manner described (*1*); also described are the analytical methods (*1, 8*). Experiments were carried out in the temperature range 5° to 27°C at temperatures held constant within 0.1°C. Evolution of oxygen was followed gasometrically. Photochemical experiments were performed by use of either (i) the light output of a medium-pressure Hg-vapor lamp at wavelengths greater than 310 nm (light of lesser wavelength being removed by a glass filter); or (ii) (particularly for the establishment of quantum yields) a Mazda-ME/D high-pressure mercury lamp, the collimated light beam being filtered by a Chance glass filter (No. OX1a) and 1 cm of a 125-g/liter solution of $CuSO_4 \cdot 5H_2O$; at 365 and 366.3 nm this transmits 65 percent of the incident light, but only 3 percent at the weaker line at 313.5 nm and 5 percent at 405 nm. The collimated beam then passed the thermostated, cylindrical quartz reaction vessel (with a light path of 5 cm), in series with the identical actinometer cell containing uranyl oxalate actinometer solution (*14*).

Light absorption in the reaction vessel was not total; it changed during the reaction with change in concentration of the complex. This change, at the concentrations of reactants employed, proved to be directly proportional to concentration of H_2O_2. Accordingly, light absorption was determined by difference between actinometer results of experiments in which the photolysis cell was filled with either distilled water or experimental solution. The integrated value of light absorbed during an experimental run was determined from actinometer data, concurrently. The value for $\phi_{\text{actinometer}}$ at the wavelength used was taken to be 0.48 (*14*). When thermal, catalytic, dark, control experiments were run in the photochemical vessel at various temperatures, the rate constants and activation energy previously obtained (*1, 13*) were confirmed. Control experiments entailed illumination of solutions of hydrogen peroxide or ferric ion; no evolution of oxygen was observed.

The thermal dark decomposition at *p*H 2.10, in solutions containing concentrations of the order of 2 to 5 $\times$ $10^{-3}M$ Fe^{3+} and, initially, of the order of $0.2M$ H_2O_2, gave first-order reaction with respect to H_2O_2. When the thermal reaction was allowed to proceed, and at the same time the vessel was illuminated, the plot of log H_2O_2 versus t again gave strictly straight lines. Thus the combination of the two reactions appears to be of first order. Using the known activation energy, 20 kcal/mole, of the thermal reaction, and subtracting at every temperature the contribution of the thermal reaction alone (thus assuming that the two reactions proceed independently of each other), we could obtain the apparent rate constant of the light-induced reaction and its activation energy. The results (Table 1) show that when one uses this procedure the rate constant of the light-induced portion of the reaction appears to be independent of temperature within experimental error. This finding contrasts with results with the thermal reaction, which shows a large activation energy. Therefore the light-induced reaction becomes dominant with decreasing temperature. Accordingly, experiments to determine the quantum yield at $\sim$ 365 nm, and the effects on it of variations in *p*H and reactant concentration, were run at a constant low temperature of 5.5°C and at constant ionic strength of 0.25. The results (Table 2) show that the quantum yield, which is greater than 1, increases both with increase in initial concentration of H_2O_2 and with decrease in *p*H. Experiments with varying concentrations of Fe^{3+} (from 2.1 to 5.4 $\times$ $10^{-3}M$), at constant initial concentration of H_2O_2, indicate an increase in chain length with decrease in concentration of Fe^{3+}. The occurrence of the temperature-independent chain reaction thus observed is consistent with the occurrence of a light-induced free-radical mechanism initiated by

$$Fe^{3+}HO_2^- \xrightarrow{h\nu} Fe^{2+} + HO_2 \qquad (5)$$

(rather than by H_2O_2 or $Fe^{3+}OH^-$) and propagated by the reactions of Fe^{2+} with H_2O_2 (*7*) and of the radical intermediates with H_2O_2. The detailed mechanism and the effects of other factors, such as light intensity and radical scavengers other than H_2O_2, on the yields remain to be investigated.

