HEAT CAPACITY OF GELS
PRELIMINARY INVESTIGATION

J.H. MENNIE

HALIFAX, 1930.

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Heat Capacity of Gels
Preliminary Investigation

By J. H. Mennie

Fish muscle consists of 15-20% protein, 1-2% inorganic salts and about 80% water. In addition, a greater or less percentage of fat may be present with a correspondingly lower percentage of water. Part of the water may be held more or less firmly, in some form of chemical combination by the protein - so called "bound" water. The remainder acts as a solvent for the inorganic salts. We have then (ignoring fat) a colloidal gel of protein permeated by a dilute salt solution.

A salt solution does not freeze completely at a fixed temperature. The presence of dissolved salt lowers the freezing point of the water. When the temperature has fallen sufficiently, ice begins to form but the removal of water in the form of ice concentrates the solution so that the freezing-point is further lowered. As the temperature continues to fall, more and more ice separates and the unfrozen solution becomes more and more concentrated. Eventually the solution becomes saturated and further removal of heat causes ice and salt to separate simultaneously from the solution without further lowering of the temperature, until the whole mass is frozen solid. The temperature at which this occurs is called the eutectic temperature.

This is presumably what occurs in the freezing of fish. Fish muscle does not begin to freeze until a temperature of about -1°C. is reached. Only part of the water is converted to ice at this temperature. As the temperature falls lower and lower, more and more ice forms. The eutectic temperature of muscle juice has not been determined. According to Plank (see Kallert, 1926), in meat 80% of the water is frozen at -10°C, 91% at -20°C., 99.9% at -50°C., and 100% only at -55°C. These figures are said to be based on heat capacity measurements. They do not give any indication of a eutectic temperature. The effect of the presence of the protein is not entirely clear. It would probably not contribute appreciably to the freezing-point lowering. On the other hand, if part of the water is "bound" to the protein, this part of the water would probably not freeze at all. Moran (1926) from experiments on gelatine gels concluded that in the case of gelatine the "bound" water amounts to 0.53 gms. water per gm. gelatine. Gels of this concentration (65.5%) remained clear and transparent showing no indication of ice formation, even at the temperature of liquid air.

Heat capacity measurements should throw some light on the mechanism of freezing in gels. It was thought desirable to make some measurements on material of more readily controllable composition than fish muscle and gelatine was selected. The heat capacity measurements were made in the usual manner in the adiabatic calorimeter used by Chipman and Langstroth (1929).

The heat capacity curve for a dilute salt solution (1.7%) was first obtained. (Table I and Figure 1). A curve was plotted from data obtained from the International Critical Tables using the method indicated by Barnes and Maass (1930). This is the curve shown in Figure 1. It will be seen that it reproduces the experimental values very closely. The break in the curve at the eutectic temperature and the effect of supercooling below the eutectic are evident.

Heat capacity curves were obtained for gelatine dried to constant weight at 100°C., and for 20%, 40% and 66% gels. These were made up by weight from granular "Bacto"-gelatine, the moisture content having been determined and allowed for. For each determination, the gel was frozen in carbon-dioxide-ether mixture and then warmed to the desired temperature. Results are shown in Table II and Figure 2. All three gels show a break in the curve resembling that at the eutectic in Figure 1. This may represent the eutectic point of the inorganic matter present in the gelatine. (ash about 3%).

For comparison, Chipman and Langstroth's curve for cod and haddock (80% water) is also shown. It will be noted that while the heat capacity above the freezing-point is identical for cod muscle and 20% gelatine, the frozen gelatine has a noticeably lower heat capacity. This suggests that in the gel a part of the water is present as "bound" water and is unfrozen, while in the fish muscle there is little or no "bound" water.

The foregoing is merely a preliminary investigation of the subject of the heat capacity of gels and no attempt at a thorough discussion of results has been made.

TABLE I

Heat Capacity to 20°C of a 1.7% Sodium Chloride Solution.

Temp.	Calories	Temp.	Calories	
0°C.	19.1	-22.2	107.9	
-1.5	54.2	-22.5	104.6	X
-1.5	61.5	-22.7	104.9	X
-2.0	63.0	-23.7	105.1	X
-5.7	86.4	-24.4	105.4	X
-10.5	95.1	-24.5	107.9	
-15.4	99.9	-24.7	108.7	
-17.3	101.4	-41.3	116.6	
-19.7	103.1	-65.4	126.1	
-21.5	107.7			

X - Supercooled.

TABLE II

Heat Capacity to 20°C of dry gelatine and 66%, 40% and 20% gels.

