APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned does not necessarily endorse or approve any statements made, opinion expressed, or conclusion drawn therein, but approves the thesis only for the purpose for which it is submitted.

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Date May 29, 1957

HEAT CAPACITIES OF AQUEOUS SOLUTIONS OF MILLING YELLOW NGS DYE

A THESIS

Submitted
to
The Department of Chemical Engineering
of the
University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree
of
Bachelor of Science

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by

Claude F. Rinehart

June 1957

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CHAPTER I

SUMMARY

The purpose of this investigation was to determine the heat capacities at constant pressure of aqueous solutions of Milling Yellow NGS dye. It was also desired to find out if a phase change occurs in dye solutions which change from non-spontaneously to spontaneously doubly refracting liquids.

The study was limited to those dye solutions which had a concentration between 1.001 per cent and 2.762 per cent dye by weight. It was also limited to a temperature range of 25° to 100°C. For this study a small calorimeter, which was operated approximately adiabatically, was assembled. The calorimeter was equipped with an electrical immersion heater which introduced energy into the dye solution under investigation.

The heat capacities of the dye solutions studied were found to be close to the heat capacity of water. They ranged from 0.994 cal/gm-°C for a 1.001 per cent dye solution to 0.980 cal/gm-°C for a 2.762 per cent dye solution. A check on several solutions showed that the results were reproduced to within 0.7 per cent or better. In two of the more concentrated solutions, phase change indications were observed. The indications, which were recognized by a

change in thermal energy at constant temperature, were rather small, only two or three calories per gram.

As a result of this investigation, it is concluded that:

1) The dye concentration has very little effect on the heat capacity of the dye solution.
2) Strong evidence points toward the existence of a phase change that is associated with the change from a non-spontaneously to a spontaneously doubly refracting dye solution.

It is recommended that a further study of the phase change be carried out with equipment that can more precisely detect small thermal changes.

CHAPTER II

INTRODUCTION

The members of the staff of the Department of Chemical Engineering of The University of Tennessee have become very much interested in aqueous solutions of Milling Yellow NGS dye. This interest originally developed when three members of the staff, Peebles, Garber, and Jury (1)*, conducted studies of flow phenomena utilizing the doubly refracting** property of aqueous Milling Yellow NGS dye solutions. Since that time, these dye solutions have been used in many investigations, including this one. It should be pointed out that these mixtures of dye dissolved in water are believed to be colloids rather than true solutions.

Most aqueous solutions of Milling Yellow NGS dye are doubly refracting. If observed under polarized light, the doubly refracting solution shows stress patterns set up in itself when in motion. The intensity of this doubly refracting property is dependent upon the salt concentration as well as the dye concentration. Solutions have been made up with the dye concentration much less than 1.0 per cent

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*Numbers in parentheses refer to Bibliography entries.

**Doubly refracting liquids produce characteristic interference patterns when viewed in polarized light while in motion. This phenomena is described in detail by Peebles, Garber, and Jury (1).

and a low salt concentration and have shown no doubly refracting property at all.

Another interesting property of aqueous Milling Yellow NGS dye solutions is that they become spontaneously doubly refracting when the dye concentration is somewhat above 2.0 per cent. A spontaneously doubly refracting liquid transmits the polarized light even though the liquid, itself, is not in motion. It is believed that some type of phase change occurs when the dye solution changes from a non-spontaneously to a spontaneously doubly refracting state. It was anticipated that such a phase change, if existing, could be detected by heat capacity measurements.

The primary purpose of this investigation was to determine the heat capacities at constant pressure of aqueous solutions of Milling Yellow NGS dye and to investigate the phase change believed to occur in the more concentrated solutions. A number of solutions were made up and studied. The concentrations were in a range from 1.001 per cent to 2.762 per cent dye by weight. The temperature range over which these solutions were studied was from 25° to 100°C.

A small, approximately adiabatic calorimeter was used to determine the heat capacity and investigate the phase change of the Milling Yellow NGS dye solutions. The thermal energy was added to the dye solution in the calorimeter by an electrical heating system.

CHAPTER III

THEORY

Heat Capacity and Thermal Transition

The heat capacity (2) of any substance is defined as the energy required to raise the temperature of a unit weight of the substance one degree. Most frequently it is expressed in calories per gram per degree centigrade or BTU per pound per degree Fahrenheit.

The heat capacities (3) are one of two types, depending upon whether the substance is heated at constant volume or at constant pressure. When a substance is heated at constant volume, all the energy supplied goes to increase the internal energy of the substance, and this increase in internal energy is called the heat capacity at constant volume, C_v. However, the substance may be heated at constant pressure where energy must be supplied not only to increase its internal energy, but also to make possible the expansion of the substance against the confining atmospheric pressure. The heat capacity at constant pressure, C_p, must therefore be larger than that at constant volume. The difference between C_p and C_v is very slight in liquids because volume changes on heating are very small.

In mathematical terms, C_p is defined by the following

equation:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

where

Q = energy added to the substance

T = absolute temperature

P = pressure

In reference to the study of a phase change, it should be pointed out that there are many different types of phase changes. But, they all have one thing in common. Each phase change is accompanied by a change in thermal energy, and this energy change may be great or very small. In view of this fact, a phase change may be determined by thermal analysis of a substance.

