0.5236	−27.7[f]
C_2H_2[e]	−76.7919	1.00058	0.0258[e]	−76.7638	−0.4296	+54.19[f]
HCN[e]	−92.8289	1.00072	0.0155[c]	−92.8111	−0.4477	+31.2[f]
N_2[b]	−108.8695	1.00061	0.0054[c]	−108.8618	−0.4596	0.0[d]
CO[b]	−112.6762	1.00003	0.0049[c]	−112.6690	−0.4670	−26.4165[f]
$HCONH_2$[n]	−168.8684	0.99975	0.0466[o]	−168.8190	−0.7980	[−50][p]
HCOOH[e]	−188.6877	0.99959	0.0326[e]	−188.6523	−0.8235	−86.67[i]
HCOF[e]	−212.6841	0.99979	0.0206[e]	−212.6607	−0.8319	[−90][f]
C_3H_6[q]	−177.0099	0.99976	0.0779[r]	−116.9292	−0.7188	+12.74[i]
C_2H_5N[s]	−132.9726	0.99937	0.0678[t]	−132.9020	−0.7466	+30.12[u]
C_2H_4O[v]	−152.8012	0.99926	0.0559[e]	−152.7425	−0.7668	−12.19[i]
CH_4N_2[w]	−148.8430	1.00037	(0.0577)[x]	−148.7825	−0.7815	?
C_3H_4[y]	−115.7655	0.99973	0.0545[z]	−115.7082	−0.6656	+66.6[aa]
CH_2N_2[bb]	−147.7287	0.99960	0.0321[cc]	−147.6938	−0.7014	+[101][dd]
CO_2[e]	−187.5377	0.99999	0.0116[e]	−187.5328	−0.7611	−94.054[i]
CH_2N_2[ee]	−147.7702	1.00006	0.0306[e]	−147.7368	−0.7071	[+71][dd]

[a] All energy quantities are in atomic units except the experimental heats of formation which are in kilocalories/mole. [b] See ref 20. [c] See ref 2. [d] Zero by definition. [e] See ref 18. [f] See ref 31. [g] See ref 12. [h] Staggered conformation; see ref 21. [i] See ref 32. [j] Hydrazine: geometry quoted in ref 23. [k] J. R. Durig, S. F. Bush, and E. E. Mercer, *J. Chem. Phys.*, **44**, 4238 (1966). [l] See ref 22. [m] R. L. Redington, W. B. Olson, and P. C. Cross, *J. Chem. Phys.*, **36**, 1311 (1962). [n] See ref 19. [o] See ref 29. [p] Estimated for the gas phase from data in ref 31 for solution and liquid phase. [q] Cyclopropane; see ref 26. [r] A. W. Baker and R. C. Lord, *J. Chem. Phys.*, **23**, 1636 (1955). [s] Ethylenimine; see ref 27. [t] See ref 30. [u] See ref 35. [v] Ethylene oxide; see ref 18. [w] Diaziridine: R(N–N) = 1.451 Å, R(C–N) = 1.485 Å, R(N–H) = 1.014 Å, R(C–H) = 1.089 Å, ∠HCH = 116°, ∠NNH = 150°, ∠CNH = 112 and 248° (staggered conformation). [x] Estimated from previous three entries. [y] Cyclopropene. [z] D. F. Eggers, J. W. Schultz, K. B. Wiberg, E. L. Wagner, L. M. Jackman, and R. L. Erskine, *J. Chem. Phys.*, **47**, 946 (1967). [aa] See ref 33. [bb] Diazirine; see ref 25. [cc] R. Ettinger, *J. Chem. Phys.*, **40**, 1693 (1964). [dd] See ref 36. [ee] Diazomethane; see ref 18.

to a minimum of three places to the right of the decimal which is one order of magnitude greater than that obtained using a minimal STO basis[28] but, on the average, one order of magnitude worse than that obtained in a DZ + P basis.[12,14] The rather uniform virial test obtained using a common basis set is taken as evidence supporting the contention that uncertainties in geometry are not factors to be considered in interpreting the computed heats of formation presented here.

As detailed earlier, the vibrational energy of a molecule (E_{vib}) is taken as one-half the sum of its fundamental vibrational frequencies.[2,18,20,29,30] In most cases, for polyatomics, the fundamental frequencies are obtained by fitting the observed infrared and Raman spectra in a normal coordinate analysis, using an assumed force field. Thus not all the normal coordinate frequencies used in computing the E_{vib} tabulated in the fourth column of Table I were observed directly. The effect of this small uncertainty in E_{vib} is expected to have a negligible effect on the computed heats of formation.

An estimate of the intraatomic correlation energy ($E_{corr-intra}$) is incorporated in Table I. The method used is discussed in section V, but the estimated values are listed here for compactness.

The experimentally observed heats of formation[31-36] are tabulated in the last column of Table I. The values in brackets are to be considered less well known. The heat of formation of formamide (−61.6 kcal/mole) was available only for the pure liquid.[32] We estimated the heat of vaporization to be +11.6 kcal/mole to obtain the gas-phase result. The heat of formation of formyl fluoride given in the JANAF Tables[31] was not directly measured but was estimated from the values for formaldehyde and fluoroformyl fluoride. Heats of formation of diazomethane and diazirine are derived from appearance potential measurements in mass spectrometry.[36] The uncertainty in the values reflects a lack of knowledge of the state of the products after electron

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impact.[36] For diazomethane, based on these data, the estimated heat of formation ranges from +31 to +104 kcal/mole. For diazirine the range is +61 to +134 kcal/mole.

