

TABLE III
MOLAL HEAT CAPACITIES IN THE HYPOTHETICAL IDEAL
GASEOUS STATE

T, °K.	HCl	C_p (cal./mole) Cl ₂	CO ₂
300	6.963	8.124	8.932
400	6.970	8.442	9.936
500	7.000	8.629	10.737
600	7.066	8.746	11.371
700	7.169	8.830	11.895
800	7.293	8.891	12.328
900	7.428	8.938	12.685
1000	7.566	8.977	12.982
1100	7.701	9.012	13.228
1200	7.830	9.043	13.433
1300	7.946	9.072	13.608
1400	8.055	9.098	13.755
1500	8.154	9.124	13.879

in the hypothetical ideal state, and that the equations, being empirical, are not suitable for ex-

trapolation. In fact the maximum deviation occurs at 300°K.

Summary

The heat capacities of equilibrium chlorine and equilibrium hydrogen chloride between 300 and 1500°K. have been calculated by use of the tables of Gordon and Barnes, and that of carbon dioxide has been calculated over the same range by use of the Planck-Einstein equation. Empirical equations of the form, $C_p = a + bT + cT^2$, have been fitted to the theoretical values of the heat capacities of the above gases and of hydrogen, oxygen, nitrogen, carbon monoxide, bromine, hydrogen bromide and water vapor, with average deviations ranging from 0.18 to 0.76%.

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Heats of Dilution of Strong Electrolytes

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Åkerlöf¹ has suggested recently that the activity coefficients of strong electrolytes of the same valence type are related to each other in a very simple way. Upon examination of existing activity coefficient measurements at 25° he finds that they obey well over a wide concentration range the rule $\log \gamma/\gamma_R = km$ where γ_R is the activity coefficient of the reference substance of a particular valence type and m is the molality.² Even if this rule is only of approximate validity, it is an extremely useful contribution to our knowledge of concentrated solutions, particularly as an aid in estimating numerical values for activity coefficients where no measurements exist.

During the past winter the possibility of the existence of some such relationship was discussed by one of us (H. S. F.) with Dr. E. Güntelberg of the Institute of Physical Chemistry, Copenhagen, Denmark. At that time Güntelberg suggested that if such a theorem were correct it might reasonably be expected to be independent of tem-

perature and that heats of dilution therefore would obey a similar rule. For, since $d \ln \gamma/dT = \bar{L}_2/2RT^2$, if $\log \gamma/\gamma_R = km$ then $\bar{L}_2 - \bar{L}_{2(R)} = km$. It can also be shown readily that integral heats of dilution ($\Delta H_\infty = -\bar{L}_2 - (55.5/m) (\bar{L}_1)$) must obey a similar relationship. Thus if Åkerlöf's rule is equally correct for several temperatures, we should get linear plots of differences of differential or integral heats of solution for electrolytes of the same valence type against the molality and these straight lines should extrapolate through the origin. The individuality of heats of dilution of strong electrolytes persists to very low concentrations where differences in activity coefficient values are within the experimental error³ and in general heats of dilution for a group of electrolytes of the same valence type show a wider dispersion than the activity coefficients. Such data are therefore well suited for the test proposed.

In Figs. 1 and 2 are plotted differences of integral heats of dilution for 7 uni-univalent and 3 bi-bivalent strong electrolytes against the molality at 25°. The data used are all comparable. The earlier measurements of Lange and co-workers

(1) (a) Åkerlöf and Thomas, *THIS JOURNAL*, **56**, 593 (1934); (b) Åkerlöf, *ibid.*, **56**, 1439 (1934); (c) Åkerlöf and Turck, *ibid.*, **56**, 1875 (1934).

(2) This relation is implied in the Hückel activity coefficient equation [Hückel, *Physik. Z.*, **26**, 93 (1925)] if the apparent ionic diameters of the two electrolytes are the same, but in this equation the concentration is expressed as molarity.

(3) Lange and Robinson, *Chem. Rev.*, **9**, 89 (1931).

extending down to concentrations of a few tenths molal have been combined with more recently obtained values for the very dilute range. The short extrapolation to $m = 0$ to obtain integral heats of dilution introduces an uncertainty of only a few calories.⁴ It is estimated that the values used for the plots are accurate to within 2%.