Thermal analysis of a substance may be carried out by heating it at a constant rate while making time and temperature measurements of the substance. Temperature is plotted versus time, and a zero slope, if one occurs, means that a phase change occurred at the corresponding temperature. One can also detect a phase change by plotting the energy added versus temperature. In this case, a phase change will be pointed out by the occurrence of an infinite slope for a portion of the curve.

Heat Transfer Coefficient

The basic law of heat transfer can be written in the form of the following rate equation:

$$\text{Rate} = \frac{\text{driving force}}{\text{resistance}}$$

The rate is the heat transfer rate, and the driving force is the temperature drop across the substance transferring the heat. The reciprocal of the resistance is the overall heat transfer coefficient, U, times the area, A, through which heat is being transferred. Thus,

$$U \times A = \frac{\text{heat transfer rate}}{\text{temperature drop}}$$

CHAPTER IV

EQUIPMENT AND MATERIALS

The equipment used in this investigation consisted of an evaporating vessel, a calorimeter, metering devices, and a laboratory oven.

The evaporating vessel was used in preparing and concentrating the dye solutions. It was an open-top container of rectangular shape, was constructed of stainless steel, and had a capacity of approximately thirty gallons. The heating element in the bottom of the container was a stainless steel pipe inside which steam was condensed.

A simple calorimeter, as shown in Figures 1 and 2, was assembled for the investigation. The body of the calorimeter was a Dewar flask. A cork stopper was chosen for the calorimeter top because of its low thermal conductivity. Calorimeter accessories were a knife-type immersion heater (115 volts, 125 watts), a partial immersion thermometer (0°-100°C, graduated to 0.1°C), and a mechanical stirrer. The stirrer was driven by a variable speed electric motor, rated at 115 volts A.C., 0.31 amp, 1/100 hp. and 0-5000 rpm.

Electrical energy was supplied to the immersion heater as shown by the circuit diagram in Figure 3. The power input was controlled by a Variac (115 volts, 60 cycles, 5 amp) and was measured with an A.C. voltmeter (0-150 volts)