IV. Quantitative Results

Earlier studies have shown that theoretical heats of reaction computed for reactions having closed-shell reactants and products are in rather good agreement with experiment when the Hartree–Fock energy is employed, and it is assumed that the correlation energy is unchanged ($\Delta E_{\text{corr}} = 0$).[2] It would indeed be fortunate if heats of reaction could equally well be predicted using our less expensive E_{DZ}. This would require that $(\Delta E_{\text{corr}} + \Delta(E_{\text{HF}} - E_{\text{DZ}})) = 0$. We have tested this possibility by assuming the above condition and employing eq 9 to compute ΔE_0 and thus $\Delta H_{\text{F}}°$ for a large set of gas-phase reactions. These results are set forth in Tables II, III, and V. Table II contains reactions in which a single hydrogen molecule is added to the reactant. Table III contains complete hydrogenations of the reactants to CH_4, NH_3, H_2O, and HF. In each table isoelectronic and chemically similar reactants are grouped together for convenient comparison. There are many ways to consider this information; one of these is given in Table V. The reactants in Table V are obtained by subtracting the first reaction in Table II from each subsequent reaction: we call the resulting processes hydrogen-transfer reactions. In all tables, bracketed experimental heats of reaction are believed to be of lower accuracy. Other heats should be accurate to at least 1 kcal/mole.

Table II. Hydrogenations

	$\Delta H°_{298}$, kcal		
Reaction	Theory	Experiment	Th − exp
$H_2 + C_2H_6 = 2CH_4$	−22.4	−15.5	−6.9
$H_2 + N_2H_4 = 2NH_3$	−48.7	−44.8	−3.9
$H_2 + H_2O_2 = 2H_2O$	−78.7	−83.2	+4.5
$H_2 + F_2 = 2HF$	−127.6	−129.6	+2.0
$H_2 + C_2H_4 = C_2H_6$	−35.4	−32.7	−2.7
$H_2 + CH_2O = 0.5C_2H_4 + H_2O$	−29.9	−24.0	−5.9
$H_2 + C_2H_2 = C_2H_4$	−47.7	−41.7	−6.0
$H_2 + HCN = 0.5C_2H_4 + 0.5N_2H_4$	+3.2	+7.4	−4.2
$H_2 + 0.5N_2 = 0.5N_2H_4$	+2.9	+11.3	−8.4
$H_2 + CO = H_2CO$	−6.2	−1.3	−4.9
$H_2 + HCONH_2 = H_2CO + NH_3$	+3.0	[+11.4]	[−8.4]
$H_2 + HCOOH = H_2CO + H_2O$	−3.9	+1.2	−5.1
$H_2 + HCOF = H_2CO + HF$	−13.2	[−2.4]	[−10.8]
$H_2 + C_3H_6 = CH_4 + C_2H_4$	−28.8	−18.2	−10.6
$H_2 + C_2H_5N = NH_3 + C_2H_4$	−45.6	−28.7	−16.9
$H_2 + C_2H_4O = H_2O + C_2H_4$	−48.1	−33.1	−15.0
$H_2 + CH_4N_2 = 0.5C_2H_4 + N_2H_4$	−100.2		
$H_2 + C_3H_4 = CH_4 + C_2H_4$	−48.6	−30.3	−18.3
$H_2 + CH_2N_2 = CH_4 + N_2$	−119.6	[−118.8]	[−0.8]
$H_2 + CO_2 = H_2O + CO$	−7.1	+9.9	−17.0
$H_2 + CH_2N_2 = CH_4 + N_2$	−92.2	[−88.8]	[−3.4]

Table III. Complete Hydrogenations

	$\Delta H°_{298}$, kcal		
Reaction	Theory	Expt	Th − exp
$H_2 + C_2H_6 = 2CH_4$	−22.4	−15.5	−6.9
$H_2 + N_2H_4 = 2NH_3$	−48.7	−44.8	−3.9
$H_2 + HOOH = 2H_2O$	−78.7	−83.2	+4.5
$H_2 + F_2 = 2HF$	−127.6	−129.6	+2.0
$2H_2 + C_2H_4 = 2CH_4$	−57.8	−48.2	−9.6
$2H_2 + CH_2O = CH_4 + H_2O$	−58.8	−48.0	−10.8
$3H_3 + C_2H_2 = 2CH_4$	−105.5	−89.9	−15.6
$3H_2 + HCN = CH_4 + NH_3$	−73.8	−60.0	−13.8
$3H_2 + N_2 = 2NH_3$	−42.9	−22.2	−20.7
$3H_2 + CO = CH_4 + H_2O$	−65.0	−49.3	−15.7
$3H_2 + HCONH_2 = CH_4 + H_2O + NH_3$	−55.8	[−36.6]	[−19.2]
$3H_2 + HCOOH = CH_4 + 2H_2O$	−62.7	−46.8	−15.9
$3H_2 + HCOF = CH_4 + H_2O + HF$	−72.0	[−50.4]	[−21.6]
$3H_2 + C_3H_6 = 3CH_4$	−86.6	−66.4	−20.2
$3H_2 + C_2H_5N = 2CH_4 + NH_3$	−103.4	−76.9	−26.5
$3H_2 + C_2H_4O = 2CH_4 + H_2O$	−105.9	−81.3	−24.6
$3H_2 + CH_4N_2 = CH_4 + 2NH_3$	−177.8		
$4H_2 + C_3H_4 = 3CH_4$	−154.1	−120.2	−33.9
$4H_2 + CH_2N_2 = CH_4 + 2NH_3$	−162.5	[−141.0]	[−21.5]
$4H_2 + CO_2 = CH_4 + 2H_2O$	−72.1	−39.4	−32.7
$4H_2 + CH_2N_2 = CH_4 + 2NH_3$	−135.1	[−111.0]	[−24.1]

