

## Acid Base Properties of Coals and Coal Liquids

by

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Solution calorimetry provides a straightforward method for comparing the acid-base properties of solids with homogeneous analogues. The presentation will describe the correlations (and lack of them) between heats of interactions of a series of acids and a corresponding series of bases with several such heterogeneous/homogeneous systems. For example, solutions of *p*-toluenesulfonic acid are compared with slurries of sulfonic acid resins in their reactions with a series of nitrogen bases. Pyridine solutions are compared with slurries of polyvinylpyridine by their reactions with a series of carboxylic and sulfonic acids. Finally, several carefully chosen coal liquids are compared with related coals of different rank and are considered in the light of the above simpler systems.

### Introduction

The classification of chemicals into acids and bases is one of the broadest in Science. It is well known that coals and the liquids derived from them include a number of functionalities and structures which are acidic (e.g., phenols, carboxylic acids) or basic (e.g., a variety of amino functions, ethers, sulfides and inorganic oxides). All types of organic functionalities are potentially basic towards protons, Lewis acids and hydrogen bond donors, and most of them are also acidic, in the Brønsted sense, if they carry protons bonded to carbon or other elements. However, only a few acidic or basic functionalities are strong enough to allow study in the familiar aqueous acid-base range of the pH meter. Over the past fifty years a variety of strategies have been developed for studying even very weak bases by reaction with strong superacids, and correspondingly weak acids with superbases. Of particular importance has been the development of gas phase techniques in the past fifteen years for studying proton transfer reactions in the gas phase which provides a very broad *inherent* scale of acid-base strengths from which all contributions due to solvation or ion-pairing effects have been completely removed.<sup>1-5</sup> The impact of gas phase studies on clarifying solvent effects can hardly be exaggerated.

The acid-base properties of solids play a fundamental role across a wide panorama of materials science, including among other matters corrosion, adhesion, the behavior of solid sensors, many biochemical medical and geochemical phenomena. Of great importance to the fossil fuel industry is the use of solid acid catalysts for a wide range of processes in the petroleum and coal derivative industries.

Unhappily, the methods for establishing quantitative acid-base scales for solids stand on a much sandier foundation than those used to compare liquid acid-base systems. A solid surface may carry a variety of basic sites in the presence of Lewis acid, Brønsted acid and hydrogen-bonding donor sites of widely different strengths and accessibilities. In solution a rapid equilibrium is established between different types of acid or basic sites and it is reasonable to de-

scribe a solution as representing a single acidity or basicity value within a very limited range. One would scarcely think that after mixing a solution of hydrochloric acid with sodium hydroxide that there would coexist in solution a number of strongly acid and strongly basic sites. However, due to the inflexible structure of solids a material such as a Zeolite, alumina or coal may carry on its surface both acidic and basic sites that are permanently separated and do not interact with each other directly.

**The Thermochemical Approach:** A number of years ago we established a very simple thermochemical method for determining the strengths of basic liquids by measuring their heats of neutralization by a common very strong acid such as sulfuric or fluorosulfuric acid.<sup>6</sup> Samples of the base were injected directly with a Hamilton syringe into a calorimeter vessel full of the pure strong acid. Alternatively, the base could be titrated using a motor-driven burette into a vessel containing a solution of the acid in some relatively inert solvent such as acetonitrile. Heats of ionization were determined in this manner for a 100 or so bases of widely different type and were shown to correlate very well with the best results obtained by other much more laborious methods. Heats of ionization are a direct measure of basicity.

The great advantage of the calorimetric method is that it can also be applied with facility to the study of solid acids and bases using a stirred slurry of the solid under an inert solvent instead of the homogeneous solution of the acid or base. The thermochemical titration method, therefore, provides a direct means for comparing the acidity or basicity of homogeneous solutions with solids which are presumed to carry the same acid or base structure. This article provides a current overview of our use of the thermochemical method to compare several types of solid acids and bases with their homogeneous cognates. As a simple prototype example of a Brønsted acid Dowex polysulfonic acid resin was compared with *p*-toluenesulfonic acid solutions. A sample of Fisher silica was examined for its hydrogen-bonding acidity compared to *p*-fluorophenol. Polyvinylpyridine was compared to solutions of pyridine as a standard base, and Carbo-pack graphitized carbon was used as a model for the dispersion force interactions which inevitably contribute to adsorption of any gas or liquid on any type of solid. Finally, several types of well-characterized coals were compared with coal liquids derived from them.