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Thermal Properties of Water: Discontinuities Questioned

Abstract. *Reports of discontinuities have been tabulated, and those dealing with vibrational spectrum and volume have been examined in detail. No evidence has been found of any discontinuity greater than experimental error.*

During the last thirty years there have been many reports (Table 1) that the physical properties of water show discontinuities at certain temperatures. The discontinuities, often described as

Table 1. Reports of thermal discontinuities for liquid water.

Temperature (°C)	Report
Vibrational spectra	
30–40, 65–75	Baistrocchi *et al.* (*8*)
37	Luck (*11*)
43	Ganz (*12*)
40	Magat (*13, 14*)
Volume and compressibility	
50	Antonoff *et al.* (*17*)
60	Tammann (*26*)
15, 30	Lavergne *et al.* (*20*)
13, 35, 60	Forslind (*22*)
10, 21, 29, 33	Qurashi (*28*)
Surface tension	
60	Tammann (*26*)
13	Forslind (*22*)
13	Timmermans *et al.* (*32*)
15, 30, 45, 60	Drost-Hansen *et al.* (*33*)
Viscosity	
35–45	Magat (*14*)
60	Tammann (*26*)
12, 35, 55	Forslind (*22*)
6, 11, 14, 19, 24, 30, 39 46, 53, 58, 66	Qurashi *et al.* (*34*)
46, 55	Antonoff *et al.* (*35*)
Other properties	
37	Magat (*14*)
60	Tammann (*26*)
35	Vlès (*6*)
15, 30, 45, 60	Drost-Hansen (*33*)
34	Franks and Ives (*1*)
30–40	Feates and Ives (*2*)
36	Othmer and Thakar (*3*)
30	Frontas'ev (*4*)

"kinks" or as transitions of higher order, have been interpreted as indicating a stepwise collapse of some sort of structural order (*1–5*). Anomalies in the growth and activity of biological systems at various temperatures have been ascribed to such transitions (*6, 7*).

The possible occurrence of discontinuities in the physical properties of liquid water should certainly be investigated with care. We have therefore reexamined the reports of discontinuities, and in this report we consider in detail those dealing with the vibrational spectrum, volume, and compressibility of water—in measuring which properties we are experienced.

Baistrocchi and Costa (*8*) reported discontinuities at 30° to 35°C and at 65° to 70°C in the wavelength and absorbance of the near-infrared band of water at 0.97 μ. The results (Fig. 1) of our restudy (*9*) of this band show no evidence of discontinuities beyond the experimental error, which is of the same order as the steplike discontinuities reported (*8*); not reported (*8*) was the experimental error, which must have been as great as ours. The uncertainty in the determination of wavelength of this band is about $\pm$ 0.003 μ; it is not a matter of technique, but is caused by the great width and the complicated changes of band shape with temperature; this is a common characteristic of the infrared bands of water in the overtone region (*10*).

The discontinuity reported (*11*, fig. 6) at about 37°C appears to be an artifact arising from Luck's plotting of the temperature dependence of the wavelength of "the most intense maximum" of the band near 1.15 μ. Our repetition of Luck's experiments on this band has shown that the intensities of the two components at about 1.19 μ and about 1.16 μ cross near 40°C, the higher-wavelength component being more intense at lower temperatures, and the lower-wavelength component more intense at higher temperatures. Wavelength and intensity of each component vary continuously with temperature.

Baistrocchi and Costa (*8*) and Ganz (*12*) reported discontinuities in the wavelength of the near-infrared band at 0.75 μ, but differed as to the kind and position of the discontinuities (Fig. 2). These discontinuities also are within the uncertainty of the wavelength determination, which we found to be within about 0.005 μ for this band.