We consider the single hydrogenations in Table II to represent a kind of unit of chemical change. However, the chemical changes occurring are rather drastic: bonds are broken, linear molecules become nonlinear, and rings are broken. Generally, the theoretical and experimental heats of hydrogenation in Table II are in good agreement. For the 16 reactions whose experimental heats are accurately known, the mean of the theoretical minus the experimental values of $\Delta H_{\text{f}}°(298°)$ is −7.5 kcal/mole; the root mean square difference is 9.7 kcal/mole.

As we have noted, the differences of theoretical and experimental heats of reaction ($\Delta H_{\text{th}} - \Delta H_{\text{exp}}$) are attributable both to changes of correlation energy (ΔE_{corr}) and to changes in the effectiveness of our DZ basis set $\Delta(E_{\text{HF}} - E_{\text{DZ}})$. Since Hartree–Fock energies are available for several of the molecules in this study,[4] we have evaluated $\Delta(E_{\text{HF}} - E_{\text{DZ}})$ and ΔE_{corr} for three independent reactions for which this is possible. This is done to give a background of reliable information for the interpretation of the pattern of $(\Delta E_{\text{corr}} + \Delta(E_{\text{HF}} - E_{\text{DZ}}))$.

Consider the reaction $H_2 + F_2 = 2HF$: we find $\Delta H_{\text{th}} - \Delta H_{\text{exp}} = +2$ kcal, $\Delta(E_{\text{HF}} - E_{\text{DZ}}) = -18.8$ kcal, and $\Delta E_{\text{corr}} = +16.8$ kcal. We have adopted Wahl's value for F_2 of $E_{\text{HF}} = -198.768$.[4] For the reactants, $E_{\text{HF}} - E_{\text{DZ}} = -51.4$ kcal. Note that agreement of theoretical and experimental heats of reaction is good because $\Delta(E_{\text{HF}} - E_{\text{DZ}})$ and ΔE_{corr} are of opposite sign. Thus an improvement of basis set could cause $\Delta H_{\text{th}} - \Delta H_{\text{exp}}$ to become negative and as large as −16.8 kcal. It is rather surprising to find the

Table IV. Bond Energies

Bond	Bond energy, kcal	Bond	Bond energy, kcal
C—C	83.1	C≡C	194
C—N	69.7	C≡N	207
C—O	84.0	C≡O	(257)
C—F	105.4	N≡N	226
N—N	38.4	H—H	104.2
O—O	33.2	C—H	98.8
F—F	36.6	N—H	93.4
C=C	147	O—H	110.6
C=O	164	F—H	134.6
N=N	100		

DZ basis set better for the reactants than the products. This may be a result of the unusually long bond of F_2 which may make F_2 resemble two spherical charge distributions so that a basis of s and p functions at their nuclear centers is rather good. The large value of ΔE_{corr} is probably due to an unusually large correlation energy of F_2, a nondynamic effect attributable to resonance with the nearby excited configuration having a pair of electrons promoted from a bonding to antibonding combination of σ p atomic orbitals.

For the reaction $N_2 + C_2H_2 = 2HCN$, which is a linear combination of reactions in Table II, we compute $\Delta H_{\text{th}} - \Delta H_{\text{exp}} = -8.7$ kcal, $\Delta(E_{\text{HF}} - E_{\text{DZ}}) = +10$ kcal, and $\Delta E_{\text{corr}} = -1.3$ kcal. Finally we find for the reaction $CO_2 + 0.5C_2H_2 = 2CO + 0.5H_2$, also a linear combination of reactions in Table II, that $\Delta H_{\text{th}} - \Delta H_{\text{exp}} = -9.1$ kcal, $\Delta(E_{\text{HF}} - E_{\text{DZ}}) = -7.5$ kcal, and $\Delta E_{\text{corr}} = +16.6$ kcal. For both these reactions we find $\Delta(E_{\text{HF}} - E_{\text{DZ}})$ and ΔE_{corr} to be of opposite sign. We believe that such a cancellation has not occurred for all reactions reported in Tables II, III, and V, and cannot always be expected to occur.