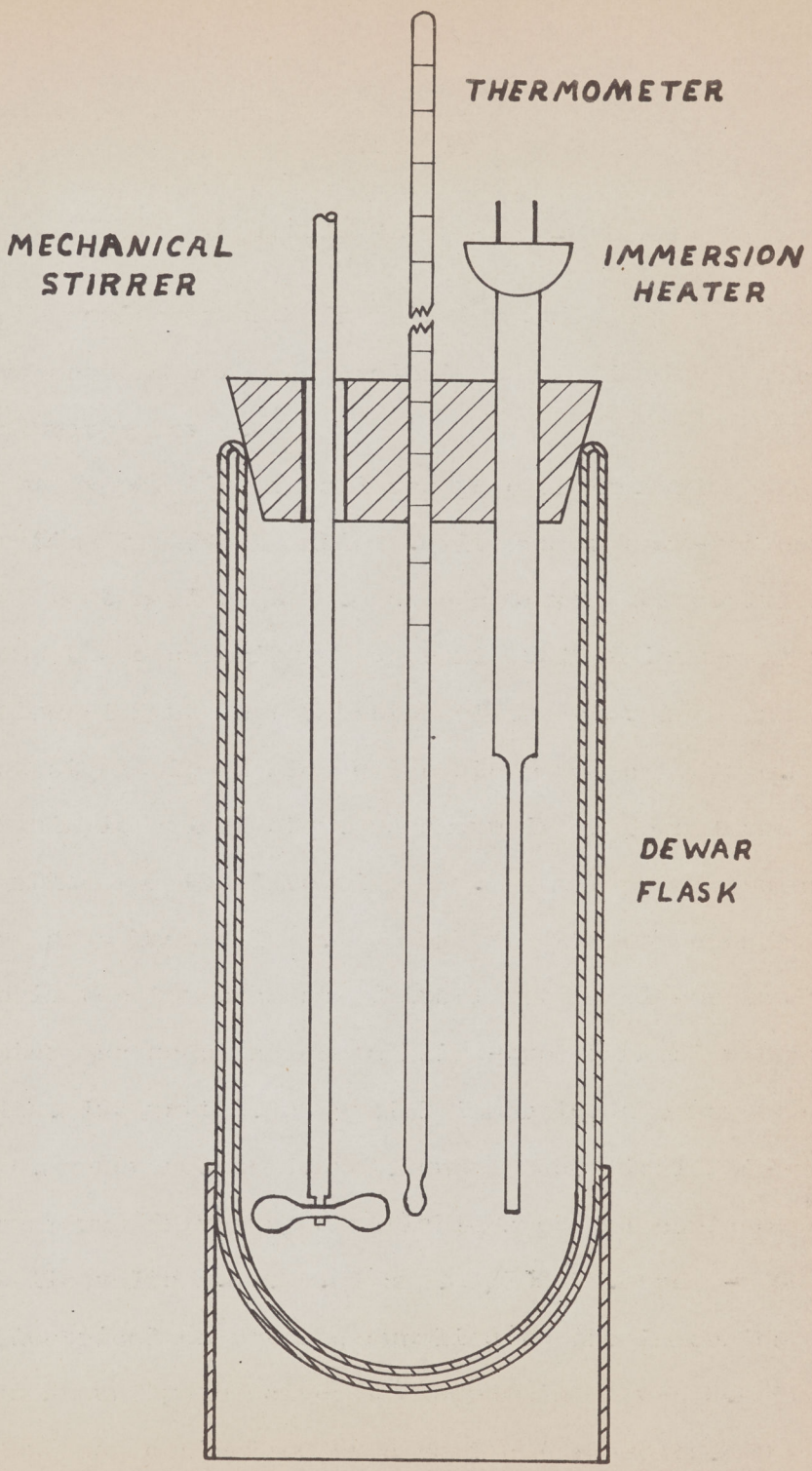


FIGURE 1
DIAGRAM OF CALORIMETER

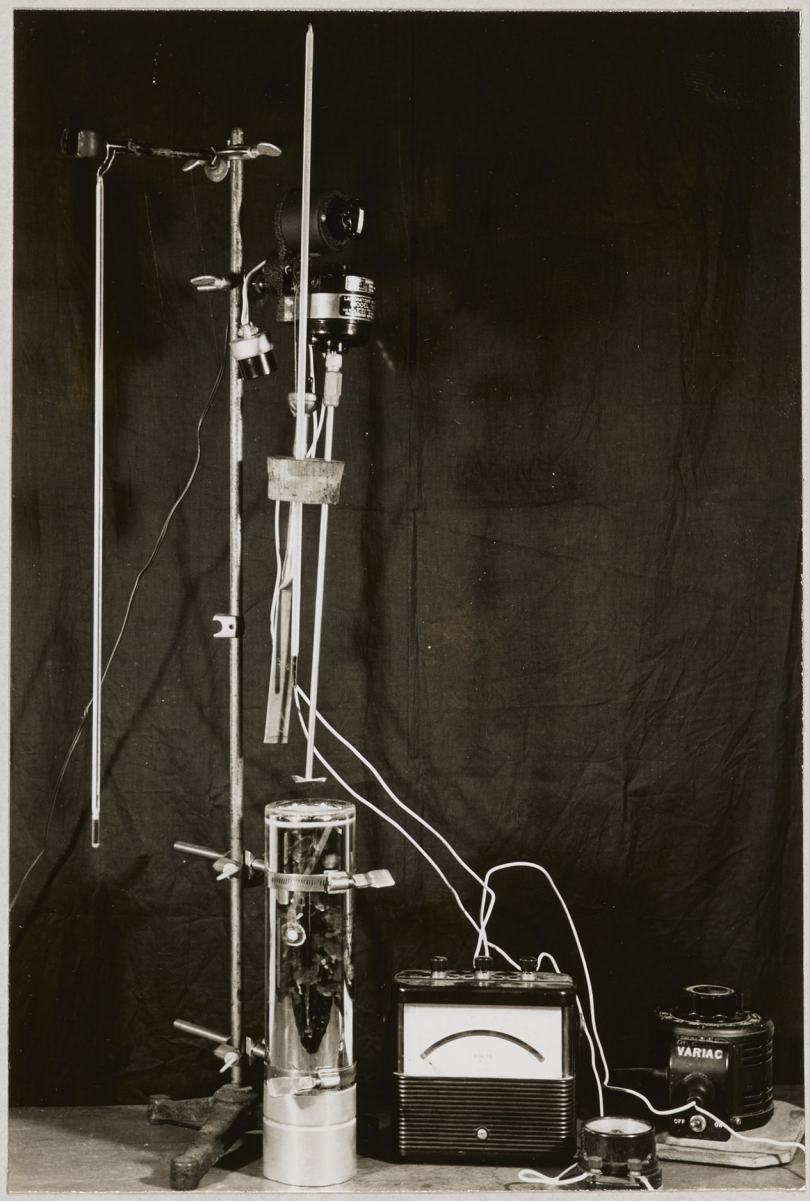


FIGURE 2
PICTURE OF CALORIMETER

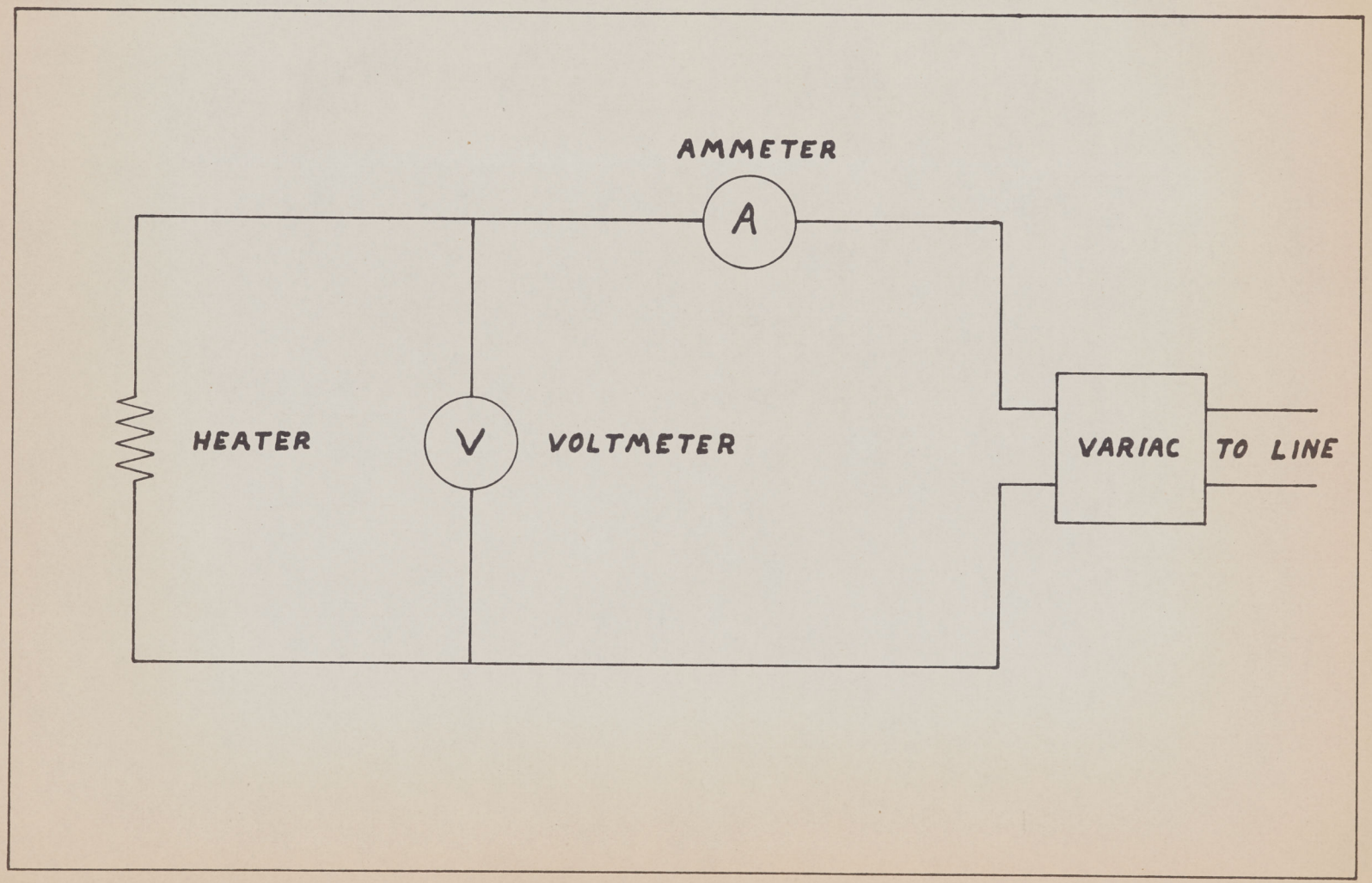


FIGURE 3

DIAGRAM OF ELECTRICAL CIRCUIT

and an A.C. ammeter (0-3 amp).

The other equipment used included a triple beam balance, a Kodak Timer clock, a chainomatic analytical balance, and a laboratory oven. The clock was used to time the experimental runs, and the samples used in the runs were weighed on the triple beam balance. The analytical balance and oven were used in determining the exact dye concentration of the solutions that were studied.

The dye used was the commercial grade of Milling Yellow NGS produced by the National Aniline Division of the Allied Chemical and Dye Corporation. The solutions were prepared from dye powder dissolved in distilled water.

CRANES CREST

CHAPTER V

PROCEDURE

It was necessary to make three types of preliminary tests on the calorimeter. They were the determination of an overall heat transfer coefficient and area product, U x A, for the calorimeter; the determination of the energy generated by the mechanical stirrer; and the determination of the heat capacity of the calorimeter. Distilled water was used as the test liquid in all three cases.

The values of U x A were determined for various temperatures in the following manner. A volume of water approximately equal to the volumes of dye samples that were used later in the investigation was placed in the calorimeter. This water was heated up to and maintained at some arbitrary temperature. The energy required to maintain the water at this temperature was measured indirectly by the power input to the immersion heater. Under these conditions, the energy that was put into the water was equal to the energy that was lost to the surroundings by the calorimeter. The water and room temperatures were recorded, and the values of U x A were calculated from the temperatures and the rate of heat transfer. A sample calculation is presented in the Appendix.