### Experimental

Surface areas were obtained by nitrogen adsorption at 77K employing the BET method and using a Quantachrome Surface area analyser. The acids and bases were obtained commercially and were used as 0.25-0.5 molar solutions in carefully purified acetonitrile or neat wherever indicated. Coal samples were obtained from Argonne Coal Bank, Exxon Research and Engineering Co. and Southern Electric International, Southern Clean Fuels Division at Wilsonville, Alabama.

Titration calorimetry using the Tronac 450 calorimeter is the most desirable technique for comparing heats of interaction of strong acids or bases with solids provided that the exothermic heats of interaction are large enough and are released in a relatively short period of time (say less than two minutes). In these cases the results can be expressed in terms of kcal/mol since it is known exactly how many moles of acid are required to titrate the solid. For titration calorimetry, the apparatus is calibrated every few weeks by measuring the heat of neutralization of aqueous sodium hydroxide by titration with standard aqueous hydrochloric acid  $\Delta H = -13.42 \pm 0.39$  kcal/mol.

For cases where relatively small heats of interaction must be compared, and the total heat is given out over a long period (say one hour), heats of immersion are measured with the Seteram C-80 heat flow calorimeter. This instrument measures heats of immersion by releasing the solid base into a solution of the liquid acid or a neat liquid acid. Heats of immersion may also be obtained by sealing the solid in an ampule which is equilibrated thermally with the acid

solution and then crushed in the stirred calorimeter. For immersion calorimetry in contrast to titration calorimetry it is more realistic to present results in  $\text{cal g}^{-1}$  of solid base since there is no direct means of knowing how many moles of acid or base were actually involved in the interaction. We have used heats of dissolution of KCl in water as the calibrating standard for immersion calorimetry.

Heats of adsorption on Carboxpack F were determined by gas-solid chromatography by the van't Hoff method previously described in which the retention volume of the adsorbate is studied as a function of temperature.

### Results and Discussion

A prototype Brønsted solid acid Dowex---polysulfonic acid resin:<sup>7</sup> In order to establish the feasibility of the thermochemical method for comparing solid and homogeneous acids and bases, Dowex polysulfonic acid resin was treated as a slurry in acetonitrile with a series of nitrogen bases whose strength cover a reasonably wide range. The same bases were again injected into solutions of *p*-toluenesulfonic acid in acetonitrile and the heats of reaction determined. Although in aqueous solution neutralization would have occurred to produce dissociated ammonium and *p*-toluenesulfonate ions in acetonitrile, there is every reason to expect that hydrogen-bonded ion-pairs were produced according to equation 1.

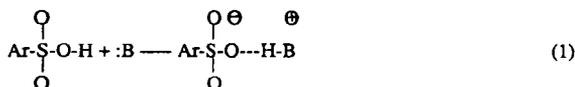


Figure 1 presents the excellent correlation between the two sets of enthalpy determinations. The quality of this correlation is of fundamental importance for our whole strategy for studying the strengths of solid acids and bases. Considering the above discussion of the real differences between the distribution of acid sites on various types of solid acids, the difference between chemisorption and physisorption, it would be possible that the difference between solid and liquid acid or base systems is inherently so great that no close correspondence between them could be found. Figure 1 emphasizes the fact that if there is ready access to surface acid sites of equivalent acidity that they respond proportionately in the same way as those same sites do if they are free molecular units in solution.

An instructive point in Figure 1 is its non-zero intercept indicating that the heats of interaction of the bases with PTSA are consistently 4-5 kcal/mol more exothermic than their interactions with Dowex resin. We have interpreted this in terms of the well-established stabilization of sulfonate anions in the presence of excess sulfonic acid according to Equation 2 which would be considerably easier in the solution phase reaction than on the solid surface where ionized sulfonate groups are separated in space from nearby unionized sulfonic acid groups. The difference of 4-5 kcal/mol is in exactly the appropriate range for the formation of such a hydrogen-bond stabilized anion.