The heats of complete hydrogenation of C_2H_4, CH_2O, and CO are given in Table III. For these reactions we compute with our DZ basis that $\Delta H_{\text{th}} - \Delta H_{\text{exp}} = -9.6$, -10.8, and -15.7 kcal, respectively. Neumann and Moskowitz have computed SCF energies for these molecules with an extended DZ basis [532/21] and find the following improvements over our energies: CH_2O (-0.0708), H_2O (-0.0403), CO (-0.0854), H_2 (-0.0046), and CH_4 (-0.231) in atomic units. Using these improved SCF energies, we compute for the heats of complete hydrogenation of C_2H_4, CH_2O, and CO, $\Delta H_{\text{th}} - \Delta H_{\text{exp}} = -6.0$, -1.9, and $+5.7$ kcal, respectively. This extension of basis is thought to recover about two-thirds of the difference between the E_{DZ} and E_{HF}. Clearly the extended basis has improved the SCF energy of the unsaturated reactants relative to the fully hydrogenated products. We note the addition of d orbitals to a set saturated in s and p orbitals improved the SCF energy of N_2 by 0.08 au, in the work of Cade, Sales, and Wahl;[37a] of CO by 0.07 au, in the study by Huo;[37b] and of F_2 by 0.02 au, in the report of Wahl.[37c] We may expect that our DZ basis is less satisfactory for unsaturated molecules.

Generally one notes that theoretical heats for a single hydrogenation are about 7 kcal more exothermic than the experimental ones. This qualitative feature may be explainable in terms of a change in the van der Waals or dispersion forces between atoms. Hydrogenation either lengthens or breaks bonds completely. The attractive van der Waals or dispersion forces, due to the correlation of the motion of electrons on different atoms, decrease rapidly with distance. The SCF energy we obtain contains no correlation energy. Thus we can expect our theoretical energy to be poorer for the reactants than for the hydrogenated products which have longer bonds. As a result, theoretical heats of hydrogenation would be predicted to be too negative, as we find in Table II. Hydrogenation of the cyclic molecules to form linear ones should be even more effective in reducing dispersion forces. We note in Table II that theoretical heats of hydrogenation for cyclic molecules are about 15 kcal/mole more negative than the experimental values. Another possible interpretation is that the DZ basis is less satisfactory for the more unsaturated reactants of a hydrogenation. This would also cause theoretical heats of hydrogenation to be too negative relative to experimental ones.

Heats of complete hydrogenation are shown in Table III. Again the theoretical heats are too exothermic by about 7 kcal for each hydrogen molecule added. These reactions are of interest because one would expect no van der Waals interactions between second-row atoms in the totally hydrogenated products. Thus one might expect large changes of interatomic van der Waals interactions for these reactions. If these were to dominate ΔE_{corr}, then there would be a strong inverse dependence of this quantity on distance. This should show itself in the complete hydrogenation of molecules containing two first-row atoms as a strong dependence of the difference of theoretical and experimental heats of reaction on the inverse power of the distance between the two bonded first-row atoms of the reactant. Figure 1 plots ΔH°_{298} (th − exp) against this distance for ten molecules. Pitzer and Catalano[38] have estimated the dispersion energy between the methyl groups of ethane to be of order 40 kcal/mole, if they are extrapolated by an inverse sixth power dependence on bond length from the values of van der Waals interactions at larger distances. Figure 1 shows little evidence for an effect of van der Waals interaction or dispersion forces.

The hydrogen-transfer reactions in Table V have been prepared by adding to each hydrogenation of Table II the dehydrogenation of methane to form ethane. In such reactions the number of bonds of hydrogen to first-row atoms is conserved. The agreement between theory and experiment is much better for the hydrogen-transfer reactions. For the reactions whose experimental heats are well known, the mean value of ΔH°_{298} (th − exp) is -0.6 kcal/mole. The root mean square deviation is 6.5 kcal/mole. This is rather good agreement and exceeds that which is attained using common empirical methods.

Chemists have developed empirical ways to summarize the results of thermochemical measurements and to estimate new values.[3] The concept of bond energy is perhaps the simplest. The idea is that a characteristic amount of energy is released in the formation of each type of chemical bond, this hopefully being independent of the types of neighboring bonds in the molecules reacting. A set of bond energies has

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(37) (a) P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.*, **44**, 1973 (1966); (b) W. M. Huo, *ibid.*, **43**, 624 (1965); (c) A. C. Wahl, *ibid.*, **41**, 2600 (1964).

(38) S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956).

been proposed by Pauling.[3] We list these in Table IV. These bond energies are a summary of thermochemical experiments. They are derived for the purpose of estimating heats of formation. We call the heats of reaction we have so derived "empirical" and list them along with the "theoretical" values from SCF calculations. We take these empirical estimates to represent the average chemist's ability to guess heats of reaction. Indeed this is the method commonly used in such estimations. More complex empirical schemes are possible, but they become less valuable as the number of parameters employed increases. The final column of Table V lists the difference of the experimental and empirical heats of reaction. These should be compared with differences of the theoretical and experimental values.

The first nine reactions in Table V involve common and stable molecules, indeed molecules from which many of the bond energies were derived. The theoretical and empirical heats of reaction are seen to be about equally close to experiment, usually within 5 kcal. However, in most cases the theoretical values are a little better. We note that these are reactions for which bond energies work best because each molecule is well represented by a single valence-bond structure.[3] They are also all molecules without strain energy due to bending of bonds.

In the reactions of methane with formamide, formic acid, and formyl fluoride, the theoretical heats are in much better agreement with experiment than the empirical ones. Again the theoretical heats are within 5 kcal of experiment. The empirical heats are about 25 kcal/mole too negative. Pauling attributes this failure to resonance: more than one valence-bond structure should contribute to the ground state of these formic acid derivatives.[3] The theoretical heats from the SCF calculations do not fail in this case: they naturally include resonance that does not produce electron correlation.