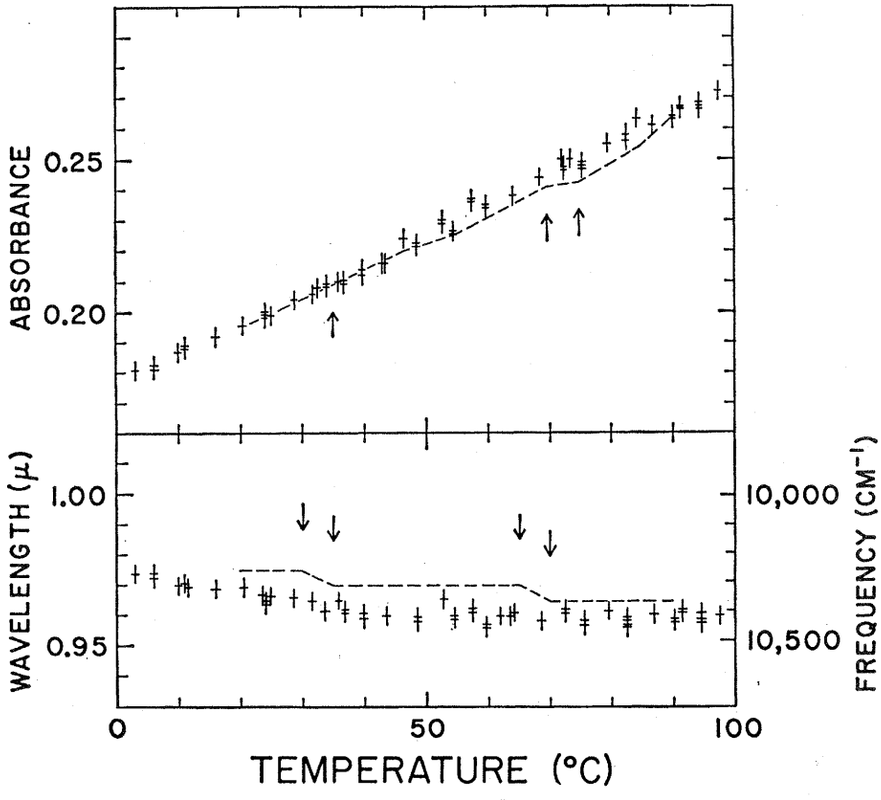

Fig. 1. Temperature variation of absorbance and wavelength of the H_2O band at 0.97 μ. Crosses, our data; broken line, replotted data of Baistrocchi and Costa (*8*); arrows indicate the supposed discontinuities.

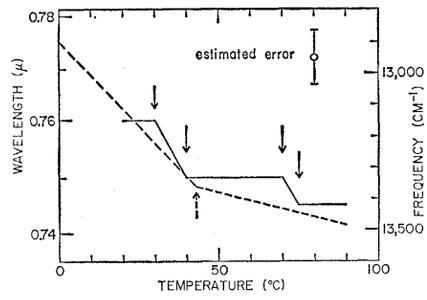

Fig. 2. Variation of wavelength of the H_2O band at 0.75 μ with temperature, as reported by Baistrocchi and Costa (*8*) (solid line) and by Ganz (*12*) (broken line). Arrows indicate the discontinuities claimed.

The finding of Magat (*13, 14*) that the Raman band at 3800 cm^{-1} and the bands below 700 cm^{-1} "disappear in the neighborhood of 40°C" is refuted by recent demonstration (*15*) that the intensity of these bands decreases gradually between 0° and 90°C.

Our recent study of many infrared bands of liquid H_2O, HDO, and D_2O between 0° and 130°C (*10, 16*) showed no evidence of discontinuities in the variation of wavelength and absorbance with temperature.

Antonoff and Conan (*17*) reported a discontinuity at 50°C in thermal expansion, with the density at that temperature about 100 parts per million higher than would be expected from a smooth curve joining the points at higher and lower temperatures. The density of water in this region has since been found, however, to be a smooth function of temperature to within 3 ppm by Kretschmer (*18*) and within 1 ppm by Kell and Whalley (*19*).

Lavergne and Drost-Hansen (*20*) have shown that 24 of the 114 points in the data of Chappuis (*21*) are better represented by three parabolic segments than by a single parabola; those data as a whole, however, do not fall into three segments. Forslind (*22*) found an indication of volume anomalies in a table in the 1912 edition of the *Landolt-Börnstein Tables* (*23*), based on a book published in 1859 (*24*); he found no such indication in Dorsey's more recent data (*25*). The reports (*14, 26*) of discontinuities in the isothermal compressibility of water are disproved by more recent studies (*19, 27*).