In order to determine the energy generated by the

mechanical stirrer, water at room temperature was placed in the calorimeter. The stirrer was adjusted to the speed used throughout the entire investigation. Then the water temperature was watched for fifteen minutes so that any temperature rise might be noted. But no temperature rise was noted, and it was assumed that the energy generated by the stirrer was negligible. Identical tests were carried out on dye solutions at a later date. The results were identical with those for water.

In determining the heat capacity of the calorimeter, a water sample of about 600 grams was weighed accurately on a triple beam balance and introduced into the calorimeter. The stirrer was put in motion, and the heater and clock were started simultaneously. The power input to the heater was adjusted to some desired value by the Variac. At regular one minute intervals, the voltmeter, ammeter, and water temperature were read and recorded. The average room temperature was read and recorded at the end of the experimental run. From these data, the heat capacity of the calorimeter was calculated. Presented in the Appendix is a sample calculation.

The aqueous solutions of Milling Yellow NGS dye were made up by dissolving the dye powder in distilled water. About one per cent dye and 99 per cent water were placed in the evaporating vessel and heated until the dye went into solution. It is very difficult to make the concentrated dye

solutions directly because Milling Yellow NGS does not dissolve readily. Therefore, the one per cent dye solution was concentrated to about 2.8 per cent by evaporating some of the water. Then solutions ranging in concentration between 1.001 per cent and 2.762 per cent dye were made by diluting the concentrated dye solution volumetrically with water. The exact concentrations of these solutions were determined by weighing a sample on an analytical balance, evaporating to dryness in an oven at 205°F, and reweighing.