The reactions of cyclopropane, ethylenimine, and ethylene oxide again show the theoretical heats of reaction to be better than the empirical. These molecules all have three-membered rings and are thus expected to be highly strained.[3] Since the empirical method omits strain energy, it underestimates the exothermicity of these reactions by 15–22 kcal/mole. These molecules are well represented by a single valence-bond structure. The theoretical heats are within 10 or less kcal/mole of the experimental. Strain energy is naturally incorporated into an SCF calculation with a sufficiently large basis. For these cyclic molecules the interatomic correlation energy may be unusually large and produce the rather poorer performance of our simple theory here.

In the two unsaturated cyclic molecules, cyclopropene and diazirine, the strain energy is expected to be even larger. We find the empirical heats in error by about 50 kcal. The error for theoretical heats is 11 or less kcal/mole.

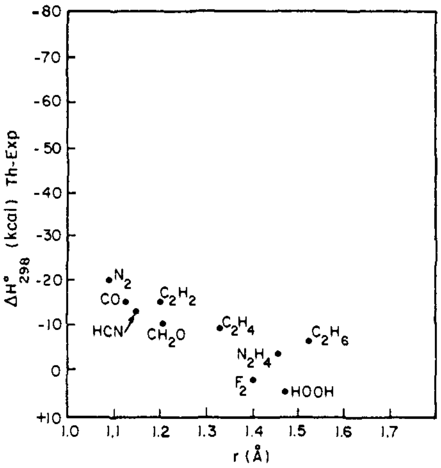

Figure 1. Plot of the theoretical minus experimental heats of complete hydrogenation against the bond distance between first-row atoms in ten compounds having one such bond. Theoretical heats assume no change of correlation energy in these reactions.

Finally, we should consider the isoelectronic molecules carbon dioxide and diazomethane. Pauling noted the four valence-bond structures which may be expected to contribute to the ground state of the symmetrical molecule CO_2. As a consequence, the empirical and experimental heats of reaction differ by 61 kcal/mole. As in previous cases, the theoretical heat is within 10 kcal/mole. In diazomethane, a single valence-bond structure much more closely represents the ground state. With our choice of the relatively uncertain experimental heat of formation, the empirical result is in rather good agreement with experiment, as is the theoretical value.

Dewar and Klopman[39] have recently proposed semiempirical SCF molecular orbital methods to estimate heats of reaction. They have extensively parameterized the Pople SCF method. They employ two molecular and four atomic parameters per atom. Heats of formation are computed from the corresponding total molecular energies. When applied to hydrocarbons, their method has predicted heats of formation from atoms for 17 hydrocarbons with a root mean square deviation from the observed of 2.7 kcal/mole. These hydrocarbons include ethane, *n*-pentane, isopentane, cyclopropane, *trans*-1,3-butadiene, and benzene. Their method did less well for molecules having shorter C–C bonds such as allene, acetylene, and methylacetylene, for which the errors were 22.0, 22.2, and 27.6 kcal/mole, respectively. One must also note that their method requires the experimental geometry as input: the minimization of the total energy with respect to bond length gives bond lengths which are much too small.[39] It is our opinion that their method will be much less satisfactory outside the set of molecules for which the parameterization has been made. Our theoretical heats of reaction are dependent on no specially chosen parameters. It is well known that *a priori* SCF calculations will give accurate molecular geometries by minimization of the total energy.[4] Thus our method can be applied to activated complexes and other unstable species for which the geometry may be experimentally unknown. Our theoretical heats must, however, be applied with caution to molecules having unusually long bonds; the correlation energy is larger in such cases.

In summary, we find rather paradoxically good agreement with experiment by theoretical heats of reaction computed with E_{DZ} and the assumption that

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(39) M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