Qurashi (*28*) found several discontinuities in the densities in the *International Critical Tables* (*29*); however, these density data for the range 0° to 40°C are the means of values from a

single equation given by Thiesen *et al.* (*30*) for 0° to 42°C, and of the values from three cubic equations used by Chappuis (*21*) to cover the ranges 0° to 10.3°, 10.3° to 13°, and 13° to 41°C. Thus these data had already been smoothed on the assumption that they were free from kinks. Had Qurashi gone directly to the equations, he would have found discontinuities only at the change of function in Chappuis's work; other kinks are computational artifacts.

The pattern common to all reports that we have examined, including those that we have not discussed in detail, is that the size of the supposed discontinuity is comparable to the degree of accuracy of the measurement. Experimenters commonly overestimate their degree of accuracy (*31*), and errors often produce odd points that do not fit a smooth plot. Accordingly, we believe that the discontinuities so far reported in the properties of liquid water are artifacts. The wide scatter of the temperatures at which discontinuities have been reported strongly supports this conclusion. The balance of evidence is that the physical properties of water *do* vary continuously with temperature.

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2 June 1966

Species Specific Effect of Acetylcholine on Bivalve Rectums

Abstract. *The pharmacology of acetylcholine and 5-hydroxytryptamine on the rectums of* Katelysia rhytiphora *and* K. scalarina *was found to be similar, in general, to that of other bivalves. However, while acetylcholine causes a fast twitch in the rectum of* K. rhytiphora, *the activity and tone of the* K. scalarina *rectum are depressed except at high concentrations of the drug. The two species can be distinguished by these responses, and, therefore, these rectums are useful experimental objects for studying the physiology of molluscan visceral muscle.*

Animal physiologists often need to compare the results of similar experiments performed on different species of animals (*1*, *2*). The usual assumption is that, if the species are sufficiently closely related and if the system under consideration is sufficiently complex, then the probability that differences are based on species is small. This report describes some relatively simple pharmacological responses of homologous tissues from two sympatric intrageneric species.

Acetylcholine (ACh) has three observed effects on the rectum of the clam *Mercenaria mercenaria*: depression of tone and rhythmic activity, phasic contraction, and tonic contraction (*1*). These effects are dependent on the dose of ACh and the tone

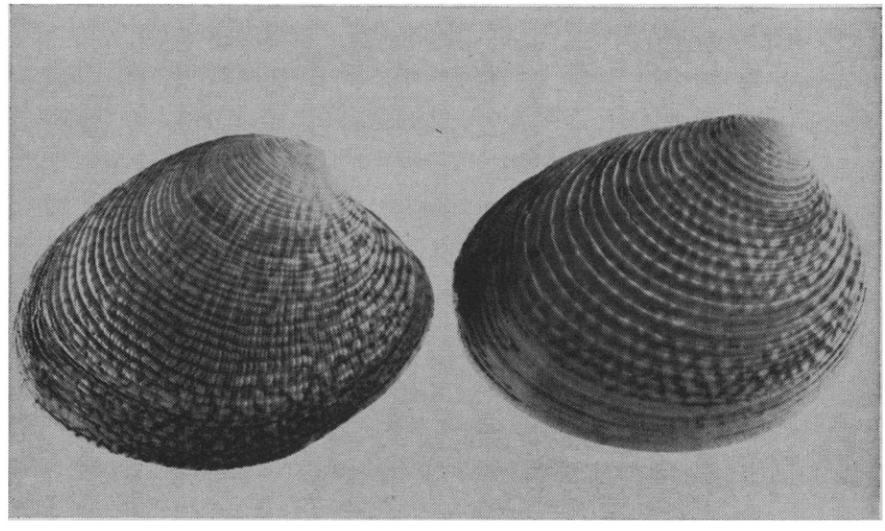

Fig. 1. *Katelysia rhytiphora* (left) is distinguished by the anastomosing concentric ridges and by the fine striations radiating from the umbo. *K. scalarina* (right) has stronger, uninterrupted, smooth concentric ridges and no radiating striations (*6*). Both specimens are right valves coming from animals collected together at Blairgowrie, Victoria, Australia. Enlarged × 1.4.