The experimental procedure for determining the heat capacities of the dye solutions was identical to that for determining the calorimeter heat capacity as described previously. In this case, the dye solution was used instead of water, and the heat capacity of the calorimeter was known.

Interest in the possibility of a phase change increased as the investigation proceeded. As a result, some visual observations were made of the change from a non-spontaneously to a spontaneously doubly refracting dye solution. A solution which was spontaneously doubly refracting at room temperature was heated up beyond the temperature at which spontaneous double refraction ceased. This heating was carried out by running hot water over the outside of a test tube containing the dye solution. A thermometer was placed in the dye solution. The solution was then allowed to cool slowly while being observed under polarized light.

When spontaneous double refraction again appeared, the temperature was read and recorded.

CHAPTER VI

RESULTS

Tabulated in Tables I-VII are the results of heat capacity measurements. Tabulations are made of the energy added to the dye solution and the temperature of the dye solution after the addition. These tabulated values were then plotted, and the resulting curves appear in Figures 4-12. The slopes of the curves which are equal to the heat capacities of the dye solutions were determined graphically and are tabulated in Table VIII. Appearing with the heat capacity values in Table VIII are the corresponding temperatures and dye concentrations of the solutions.

In Table IX, the results of the phase change investigation are presented. A thermal analysis was made on Figures 4-12, and phase change indications appeared for the 2.501 per cent and the 2.762 per cent dye solutions. The temperatures corresponding to the phase change indications are tabulated in Table IX. Also tabulated are the temperatures at which the same solutions were visually observed to change to the spontaneously doubly refracting state.

TABLE I

TABULATED RESULTS - 1001 PER CENT DYE

Run 1		Run 2	
Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm	Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
23.65	0	23.35	0
25.80	2.62	25.50	2.77
28.30	5.26	28.20	5.44
30.90	7.85	30.90	8.11
33.70	10.35	33.70	10.75
36.30	12.88	36.40	13.41
39.00	15.44	39.10	16.07
41.80	17.93	42.00	18.68
44.40	20.50	44.70	21.29
47.10	23.04	47.40	23.90
49.70	25.56	50.10	26.54
52.40	28.22	52.90	29.16
55.00	30.89	55.50	31.81
57.70	33.51	58.10	34.41
60.30	36.12	60.70	36.96
62.90	38.73	63.30	39.56
65.60	41.32	65.90	42.16
68.20	43.93	68.50	44.78
70.90	46.52	71.10	47.37
73.50	49.11	73.70	49.95
76.00	51.73	76.30	52.57
78.70	54.35	78.90	55.18
81.20	56.94	81.50	57.75
83.80	59.52	84.00	60.37
86.30	62.12	86.60	63.07
88.90	64.73	89.10	65.64
91.50	67.34	91.80	68.17
94.00	69.97	94.30	70.73
96.60	72.53	96.90	73.30
99.10	75.09	99.30	75.91

TABLE II

TABULATED RESULTS - 1.218 PER CENT DYE

Run 1		Run 2	
Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm	Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
24.20	0	23.60	0
26.40	2.82	25.70	2.90
29.20	5.53	28.50	5.58
32.00	8.24	31.40	8.33
35.80	10.76	34.30	11.08
37.70	13.63	37.20	13.82
40.60	16.30	40.10	16.56
43.40	19.00	43.00	19.29
46.20	21.69	45.90	22.02
49.10	24.36	48.80	24.74
51.90	27.04	51.60	27.42
54.60	29.73	54.20	30.19
57.30	32.42	56.90	32.94
60.00	35.11	59.70	35.67
62.70	37.79	62.50	38.39
65.40	40.47	65.30	41.11
68.20	43.12	68.00	43.84
70.80	45.81	70.70	46.57
73.50	48.47	73.40	49.29
76.20	51.13	76.20	51.99
78.90	53.79	78.90	54.70
81.50	56.45	81.60	57.41
84.30	59.08	84.40	60.09
87.00	61.72	87.00	62.80
89.60	64.37	89.70	65.49
92.20	67.02	92.40	68.18
94.80	69.66	95.10	70.86
97.50	72.28	97.70	73.53
100.00	75.01		

TABLE III

TABULATED RESULTS - 1.615 PER CENT DYE

Temperature of Dye Solution, °C	Energy Added of Dye Solution, cal/gm
23.10	0
23.30	3.27
24.40	6.38
31.80	8.30
33.80	11.22
36.70	13.97
39.60	16.72
42.50	19.46
45.40	22.20
48.30	24.94
51.20	27.67
54.00	30.42
56.70	33.18
59.50	35.91
62.30	38.64
65.10	41.37
67.90	44.09
70.70	46.81
73.50	49.52
76.20	52.25
78.90	54.97
81.60	57.68
84.30	60.39
87.00	63.10
89.70	65.80
92.30	68.51
95.00	71.20
97.60	73.90