Table V. Hydrogen-Transfer Reactions

Reaction	ΔH°_{298}, kcal				
	Theory	Empirical	Experiment	Th − exp	Emp − exp
$2CH_4 + N_2H_4 = C_2H_6 + 2NH_3$	−26.3	−33.9	−29.3	+3.0	−4.6
$2CH_4 + H_2O_2 = C_2H_6 + 2H_2O$	−56.3	−73.5	−67.7	+11.4	−5.8
$2CH_4 + F_2 = C_2H_6 + 2HF$	−105.2	−118.1	−114.1	+8.9	−4.0
$2CH_4 + C_2H_4 - 2C_2H_6$	−13.0	−19.2	−17.2	+4.2	−2.0
$2CH_4 + CH_2O = C_2H_6 + 0.5C_2H_4 + H_2O$	−7.5	−16.2	−8.5	+1.0	−7.7
$2CH_4 + C_2H_2 = C_2H_6 + C_2H_4$	−25.3	−36.1	−26.2	+0.9	−9.9
$2CH_4 + HC{\equiv}N = C_2H_6 + 0.5C_2H_2 + 0.5N_2H_4$	+25.6	+18.5	+22.9	+2.7	−4.4
$2CH_4 + 0.5N_2 = C_2H_6 + 0.5N_2H_4$	+25.3	+21.5	+26.8	−1.5	−5.3
$2CH_4 + CO = C_2H_6 + H_2CO$	+16.2	+9.9	+14.2	+2.0	−4.3
$2CH_4 + HCONH_2 = C_2H_6 + H_2CO + NH_3$	+25.4	−8.0	[+26.9]	[−1.5]	[−34.9]
$2CH_4 + HCOOH = C_2H_6 + H_2CO + H_2O$	+18.5	−10.9	+16.7	+1.8	−27.6
$2CH_4 + HCOF = C_2H_6 + H_2CO + HF$	+9.2	−13.5	[+13.1]	[−3.9]	−26.6
$2CH_4 + C_3H_6 = C_2H_6 + CH_4 + C_2H_4$	−6.4	+19.2	−2.7	−3.7	+21.9
$2CH_4 + C_2H_5N = C_2H_6 + NH_3 + C_2H_4$	−23.2	+3.2	−13.2	−10.0	+16.4
$2CH_4 + C_2H_4O = C_2H_6 + H_2O + C_2H_4$	−25.7	−2.6	−17.6	−8.1	+15.0
$2CH_4 + CH_4N_2 = N_2H_4 + CH_4 + C_2H_4$	−71.3	+3.6			
$2CH_4 + C_3H_4 = C_2H_6 + CH_4 + C_2H_2$	−26.2	+36.1	−14.8	−11.4	+50.9
$2CH_4 + CH_2N_2 = C_2H_6 + CH_4 + N_2$	−97.2	−69.7	[103.3]	[+6.1]	[+33.6]
$2CH_4 + CO_2 = C_2H_6 + H_2O + CO$	+15.3	−35.7	+25.4	−10.1	+61.1
$2CH_4 + CH_2N_2 = C_2H_6 + CH_4 + N_2$	−69.8	−62.1	[−73.3]	[+3.5]	[+11.2]

Table VI. Atomic Orbital Pair Correlation Energies

Pair	Atomic ϵ_{ij}, au					
ij	C	N	O	F	Ne	H
1s1s	−0.0409	−0.0409	−0.0402	−0.0398	−0.0399	−0.0409
1s2s	−0.0015	−0.0013	−0.0014	−0.0014	−0.0013	
1s2p	−0.0015	−0.0014	−0.0012	−0.0016	−0.0017	
2s2s	−0.0284	−0.0136	−0.0129	−0.0119	−0.0108	
2s2p	−0.0139	−0.0139	−0.0118	−0.0084	−0.0068	
2p2p	−0.0258	−0.0258	−0.0258	−0.0258	−0.0258	
2p2p′	−0.0123	−0.0123	−0.0123	−0.0123	−0.0123	

$(\Delta E_{\text{corr}} + \Delta(E_{\text{HF}} - E_{\text{DZ}})) = 0$. Many considerations would argue against the possibility of such agreement. The values of E_{DZ} are about 100 au for the reactants or products. An unbalanced error in E_{DZ} of only 0.01% would produce an effect of 6 kcal on computed heats of reaction. A value for ΔE_{corr} equal to 2% of the total correlation energy would also shift theoretical heats of reaction by 6 kcal or more. It is clear that in some reactions ΔE_{corr} and $\Delta(E_{\text{HF}} - E_{\text{DZ}})$ have been of opposite sign to enhance the agreement with experiment. We would be surprised if this has happened for most of the reactions reported here. In section V we shall try to more quantitatively examine the structure of correlation energy and its relation to these results.

V. The Structure of Correlation Energy

Hollister and Sinanoğlu[40] have suggested a method of estimating the correlation energy in molecules. The method, which they call the "pair population" method, assigns a number of pairs of electrons to each atomic orbital employed in a minimum basis set SCF wave function for a molecule. The total correlation energy is then evaluated as a sum over all atomic orbitals and pairs of atomic orbitals, of atomic pair correlation energies, ϵ_{ij}, weighted by the atomic orbital pair populations.

A Mulliken population analysis[41] of the molecular orbital wave function provides a convenient method to define atomic orbital charge densities, ρ_i, which may be interpreted as the number of electrons in atomic orbital i. The atomic orbital pair population of orbital i is then $\frac{1}{2}\rho_i$.

An atomic orbital pair correlation energy ϵ_{ij} is the correlation energy of a pair of electrons in the same or different atomic orbitals; the indices refer to the atomic orbitals. For a given pair of orbitals the pair correlation energy depends on the relative spin of the two electrons, as has been shown in recent calculations by Nesbet.[42] At the time of Sinanoğlu and Hollister's work, knowledge of atomic orbital pair correlation energies was incomplete and to a large degree based on empirical analysis of total correlation energies of atoms.[43] Recently Nesbet has completed Bethe–Goldstone calculations of pair correlation energies for all pairs of electrons in first-row atoms. His calculations were for a basis of complex atomic orbitals. We have used Nesbet's[42] work to guide us in preparing a set of ϵ_{ij}'s for real atomic orbitals. We list the values employed in Table VI.

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(40) C. Hollister and O. Sinanoglu, *J. Am. Chem. Soc.*, **88**, 13 (1966).

(41) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(42) R. K. Nesbet, Paper BE4, American Physical Society Meeting, March 1968, Berkeley, Calif.; R. K. Nesbet, *Phys. Rev.*, **155**, 56 (1967).

(43) L. C. Allen, E. Clementi, and H. M. Gladney, *Rev. Mod. Phys.*, **35**, 465 (1963).

