There has been some question regarding the original anchoring of the gas phase acidity scale based on ICR measurements in the region of the aliphatic alcohols. The data for methanol from this scale differ by 2.2 kcal/mol from the value from the thermochemical cycle based on bond strength and electron affinity. Moylan and Brauman have questioned the values for the relative acidities of HF, tBuCH2OH, and PhCH2OH. The acidity scale presented in 1979 is based on two assumptions. First, the ion temperature is assumed to be equal to the cell temperature of 320K, so that the slope of a plot of the relative ICR acidities vs. the D-EA absolute values (converted to $\Delta G^0_{\text{acid}}$ as in equation 1) should be unity. Secondly, hydrogen fluoride, with the most accurately known acidity from the D-EA thermochemical cycle, is properly related to the rest of the acidity ladder, so that it may serve as a single point anchor for the whole scale.

$$\Delta G^0_{\text{acid}}(A-H) = DH^0(A-H) + IP(H^+) - EA(A') + T\Delta S^0_{\text{acid}}$$ (1)

In order to find the source of the discrepancies, we have re-examined the primary data for the ICR acidity scale. The original ladder of relative acidities was constructed from the individual equilibria "by eye": the single equilibrium measurement for two acids was assumed to be the most accurate, and other multiple equilibria pathways between those two acids were used to bias that value slightly if the numbers did not add up exactly right. This method may result in an expansion or contraction of the scale, depending on what choices are made for given values. For example, the free energy corresponding to the D-EA difference for methanol and phenol is 36 kcal/mol, while the relative ICR scale gives 28.1 kcal/mol. We have written a computer program that constructs the equilibria ladder on a rational basis, averaging the difference between two acids over all pathways out to n successive overlaps, where n is up to 10. A number of different weighting methods for the less direct paths have been tried, such as by length in kcal/mol, number of paths, or the square of these. The results of all these schemes consistently give 24.5±0.5 kcal/mol for the $\delta \Delta G^0_{\text{acid}}$ difference between methanol and phenol, with negligible

variation in the results for n greater than 4. This indicates that there was bias in the original ladder construction, but makes the fit of the ICR data to the D-EA values even worse.

A least-squares correlation of these "new" ICR $\delta \Delta G_{\text{acid}}$ values (at an assumed 320K) vs. the $\delta \Delta G_{\text{acid}}$ values calculated from equation (1) results in a non-unity slope, implying an effective temperature of 409K for the species in the ICR cell. Hydrogen fluoride is not included in the correlation, since its value is clearly outside the error limits. There is justification given below for this. While there is some question of the exact temperature of the cell walls in the original experiments, due to heating by the electron beam filament in the original McIver cell design, the 409K value derived here is well outside the range of macroscopic temperatures ever measured by thermocouple on the cell itself. Using the 409 effective temperature and the least-squares anchoring as described, we thus have a re-anchored scale. As further support for this realignment of the acidity scale, we find that:

1) Acidities obtained at 500 to 600K in a pulsed high pressure mass spectrometer now agree with the "new" ICR scale to within 0.4 kcal/mol for acids that are common to both scales.

2) If the acidity of HF is set not by the ICR equilibrium experiments, but only by the D-EA number, it now becomes 0.9 kcal/mol more acidic than neopentyl alcohol. It was 0.5 kcal/mol less acidic in free energy than tBuCH2OH in the old scale. This is consistent with the observations of Moylan and Brauman concerning the kinetics of fluoride reacting with tBuCH2OH and PhCH2OH, and with the acidity overlaps of HF, HCF3, and H2O2 measured in the flowing afterglow. We believe that the pressure of the HF in the ICR spectrometer was not accurately measured during the original experiments, due to vacuum system conditioning.

What is the source of this temperature discrepancy? There has long been debate on whether the ions in the ICR spectrometer are thermalized, with respect to those in "high pressure" techniques such as the flowing afterglow and pulsed CI mass spectrometry. The present results seem to be evidence for that contention, but the source of the excess energy is not clear. It is possible that the "equilibria" measured are not true equilibria, but steady state populations. However, the cationic equilibria scales in the ICR spectrometer agree quite well with those from high pressure techniques over large energy differences. This may be due to the presence of barriers on the reaction surface being prevalent in the π-π proton transfers that predominate in the anion reactions. For the cationic basicity scale, it is expected that any barriers will be much smaller, since most proton transfers are between non-bonding lone pairs that are not delocalized. A second source of excess energy may be from the axial electrostatic trapping well.

In order to quantitate such internal temperature effects, an ad hoc group has been formed at this meeting to determine reactions and equilibria which can function as "thermometer" reactions. These are reactions with rate or equilibrium constants that are sensitive and well established functions of temperature. The reactions suggested are merely first round possibilities; based on the experimental outcome in the collaborators' laboratories, other reactions may be put forward.