Temp.	Dry	66%	40%	20%
0°C	5.6	13.0	15.5	17.6
0				17.8
0				17.8
-1				50.2
-1.5				55.7
-2		16.5	25.3	59.8
-3			33.7	
-4			39.0	
-5		17.9		72.9
-6			X20.4	
-6			44.8	
-8	7.7			
-8	7.9			
-9			49.0	
-10		X19.6	50.7	77.2
-10		20.9	50.8	
-10		21.1	50.9	
-12			51.1	
-12			51.8	
-15.1				81.7
-15.5			53.6	
-20.2				84.5

Continued on Page 4.

Table II (continued)

Temp.	Dry	66%	40%	20%
-20.3	11.2	27.6		83.4
-20.4			55.9	
-30.2				89.2
-30.3				87.0
-30.5		31.7		
-30.6			60.7	
-40.2				91.3
-40.2				92.8
-40.4			63.8	
-40.5		35.4		
-40.6	16.4			
-50.2		39.7		
-50.4			68.0	96.3
-60.4		43.5		
-60.6	20.2			100.3
-60.8			72.2	
-70.9				103.2
-78.5	22.4	47.9	77.5	105.9

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FIG. I.

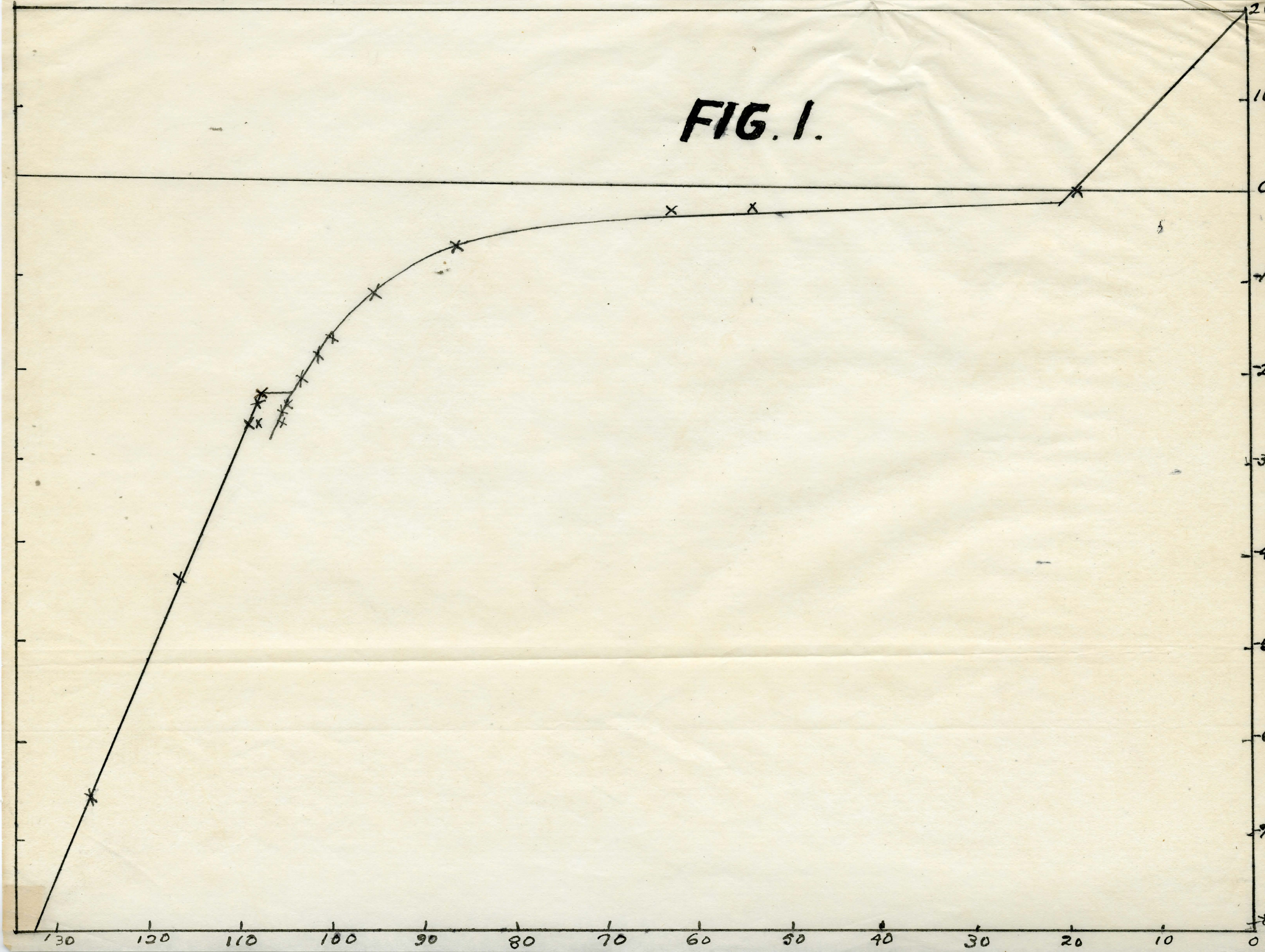
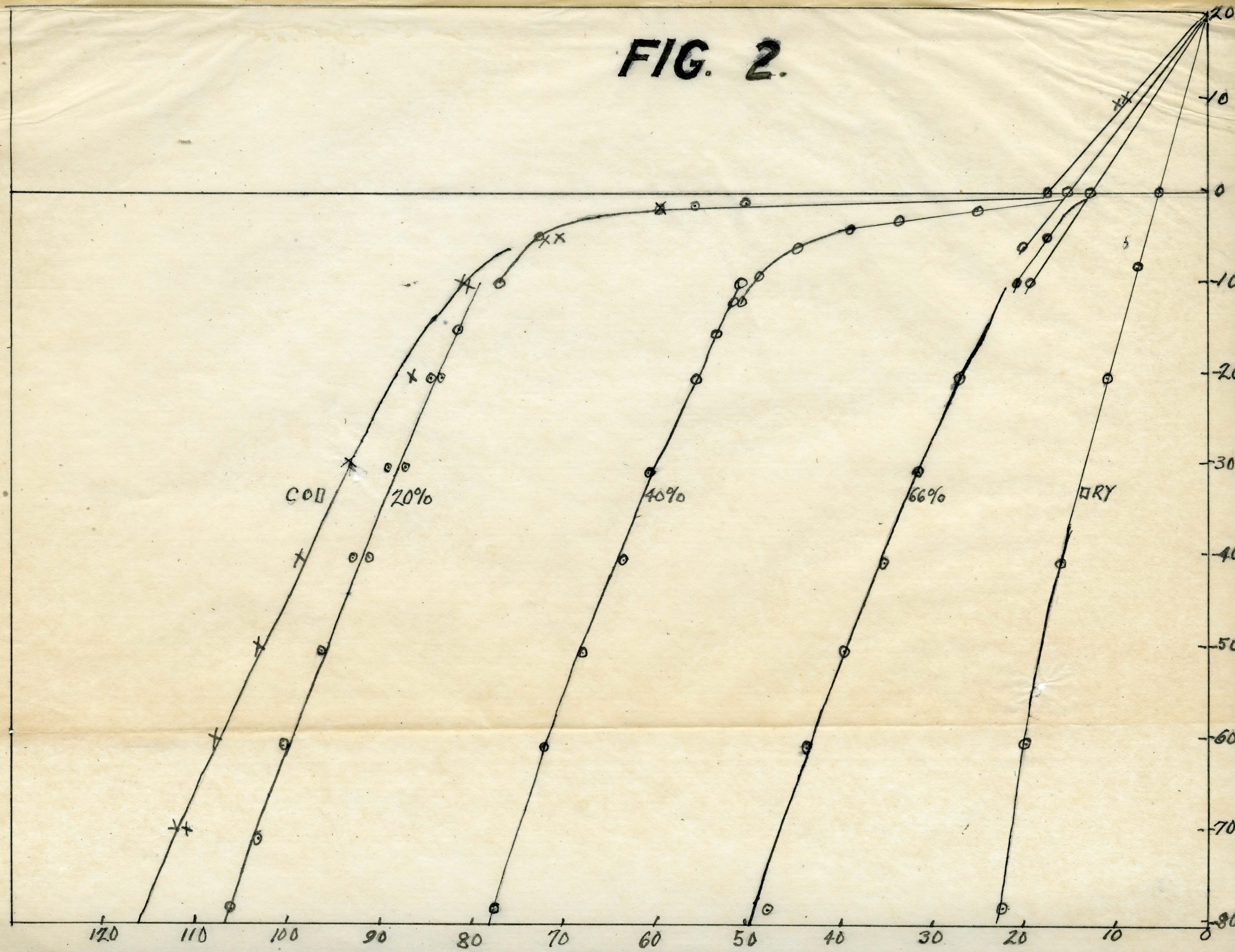


FIG. 2.



COII
20%
40%
66%
DRY
120
110
100
90
80
70
60
50
40
30
20
10
0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80