Polyvinylpyridine a prototype solid base: Following the strategy described above, a thermochemical comparison has been made between solutions of pyridine and polyvinylpyridine

in which pyridine units are attached to an extended carbon framework. Figure 2 provides exactly the same type of correlation for these liquid and solid basic systems as those presented in Figure 1 for liquid and solid acids. We believe that it is significant that in this case the intercept is within experimental error of zero which helps to support the explanation given above for the non-zero intercept in the case of the sulfonic acids. In the case of protonating the pyridines the sulfonate and carboxylate anions are left free in solution where they can be stabilized in exactly the same way (Equation 2) after reaction with free pyridine molecules or pyridine units attached to the polymeric framework.

Silica a hydrogen-bonding acid: Silica is probably one of the best characterized and best understood of solid acids.<sup>9</sup> Its interaction with bases, unless they are unusually strong, is usually through hydrogen-bonding from the hydroxyl groups on the silica surface. In order to probe the use of silica as a prototype hydrogen-bonding acid, a standard sample of Fisher silica was treated with a series of nitrogen and oxygen bases which are well-established as hydrogen-bond acceptors.<sup>10</sup> Figure 3 shows the relationship between these heats of interaction and the corresponding heats of interaction for the same series of bases with *p*-fluorophenol, a well-established hydrogen-bonding acid. Although the correlations are not as good as those shown in Figures 1 and 2, it is apparent that the heats of interaction of the bases with silica is indeed largely determined by hydrogen-bonding.

Since hydroxyl groups are amphiprotic, amphoteric functionalities, we tried examining silica as an acceptor base for hydrogen bonds or protons from the same series of acids used with pyridine and polyvinylpyridine.<sup>11</sup> To our surprise, the heats of interaction followed an entirely different pattern than would have been expected if the acids were donating protons or hydrogen bonds to silica. Instead, the simplest interpretation of the results was that the silica was actually serving as a strong hydrogen-bonding acid that it was donating hydrogen bonds to the carbocyclic and sulfonic acid functionalities instead of receiving protons from them.

Physisorption on Carboxpack carbon: All matter attracts all matter through dispersion force interactions and accordingly, in the absence of all other types of interactions, gases and liquids will be adsorbed on any kind of solid. As a prototype dispersion force adsorbent we chose Carboxpack F, a graphitized carbon, and determined the heats of adsorption of a variety of compounds on the surface using the van't Hoff equation and the temperature dependence of gas chromatographic retention volumes as the experimental tool.<sup>12</sup> It was immediately apparent from the results when compared with those presented in Figures 1 and 2 that the heats of adsorption had absolutely no relation whatsoever to the basicities or acidities of the adsorbed molecules. Instead, excellent correlations were found (Figures 4 and 5) between the simple number of main group atoms in the adsorbates and their total polarizabilities (the dipole polarizability plus the electronic polarizability).

Comparison of solid coals and coal liquids: The rest of this paper will present work mainly acquired during the summer from the heats of reaction of several well-classified coal liquids received from the Southeast Regional Laboratory at Wilsonville, Alabama and titration of slurries with the corresponding coals from which the coal liquids were derived.