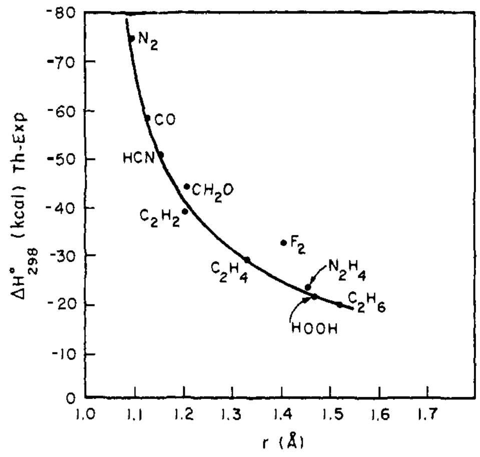

Figure 2. Plot of the theoretical minus experimental heats of complete hydrogenation against the bond distance between first-row atoms. The theoretical heats include the estimated change in intraatomic correlation energy. The change of interatomic correlation energy is not included.

The total correlation energy in a molecule is taken to be given by

$$E_{\text{corr}} = \sum_i \epsilon_{ii}{}^1/_2\rho_i + \sum_{i>j} \epsilon_{ij}\rho_i\rho_j \tag{10}$$

This equation can very accurately reproduce E_{corr} if the sums are taken over the molecular orbitals of the determinental SCF wave function. In this study using the "pair population" method, the sums are over atomic orbitals. We note that some ϵ_{ij}'s correspond to atomic orbitals on the same atom; we interpret these as contributing intraatomic correlation energy $E_{\text{corr-intra}}$. Other ϵ_{ij}'s correspond to pairs of atomic orbitals on different atoms; we interpret these as contributing to dispersion forces or interatomic correlation $E_{\text{corr-inter}}$. Only the intraatomic ϵ_{ij}'s may be estimated from Nesbet's work. We have used them to evaluate the sum (eq 10) and obtain our estimates in Table I of the intraatomic correlation energy of the molecules in this study. We note that in evaluating (10) we have taken ρ for all 2p orbitals on atoms equal to one-third of the total 2p atomic orbital density on the atom. When eq 10 is applied for the neon atom, we obtain Nesbet's result of -0.3829 au or 97.3% of the correlation energy.[42]

Our estimates of the intraatomic correlation energy are rather close to estimates of the total correlation energy published by Ritchie and King for H_2O, NH_3, and CH_4; they found 0.38, 0.33, and 0.28 au, respectively.[44]

The previous theoretical heats of reaction may now be improved by adding our estimates of the change in intraatomic correlation energy ($\Delta E_{\text{corr-intra}}$). We have completed these revised theoretical heats of reaction for the set of complete hydrogenations. The mean value of the theoretical minus the experimental value of ΔH is now -52 kcal/mole. The root mean square deviation for the difference is now 56 kcal/mole. The addition of our estimate of the change in intraatomic correlation energy to the theoretical heat of reaction has made the agreement between theory and experiment much worse. We note that in all cases the intraatomic correlation energy is larger in the hydrogenated products. The electrons of the added H_2 correlate with the many electrons of the first-row atoms to which it bonds. To aid in interpreting this result, we plot in Figure 2 the difference between the theoretical and experimental heats of complete hydrogenation for the first ten reactions of Table III against the distance between bonded first-row atoms of the reactants. Our estimate of $\Delta E_{\text{corr-intra}}$ has been included in the theoretical heats of reaction. The difference increases rapidly with decreasing bond length, approximately as the inverse fourth power. This is qualitatively what one would expect if the error were due to the so-far neglected changes of interatomic correlation energy, the van der Waals or dispersion interactions. The magnitude of the interatomic correlation energy is not known. As noted, Pitzer and Catalano probably overestimate it by extrapolation of van der Waals interactions to bonding distances.[38] Kestner and Sinanoğlu[45] showed that for two helium atoms, the interatomic correlation energy increases at a rate less than r^{-6} at bonding distances. Indeed if all interatomic pair correlations in ethane could be approximated by those of two helium atoms at 1.54 Å, then the interatomic correlation energy (between electrons of the methyl groups) would be about 5 kcal/mole. This is probably a lower limit. The estimate of about 40 kcal based on Pitzer and Catalano's work is probably too large. If the entire difference between theory and experiment in Figure 2 can be attributed to $\Delta E_{\text{corr-inter}}$, then our estimate is 19.9 kcal for ethane. In fact, the difference is equal to $\Delta E_{\text{corr-inter}} + \Delta(E_{\text{HF}} - E_{\text{DZ}})$ if our estimate of $\Delta E_{\text{corr-intra}}$ has been correct.

As previously mentioned, we have recomputed several heats of reaction using the energies obtained with the considerably enlarged basis set of Neumann and Moskowitz[12] to more closely approach E_{HF}. The resulting changes in theoretical heats for the complete hydrogenations of CO, CH_2O, and C_2H_4 would lower the curve in Figure 2 by 33%. We conclude that a relatively small part of our apparent change in van der Waals energy is due to an increasing inadequacy of our DZ basis set with increasing unsaturation.

