formation does not necessarily involve the i-steroid structure.

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Change with Temperature of the Heat of Wetting of Dry Cellulose in Water, and its Bearing on the Specific Heat of the Adsorbed Water and of the Swollen Cellulose

THE heat of wetting of dry standard cellulose in water was measured at temperatures between 0° C. and 40° C. The cellulose and the experimental technique were those described previously[1]. The heat of wetting decreases with the rise of temperature as shown by the following values, which represent the means of several experimental results at each temperature :

Temperature	Heat of wetting (cal./gm. dry cellulose)
0° C.	11·84
10	11·51
20	11·01
25	10·80
30	10·70
40	10·14

The decrease appears to be linear in the range tested, and amounts to about 0·042 cal./degree/gm. cellulose.

The heat of wetting represents the decrease in the heat content $(-\Delta H)$ of the 'dry cellulose–water' system through the wetting process. The variation of the change of heat-content with temperature represents the difference between the heat capacity of the system before and after wetting as given by Kirchhoff's equation :

$$d(\Delta H)/dT = \Delta C_p.$$

$d(\Delta H)/dT$ here is positive. It means that the heat capacity of the system after wetting (swollen cellulose-adsorbed water) is more than its heat capacity before wetting, that is, more than the sum of the heat capacity of the dry cellulose and that of the water it can adsorb. Such increase in the heat capacity of the system resulting from wetting may be due to some change either in the water, on being taken up by the dry cellulose, or in the cellulose itself, on swelling, or due to a change in both.

As to the water, it may be suggested that adsorption causes some depolymerization of the liquid. This may take place either directly by the splitting of the adsorbed polymerized molecules on the surface of the cellulose, or indirectly by the selective adsorption of the simple molecules, and thus disturbing the equilibrium between the simple and the polymerized molecules of the liquid. Depolymerization of liquid water seems to cause an increase in its specific heat, as suggested by the thermal measurements by Koch[2]. These show that the specific heat C_p of the liquid decreases with the increase of pressure at constant temperature. At the same time, it is reasonable to think that the increase of pressure would cause an increase in the degree of polymerization. Again, Koch's measurements show that C_p increases with the rise of temperature, while this would decrease the degree of polymerization. Thus it may be con-

cluded that the adsorbed water has a higher specific heat than that of ordinary liquid water due to a smaller degree of polymerization.

As to the cellulose, its swelling is a process analogous to depolymerization, since it represents a partial separation of the cellulose micelles. Thus it may be expected that the swollen cellulose would also have a higher specific heat than that of dry cellulose.

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Stability of Complex Salts of Bivalent Metals

IN the study of absorption spectra of inner complex salts of acetylacetone with bivalent metals, we have found the absorption maximum shifts towards longer wave-lengths in the following order :

Acetylacetone	273 mμ	
Zn(acetylacetone)$_2$	280 ,,	alcoholic
Co(acetylacetone)$_2$	282 ,,	solution
Ni(acetylacetone)$_2$	294 ,,	
Cu(acetylacetone)$_2$	296 ,,	

The above absorption bands of complex salts are due to the acetylacetone molecules co-ordinated to the central metal, and the displacement of the position indicates the degree of deformation or polarization of ligand molecules. In other words, the copper complex salt, which shows the largest displacement, combines with acetylacetone most firmly and is most stable. The chemical properties, such as stability against alkali, thermal decomposition, exchange of central metal with other metals in the aqueous solution, etc., also show the remarkable stability of the copper complex salt. The manganous and ferrous complexes are very unstable and easily oxidized to the trivalent state. Arranged in order of stability, the series is, therefore,

$$Cu > Ni > Co > Zn > Fe, Mn.$$
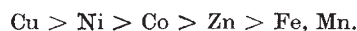
Recently, several studies on the stability of complex salts of bivalent metals with salicylaldehyde[1,2], sodium salicylaldehyde sulphonate[3], o-formylnaphthoxide[3] and β,β',β"-triaminotriethylamine[4] have been published. These studies gave the nearly identical stability series of bivalent metals, namely,

$$Zn < Cu > Ni > Co > Fe > Mn.$$

Our results are also in accord with these results, and add another example to the stability series of bivalent metals.

A part of these results were published in Japanese (J. Chem. Soc. Japan, 69, 70 (1948)).

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