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Figure 1

Plot of  $\Delta H_{Dowex}$  Vs.  $\Delta H_{PTSA}$  with various bases at 25° C

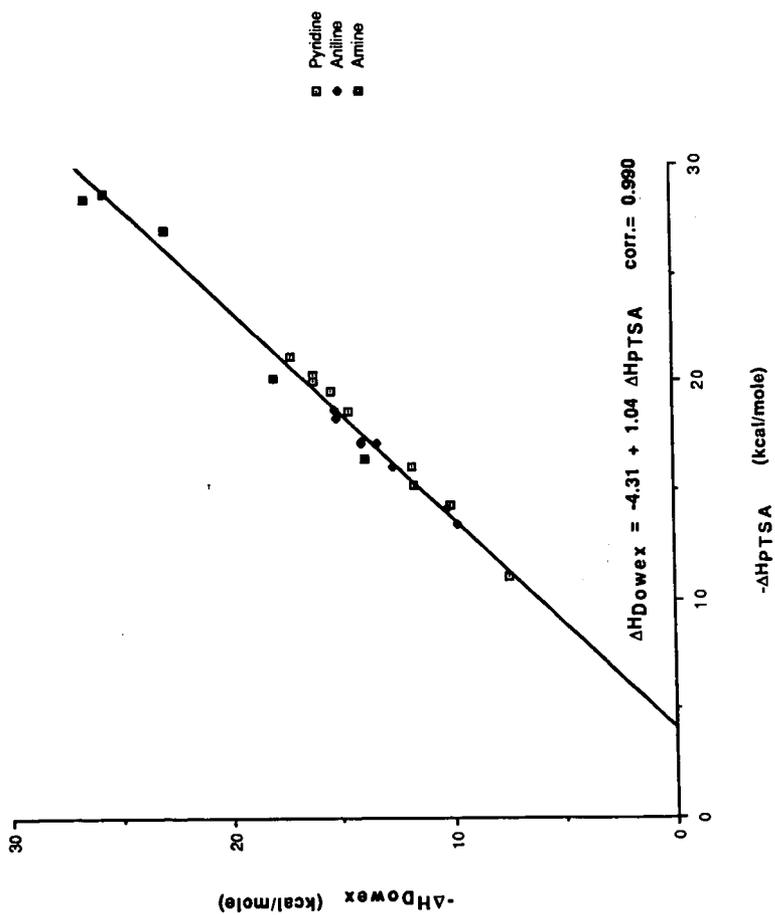


Figure 2

Plot of  $\Delta H_{\text{PVP}}$  Vs.  $\Delta H_{\text{PYR}}$  with some strong acids