TABLE IV

TABULATED RESULTS - 2.003 PER CENT DYE

Run 1		Run 2	
Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm	Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
23.80	0	24.40	0
23.85	3.88	25.10	3.43
24.50	7.64	26.60	4.90
25.80	11.26	28.30	6.33
35.10	13.14	29.70	7.82
40.00	15.96	31.00	9.33
42.90	19.21	32.00	10.90
46.60	22.27	33.40	12.39
49.40	25.53	35.50	13.73
52.60	28.69	38.00	14.99
55.90	31.83	41.00	16.14
59.20	34.96	42.90	17.52
62.30	38.13	43.80	19.10
65.60	41.24	45.10	20.60
68.70	44.40	46.60	22.14
71.90	47.52	48.10	23.60
75.10	50.64	51.40	26.44
78.30	53.76	54.40	29.34
81.50	56.86	57.80	32.16
84.60	59.98	60.30	35.15
87.70	63.10	63.30	38.04
90.80	66.20	66.30	40.92
93.70	69.34	69.30	43.80
96.70	72.46	72.20	46.69
		75.20	49.55
		78.20	52.40
		81.10	55.28
		84.00	58.14
		86.90	61.00
		89.80	63.85
		92.70	66.70
		95.50	69.55
		98.30	72.41

TABLE V

TABULATED RESULTS - 2.248 PER CENT DYE

Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
22.85	0
23.10	1.97
25.00	3.60
27.10	5.19
29.40	6.73
31.50	8.31
33.50	9.90
34.90	11.62
36.40	13.32
38.50	14.89
40.50	16.48
41.80	18.21
43.30	19.90
44.80	21.58
46.60	23.20
48.60	24.77
50.20	26.43
51.90	28.06
53.50	29.71
56.30	32.80
59.50	35.81
62.60	38.83
65.70	41.85
68.80	44.86
71.90	47.86
75.00	50.86
78.00	53.87
81.00	56.88
84.10	59.85
87.10	62.85
90.20	65.81
93.20	68.79
96.10	71.78

TABLE VI

TABULATED RESULTS - 2.501 PER CENT DYE

Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
22.45	0
22.55	2.02
24.00	3.76
25.70	5.44
27.60	7.08
29.30	8.76
31.10	10.42
32.00	12.26
34.00	13.87
34.00	15.89
35.60	17.58
38.90	18.91
42.50	20.17
46.00	21.45
46.40	23.37
48.60	24.92
50.40	26.54
52.00	28.21
53.80	29.83
56.50	32.97
59.70	36.00
62.90	39.05
66.00	42.09
69.10	45.12
72.20	48.15
75.30	51.17
78.40	54.18
81.50	57.19
84.50	60.21
87.50	63.23
90.50	66.24
93.50	69.24
96.50	72.23

TABLE VII

TABULATED RESULTS - 2.762 PER CENT DYE

Run 1		Run 2	
Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm	Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
23.30	0	24.25	0
23.30	1.87	24.70	1.74
24.00	3.59	26.90	3.15
25.60	5.12	28.80	4.61
27.60	6.56	30.50	6.10
29.10	8.12	32.40	7.56
30.60	9.66	34.00	9.08
32.00	11.23	35.50	10.60
33.50	12.78	37.10	12.11
35.10	14.30	38.30	13.69
36.60	15.85	39.00	15.36
38.30	17.35	38.50	17.26
39.40	18.89	40.20	18.75
40.70	20.47	42.90	20.04
42.30	21.99	45.00	21.44
44.40	23.40	46.70	22.92
47.80	24.54	49.00	24.28
50.40	25.84	51.00	25.69
52.50	27.25	53.10	27.08
53.50	28.89		
54.50	30.52		
56.00	32.05		
57.50	33.58		
59.10	35.08		
60.70	36.58		
62.40	38.06		
63.90	39.58		
65.50	41.12		
67.10	42.62		
68.60	44.14		
70.20	45.63		
71.80	47.12		
73.30	48.64		
74.80	50.12		
76.40	51.63		

TABLE VII (continued)

TABULATED RESULTS - 2762 PER CENT DYE

Run 1		Run 2	
Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm	Temperature of Dye Solution, °C	Energy Added to Dye Solution, cal/gm
77.90	53.14		
79.40	54.64		
80.90	56.15		
82.40	57.65		
83.90	59.15		
85.50	60.63		
87.00	62.13		
88.50	63.62		
90.00	65.12		
91.50	66.61		
92.90	68.12		
94.40	69.61		
95.80	71.11		
97.30	72.60		