To test the possibility that there is a single function of bond length between bonded first-row atoms, which we can employ to correct theoretical heats of reaction, we have used the solid curve of Figure 2 to represent the "interatomic" correlation energy between a bonded pair of first-row atoms. This curve of Figure 2 uses the complete hydrogenation data on all compounds which have a single pair of bonded first-row atoms. The curve has been used to correct the theoretical heats of reaction for the complete hydrogenation of all remaining molecules which have more than one pair of first-row atoms bonded. These corrected theoretical heats of reaction are denoted by Theory'' in Table VII. They are obtained by using our previous estimates of $\Delta E_{\text{corr-intra}}$ and the empirical correction $\Delta E_{\text{corr-inter}}$ from Figure 2 to compute the theoretical heats of reaction. Of course, it must be remembered that the correction we call $\Delta E_{\text{corr-inter}}$ also must incorporate a correction for $\Delta(E_{\text{HF}} - E_{\text{DZ}})$. For the complete hydrogenations of Table VII, the mean value of ΔH (th'' $-$ exp) is $+1.4$ kcal/mole. The root mean square deviation is $+4.4$ kcal/mole. The RMS calculations exclude all reactions for which the experimental heat is in doubt. The

[44] C. D. Ritchie and H. F. King, *J. Chem. Phys.*, **47**, 564 (1967).
[45] N. R. Kestner and O. Sinanoğlu, *ibid.*, **45**, 194 (1966).

Table VII. Complete Hydrogenations

Reaction	$\Delta E_{\text{corr-intra}}$	$\Delta E_{\text{corr-inter}}$	ΔH°_{298}, kcal Theory″	 Experiment	Th″ − exp
$H_2 + C_2H_6 = 2CH_4$	−13.0	+19.7	−15.7	−15.5	−0.2
$H_2 + N_2H_4 = 2NH_3$	−19.1	+22.4	−45.4	−44.8	−0.6
$H_2 + HOOH = 2H_2O$	−25.7	+21.7	−82.7	−83.2	+0.5
$H_2 + F_2 = 2HF$	−34.8	+25.0	−137.4	−129.6	−7.8
$2H_2 + C_2H_4 = 2CH_4$	−19.7	+29.2	−48.3	−48.2	−0.1
$2H_2 + CH_2O = CH_4 + H_2O$	−34.1	+41.7	−51.2	−48.0	−3.2
$3H_2 + C_2H_2 = 2CH_4$	−23.9	+41.7	−87.7	−89.9	+2.2
$3H_2 + HCN = CH_4 + NH_3$	−37.8	+51.5	−60.1	−60.0	−0.1
$3H_2 + N_2 = 2NH_3$	−55.5	+76.0	−22.4	−22.2	−0.2
$3H_2 + CO = CH_4 + H_2O$	−43.9	+59.0	−49.9	−49.3	−0.6
$3H_2 + HCONH_2 = CH_4 + H_2O + NH_3$	−46.7	+67.0	−35.1	[−36.6]	[+1.1]
$3H_2 + HCOOH = CH_4 + 2H_2O$	−48.9	+72.0	−39.6	−46.8	+7.2
$3H_2 + HCOF = CH_4 + H_2O + HF$	−48.9	+75.5	−45.4	[−50.4]	[+5.0]
$3H_2 + C_3H_6 = 3CH_4$	−27.7	+59.1	−55.2	−66.4	+11.2
$3H_2 + C_2H_5N = 2CH_4 + NH_3$	−35.5	+64.5	−74.4	−76.9	+2.5
$3H_2 + C_2H_4O = 2CH_4 + H_2O$	−41.0	+68.5	−78.4	−81.3	+2.9
$3H_2 + CH_4N_2 = CH_4 + 2NH_3$	−38.8	+67.0	−149.6		
$4H_2 + C_3H_4 = 3CH_4$	−35.4	+73.0	−116.5	−120.2	+3.7
$4H_2 + CH_2N_2 = CH_4 + 2NH_3$	−63.4	+83.0	−142.9	[−141.0]	[−1.9]
$4H_2 + CO_2 = CH_4 + 2H_2O$	−62.4	+100.0	−34.5	−39.4	+4.9
$4H_2 + CH_2N_2 = CH_4 + 2NH_3$	−59.8	+92.6	−102.3	[−111.0]	[+8.7]

improved agreement of the theoretical and experimental heats of complete hydrogenation at least indicates that the correction has the right dependence on distance.

VI. Summary

For chemical reactions in which closed-shell reactants form closed-shell products, fairly accurate theoretical standard heats of reaction can be computed with SCF energies in a DZ basis of gaussian orbitals and the assumption that the relativistic energy does not change and that $(\Delta E_{\text{corr}} + \Delta(E_{\text{HF}} - E_{\text{DZ}})) \cong 0$. These theoretical heats of reaction are more accurate than those obtained using semiempirical relations of bond energies for reactions of strained molecules, or those not well represented by a single valence-bond structure. We also believe that our theoretical heats of reaction will be more accurate than those of parameterized SCF molecular orbital treatments[39] when molecules outside the set parameterized are considered.

If an attempt is made to add a theoretical estimate of the change in correlation energy, the agreement with experiment is likely to become worse unless this estimate is quite good. In particular, the addition of a pair population estimate of the change of intraatomic correlation energy causes the agreement with experiment to become much worse. The estimate suggests that intraatomic correlation energy increases considerably in a hydrogenation. Apparently this increase is compensated for by a decrease in interatomic correlation energy as bonds lengthen in hydrogenated products. This study gives a correction, which we attribute mainly to interatomic correlation energy, as a function of the length of bonds between first-row atoms. The addition of this correction improves the theoretical values for heats of reaction.

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