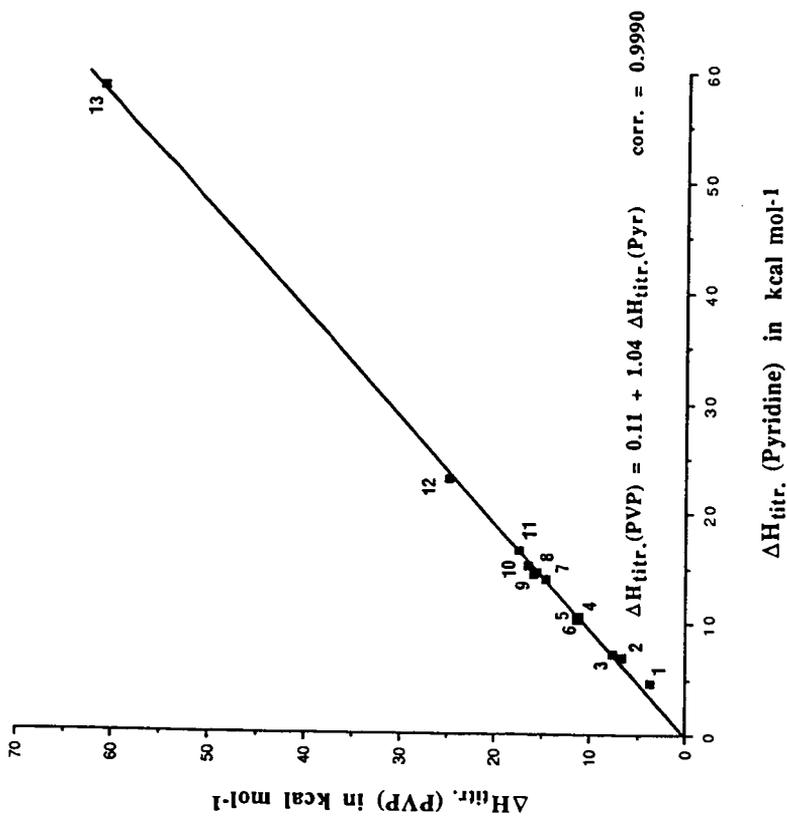


Figure 3

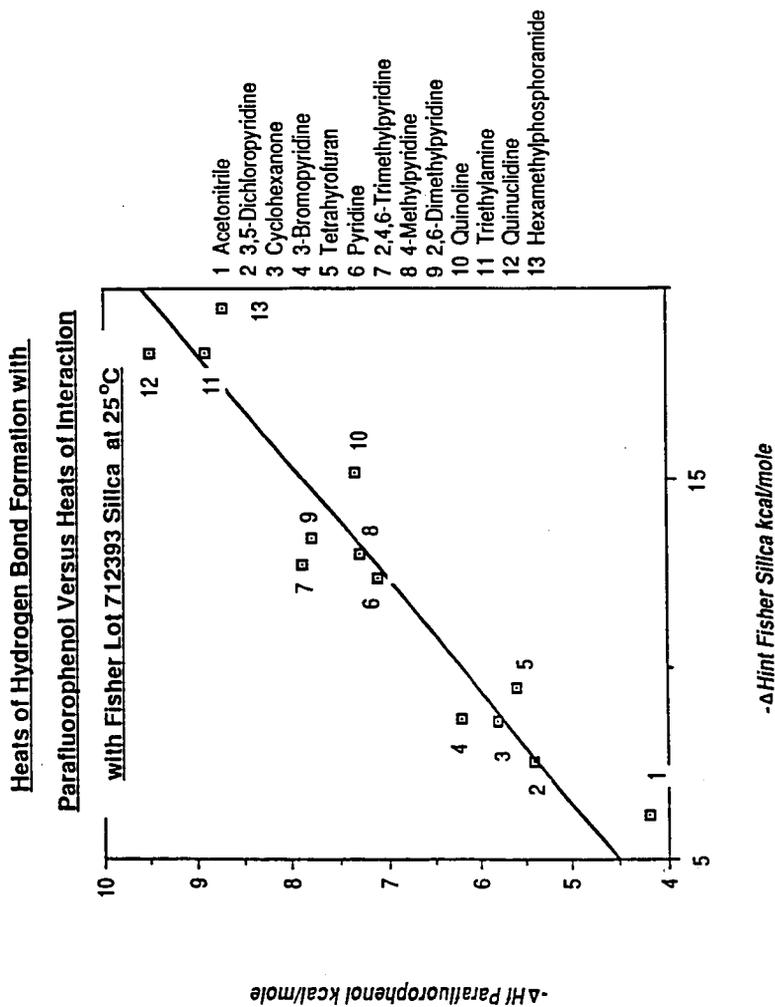
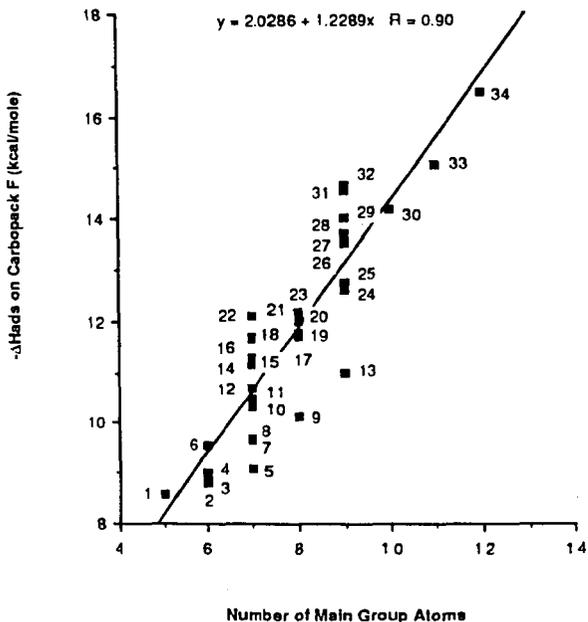