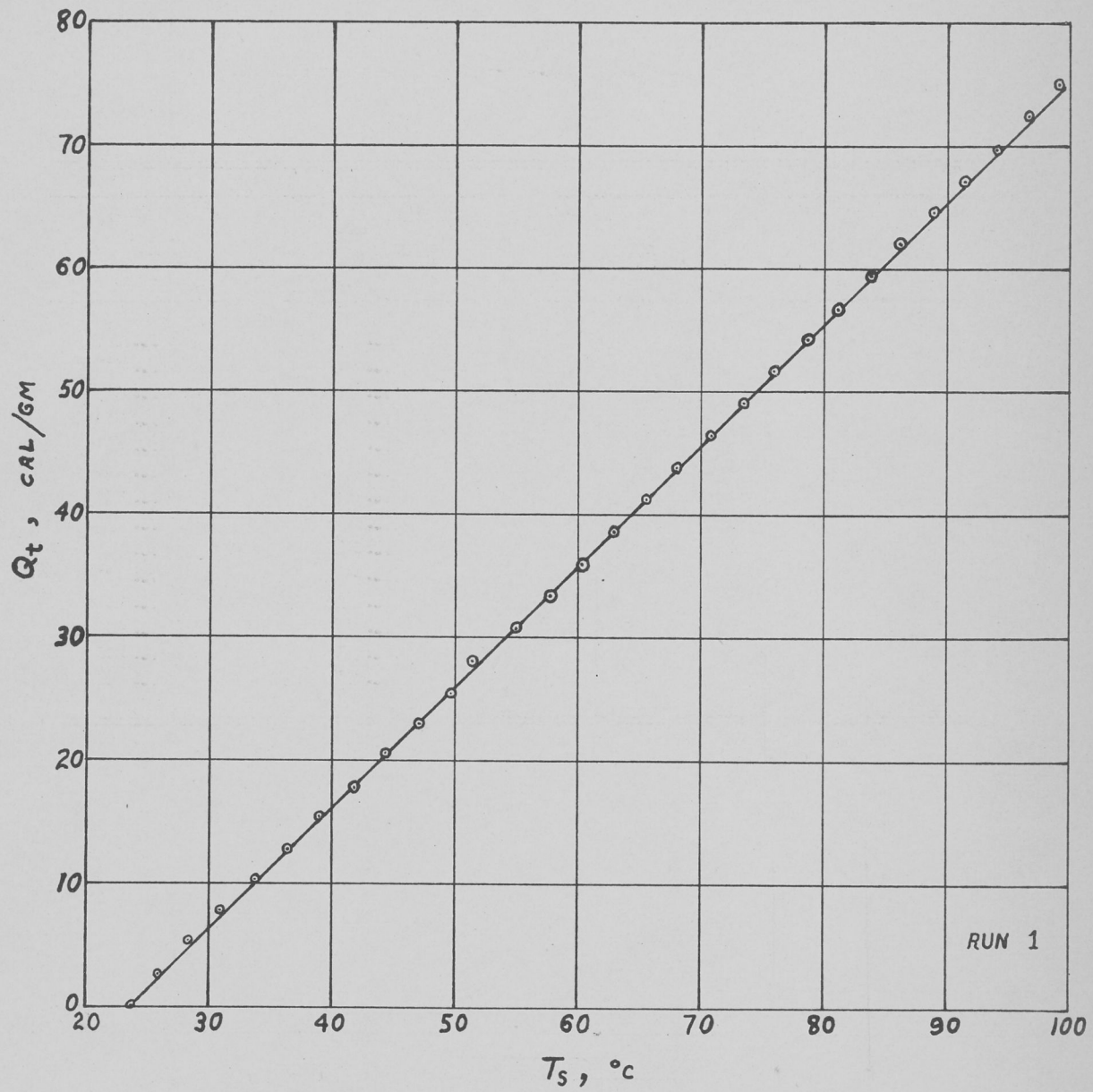


FIGURE 4

Q_t VERSUS T_S — 1.001% DYE

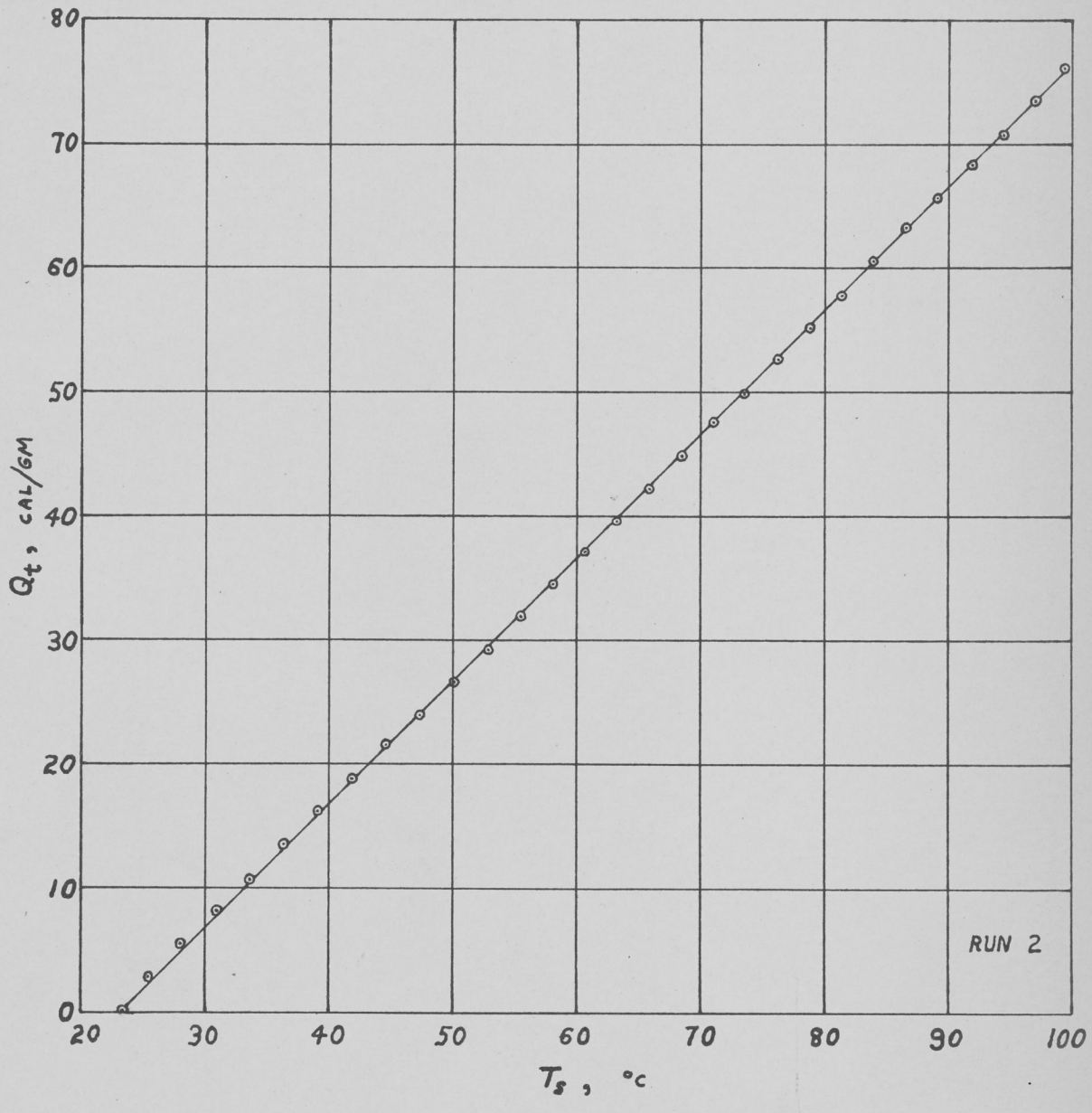


