

Errata: Thermodynamic Functions of the Chloro- and Bromomethanes, Formaldehyde and Phosgene

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Citation: [The Journal of Chemical Physics](#) **6**, 108 (1938); doi: 10.1063/1.1750198

View online: <http://dx.doi.org/10.1063/1.1750198>

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Alterations in the Infrared Absorption Spectrum of Water in Gelatin

The absorption spectra in the region 1–2.5 μ have been recorded in the four following instances with a self-registering instrument of slit widths equivalent to 0.003 μ : (1) a 0.20 mm specimen of gelatin dried to constant weight at 120°C; (2) a portion of the same specimen after it had absorbed an amount of water equal to 35.7 percent of the total weight and swollen to a thickness of 0.28 mm; (3) a 0.09 mm cell of water at room temperature; (4) a 0.17 mm cell of water. The spectrum of (1), in spite of the complexity of the protein molecules involved, can readily be interpreted in terms of CH and NH vibrations; any absorption by OH groups or by possible residual water is not observable. Although there may be slight changes in the NH bands, the main differences in the percentage transmission curves obtained from the reduction of (1) and (2) and of (3) and (4) can fairly certainly be ascribed to alterations in the water spectrum. Since equal effective thicknesses (0.08 mm) of water were involved, these alterations must arise from differences in the structure or in the environment of the water. The following modifications are observed, and provisional causes are assigned.

(a) The 1.44 μ band ($\nu_{\pi} + \nu_{\sigma}$). The maximum absorption is slightly shifted to a longer wave-length in the gelatin specimen, apparently owing to the partial or complete removal of the short wave portion of the band usually associated with the water vapor molecule. This indicates that most or all of the water molecules are bound molecules. Absorption at the maximum is increased but total absorptions in the two instances are comparable owing to a diminution of continuous absorption in the 1.65 μ region.

(b) The 1.96 μ band ($\nu_{\pi} + \nu_{\delta}$). The location of the maximum is practically unaltered. This need not be construed as indicating that unbound molecules are present. For, since this band is a combination of the fundamental deformation frequency (6.1 μ) and the fundamental asymmetric valence frequency (2.7 μ), it should show the characteristics of both fundamentals; and the temperature effects and the hydration studies of Ganz,¹ as well as vapor-liquid band shifts, clearly show opposite behaviors in these two bands. A statement analogous to the last sentence of (a) can also be made in connection with this band.

(c) The 1.79 μ band ($\nu_{\pi} + \nu_{\delta} + \nu_R$). This band, whose frequency differs from that of 1.96 μ by an amount equal to the frequency of "hindered rotation," ν_R ,² is stronger and sharper than in pure water. This seems to indicate, first, that at least some of the water molecules are bound in such a way as to permit hindered rotation about the axis of least inertia and, second, that the average field of potential energy is equivalent to that in pure water but that it is more homogeneous.

(d) A new 1.35 μ band ($\nu_{\pi} + \nu_{\sigma} + \nu_R$). This band is analogous to the 1.79 μ band and is doubtless observable in the gelatin specimen but not in pure water because of a greater homogeneity in the field.

(e) The 2.4 μ region. The absorption in this broad region,

more intense in the gelatin instance, is probably to be interpreted in terms of $\nu_{\pi} + \nu_R$.

(f) The absorption bands at 4.7 μ ($\nu_{\delta} + \nu_R$) and 20 μ (ν_R) should, if observed in gelatin, be sharper than in pure water.

It is the authors' opinion that the absorption at 3 μ found by Buswell, Krebs and Rodebush³ in a gelatin specimen dried for 14 hours at 122°C is caused by protein NH groups rather than by residual water.

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January 13, 1938.

¹ Ganz, Ann. d. Physik. **28**, 445 (1937).

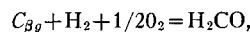
² Ellis, Phys. Rev. **38**, 693 (1931); Cartwright, Phys. Rev. **49**, 470 (1936).

³ Buswell, Krebs and Rodebush, J. Am. Chem. Soc. **59**, 2603 (1937).

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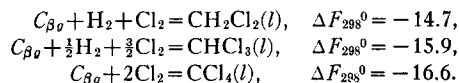
(J. Chem. Phys. **6**, 25 (1938))

Because of a systematic error the values of $-(F^0 - E_0^0)/T$ in Tables VI and VIII are too large by 1.987 cal./°K mole. The value of ΔE_0^0 for the reaction



as calculated from the work of Newton and Dodge should be -26.0 kcal./mole instead of -27.0 kcal./mole. This leads to a final value of ΔE_0^0 for this reaction of -26.5 kcal./mole in place of -27.2 kcal./mole.

For the free energy of formation of the liquid chloro-methanes



The free energies of formation of the gases are given in Table X.

TABLE X. ΔF^0 of ideal gases.

T	H ₂ CO	COCl ₂	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄
298.1	-25.2	-49.7	-13.0	-14.3	-15.1	-15.5
350	-24.8	-49.1	-11.8	-13.1	-13.7	-13.8
406	-24.4	-48.4	-10.6	-11.3	-12.3	-12.1
500	-23.5	-47.2	-8.0	-9.2	-9.5	-8.9
600	-22.5	-45.9	-5.4	-6.6	-6.7	-5.5
700	-21.5	-44.7	-2.6	-4.0	-3.8	
800	-20.5	-43.4	+0.1	-1.3	-0.7	
900	-19.4	-42.0	+3.0			
1000	-18.3		+5.8			
1100	-17.2		8.7			
1200	-16.1		11.5			
1300	-15.0					
1400	-13.9					
1500	-12.8					

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January 14, 1938.