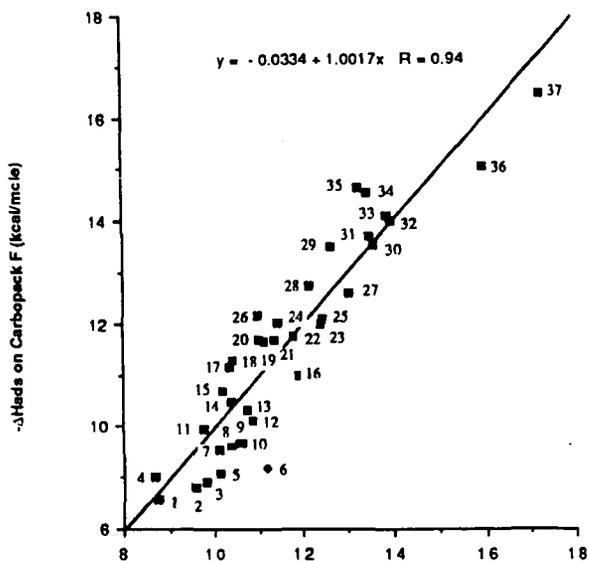
Figure 4



- |                         |                          |                            |
|-------------------------|--------------------------|----------------------------|
| 1. <i>n</i> -Butylamine | 12. 2-Methylpyridine     | 23. Anisole                |
| 2. <i>n</i> -Pentanol   | 13. Methyl caproate      | 24. <i>n</i> -Octanol      |
| 3. Pyridine             | 14. 3-Methylpyridine     | 25. Nitrobenzene           |
| 4. Benzene              | 15. 4-Methylpyridine     | 26. 2,4,6-Collidine        |
| 5. Cyclohexanol         | 16. <i>n</i> -Hexylamine | 27. Nonane                 |
| 6. Hexane               | 17. <i>m</i> -Cresol     | 28. Octylamine             |
| 7. Cyclohexanone        | 18. Bromobenzene         | 29. 1-Chlorooctane         |
| 8. Cyclohexylamine      | 19. Benzonitrile         | 30. <i>n</i> -Butylbenzene |
| 9. Methyl valerate      | 20. Octane               | 31. <i>o</i> -Bromoanisole |
| 10. <i>n</i> -Hexanol   | 21. 2,6-Lutidine         | 32. <i>p</i> -Bromoanisole |
| 11. Toluene             | 22. 1-Bromohexane        | 33. Undecane               |
|                         |                          | 34. Dodecane               |

Heats of Adsorption of a Variety of Adsorbates on Carpack F versus the Number of Main Group Atoms.

Figure 5



$$-\Delta H_{ads} = 0.648(\text{electronic polarizability}) + 0.015(\text{orientation polarizability}) + 2.410$$

- |                         |                          |                            |
|-------------------------|--------------------------|----------------------------|
| 1. <i>n</i> -Butylamine | 14. Toluene              | 27. <i>n</i> -Octanol      |
| 2. <i>n</i> -Pentanol   | 15. 2-Methylpyridine     | 28. Nitrobenzene           |
| 3. Pyridine             | 16. Methyl caproate      | 29. 2,4,6-Collidine        |
| 4. Benzene              | 17. 3-Methylpyridine     | 30. Nonane                 |
| 5. Cyclohexanol         | 18. 4-Methylpyridine     | 31. Octylamine             |
| 6. Triethylamine        | 19. <i>n</i> -Hexylamine | 32. 1-Chlorooctane         |
| 7. Hexane               | 20. <i>m</i> -Cresol     | 33. <i>n</i> -Butylbenzene |
| 8. Cyclohexanone        | 21. Bromobenzene         | 34. <i>o</i> -Bromoanisole |
| 9. Dimethyl sulfoxide   | 22. Benzonitrile         | 35. <i>p</i> -Bromoanisole |
| 10. Cyclohexylamine     | 23. Octane               | 36. Undecane               |
| 11. Propylene carbonate | 24. 2,6-Lutidine         | 37. Dodecane               |
| 12. Methyl valerate     | 25. 1-Bromohexane        |                            |
| 13. <i>n</i> -Hexanol   | 26. Anisole              |                            |

Heats of Adsorption on Carbopeak F versus Electronic plus Orientation Polarizability.