

Free energies and heats of formation have been calculated.

Attempts to measure the equilibrium constant, starting with vanadium tetroxide obtained by oxidation of the tetroxide in air, gave high values

of the carbon dioxide-carbon monoxide ratio, which decreased with continued reduction. This "surface effect" is somewhat similar to that noted by other investigators.

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## Empirical Heat Capacity Equations for Simple Gases

BY HUGH M. SPENCER AND JOHN L. JUSTICE

The determination of the thermodynamic properties of the simple diatomic gases from the application of statistical mechanics to spectroscopic data by the accurate summation and approximation methods, in the hands of Giauque, Johnston, Gordon and others, has proved to be an important and powerful method. While for gaseous equilibria (and certain gas-solid equilibria where the solids have been investigated thoroughly to temperatures approaching the absolute zero) the results of these calculations may be used and tested directly without even the calculation of the heat capacities, the heat capacity data should be of great utility in the interpretation of many heterogeneous equilibria if they were available in the form of convenient empirical equations.

Some time ago, after these calculations were commenced, Bryant<sup>1</sup> published a series of equations fitted to values derived by the Planck-Einstein equation. In view of the insufficiencies of this equation for such gases as hydrogen, it has seemed worth while to present the equations based upon the more accurate calculations.

Table I presents the results of least square solutions of the data in the form,  $C_p = a + bT + cT^2$ ,

Substance	$a$	$b \times 10^3$	$c \times 10^7$	% deviation		Source
				Max.	Av.	
H <sub>2</sub>	6.9469	-0.1999	4.808	0.49	0.19	(2a)
O <sub>2</sub>	6.0954	3.2533	-10.171	.57	.23	(2b)
Cl <sub>2</sub>	7.5755	2.4244	-9.650	1.13	.59	(2c)
Br <sub>2</sub>	8.4228	0.9739	-3.555	.71	.25	(2d)
N <sub>2</sub>	6.4492	1.4125	-0.807	1.35	.54	(2e)
CO	6.3424	1.8363	-2.801	1.38	.47	(2e)
HCl	6.7319	0.4325	3.697	0.98	.48	(2c)
HBr	6.5776	0.9549	1.581	1.23	.54	(2d)
H <sub>2</sub> O	7.1873	2.3733	2.084	1.05	.38	(2f)
CO <sub>2</sub>	6.3957	10.1933	-35.333	2.17	.76	(2c)

(1) W. D. M. Bryant, *Ind. Eng. Chem.*, **25**, 820 (1933).

(2) (a) C. O. Davis and H. L. Johnston, *THIS JOURNAL*, **56**, 1045 (1934); (b) H. L. Johnston and M. K. Walker, *ibid.*, **55**, 172 (1933); (c) calculated by the authors; (d) A. R. Gordon and C. Barnes, *J. Chem. Phys.*, **1**, 692 (1933); (e) H. L. Johnston and C. O. Davis, *THIS JOURNAL*, **56**, 271 (1934); (f) A. R. Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

at even hundreds from 300 to 1500°K., which is a useful range for heterogeneous equilibria.

The theoretical values for chlorine and hydrogen chloride were calculated by the method of Gordon and Barnes<sup>3</sup> and are for the equilibrium mixtures of the chlorine isotopes. The molecular constants given in Table II were derived from those of Elliott<sup>4</sup> and of Kemble<sup>5</sup> for Cl<sup>35</sup>Cl<sup>35</sup> and HCl<sup>35</sup>, respectively.

TABLE II  
MOLECULAR CONSTANTS OF EQUILIBRIUM CHLORINE AND HYDROGEN CHLORIDE

	Chlorine	Hydrogen chloride
$\omega_e$	561.2	2993.78
$x_e\omega_e$	3.9	53.56
$B_e$	0.2406	10.6041
$\alpha$	0.0017	0.3279
$\zeta$	0	0.01194
$D_e$	$-1.768 \times 10^{-7}$	$-5.326 \times 10^{-4}$
$\beta$	$-3.0 \times 10^{-9}$	$1.209 \times 10^{-5}$
$F_v$	$-9.0 \times 10^{-14}$	$1.46 \times 10^{-8}$

Since the complete treatment of carbon dioxide is not available at present, values were derived on the basis of a linear molecule with completely excited rotational energy, by means of the Planck-Einstein equation (actually derived by use of Table I of Reference 3), using the fundamental frequencies  $\nu_2 = 667.5$ ,  $\nu_1 = 1285$  and  $\nu_3 = 2350.1$  cm.<sup>-1</sup>,<sup>6</sup> the first of which is doubly degenerate. The theoretical values thus calculated are given in Table III ( $R = 1.9869$  cal.).

The theoretical values derived by Gordon and Barnes<sup>2d</sup> for bromine and hydrogen bromide are equivalent to those for the equilibrium mixtures. For the latter this follows because the reduced masses of HBr<sup>79</sup> and HBr<sup>81</sup> are very nearly equal.

Attention may be called to two facts, namely, that the theoretical values are those of the gases

(3) A. R. Gordon and C. Barnes, *J. Chem. Phys.*, **1**, 297 (1933).

(4) A. Elliott, *Proc. Roy. Soc. (London)*, **A127**, 638 (1930).

(5) E. C. Kemble, *J. Opt. Soc. Am.*, **12**, 1 (1926).

(6) P. E. Martin and E. F. Barker, *Phys. Rev.*, **41**, 291 (1932).

TABLE III  
MOLAL HEAT CAPACITIES IN THE HYPOTHETICAL IDEAL  
GASEOUS STATE

T, °K.	HCl	$C_p$ (cal./mole) Cl <sub>2</sub>	CO <sub>2</sub>
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

BY A. L. ROBINSON AND HENRY S. FRANK

Åkerlöf<sup>1</sup> 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  $\gamma_R$  is the activity coefficient of the reference substance of a particular valence type and  $m$  is the molality.<sup>2</sup> 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 error<sup>3</sup> 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).