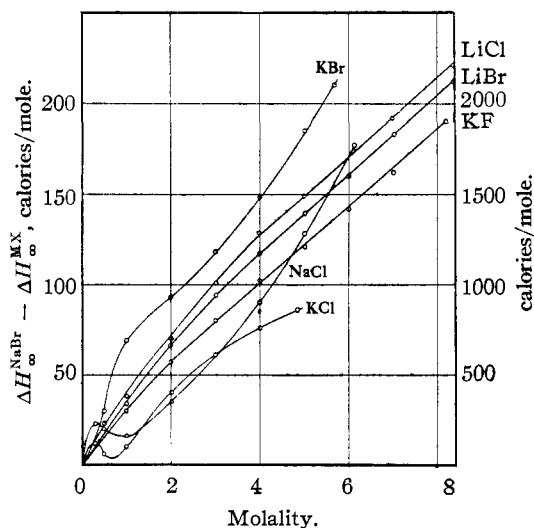


Fig. 1.—Heats of dilution of sodium bromide (reference electrolyte): Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925); Hammerschmid and Robinson, *THIS JOURNAL*, **54**, 3120 (1932). Heats of dilution of sodium chloride: Wüst and Lange, *loc. cit.*; Robinson, *ibid.*, **54**, 1311 (1932). Heats of dilution of potassium chloride: Wüst and Lange, *loc. cit.*; Lange and Leighton, *Z. Elektrochem.*, **34**, 566 (1928); Lange and Monheim, *Z. physik. Chem.*, **150A**, 349, (1931). Heats of dilution of potassium bromide: Wüst and Lange, *loc. cit.*, Hammerschmid and Robinson, *loc. cit.* Heats of dilution of lithium bromide: Lange and Schwarz, *Z. physik. Chem.*, **133**, 129 (1928); Lange and Messner, *Z. Elektrochem.*, **33**, 439 (1927). Heats of dilution of lithium chloride: Lange and Dürr, *Z. physik. Chem.*, **121**, 361 (1926); the results of Lange and Dürr have been extrapolated to $m = 0$ by interpolation of the results on dilute solutions of lithium fluoride and lithium bromide (see *Chem. Rev.*, **9**, 89 (1931)). Heats of dilution of potassium fluoride: Lange and Eichler, *Z. physik. Chem.*, **129**, 285 (1927); Lange and Messner, *Z. Elektrochem.*, **33**, 439 (1927). The sign of $\Delta H_{\infty}^{\text{NaBr}} - \Delta H_{\infty}^{\text{KBr}}$ has been changed for convenience of plotting.

Although in a number of cases the curves of Figs. 1 and 2 are approximately linear at higher concentrations, in no instance do these linear portions extrapolate through the origin as would

(4) The actual measurements (intermediate heats of dilution) extend to about 0.0002 m for 1-1 salts and 0.00005 m for the 2-2 salts. Åkerlöf's activity coefficient plots stop at 0.5 m .

be required if Åkerlöf's rule were equally valid at temperatures above and below 25°. Åkerlöf^{1a} observed this for his activity coefficient plots but only for electrolytes of valence type higher than 1-1. It is felt that the S-shaped portions of the curves of Fig. 1 below 1 m are real and not due to experimental errors. The intersecting of the heats of dilution curves for electrolytes of the same valence type has frequently been observed at low concentrations³ and the selection of another reference salt, such as rubidium fluoride,⁵ would give curves similar to those of Fig. 1 but intersecting the molality axis below 0.5 m .

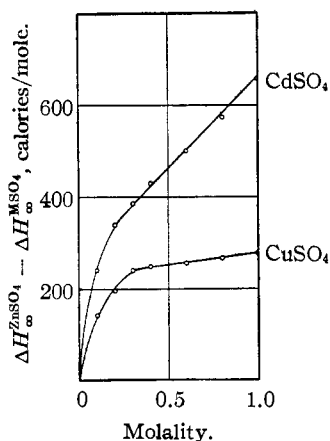


Fig. 2.—Heats of dilution of zinc sulfate (reference electrolyte), cadmium sulfate and copper sulfate: Lange, Monheim and Robinson, *THIS JOURNAL*, **55**, 4733 (1933).

Åkerlöf's rule is therefore not equally valid at all temperatures. Accurate heat of dilution values at temperatures other than 25° are too few to test this point further. The approximate linearity of the curves presented here in the region of higher concentrations is interesting although its significance is not clear and its usefulness is limited by the fact that the linear portions of the curves do not extrapolate through the origin.

Summary

Integral heats of dilution data have been examined to test an extension of a rule proposed by Åkerlöf for activity coefficients of strong electrolytes. The validity of the rule seems to depend upon the temperature.

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(5) Lange and Monheim, *Z. physik. Chem.*, **150A**, 349 (1931).