FIGURE 5

Q_t VERSUS T_s — 1.001 % DYE

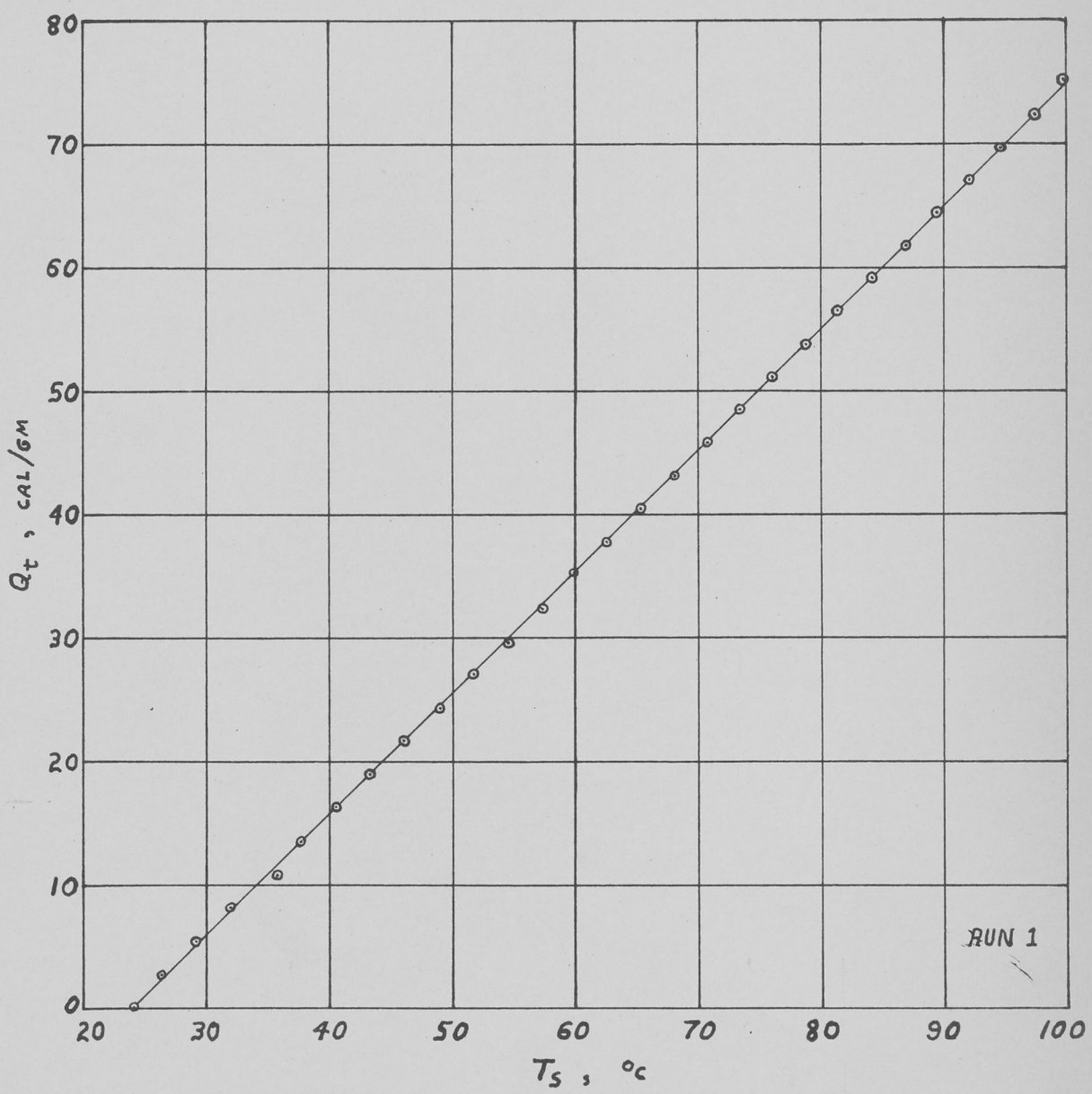


FIGURE 6

Q_t VERSUS T_S – 1.218 % DYE

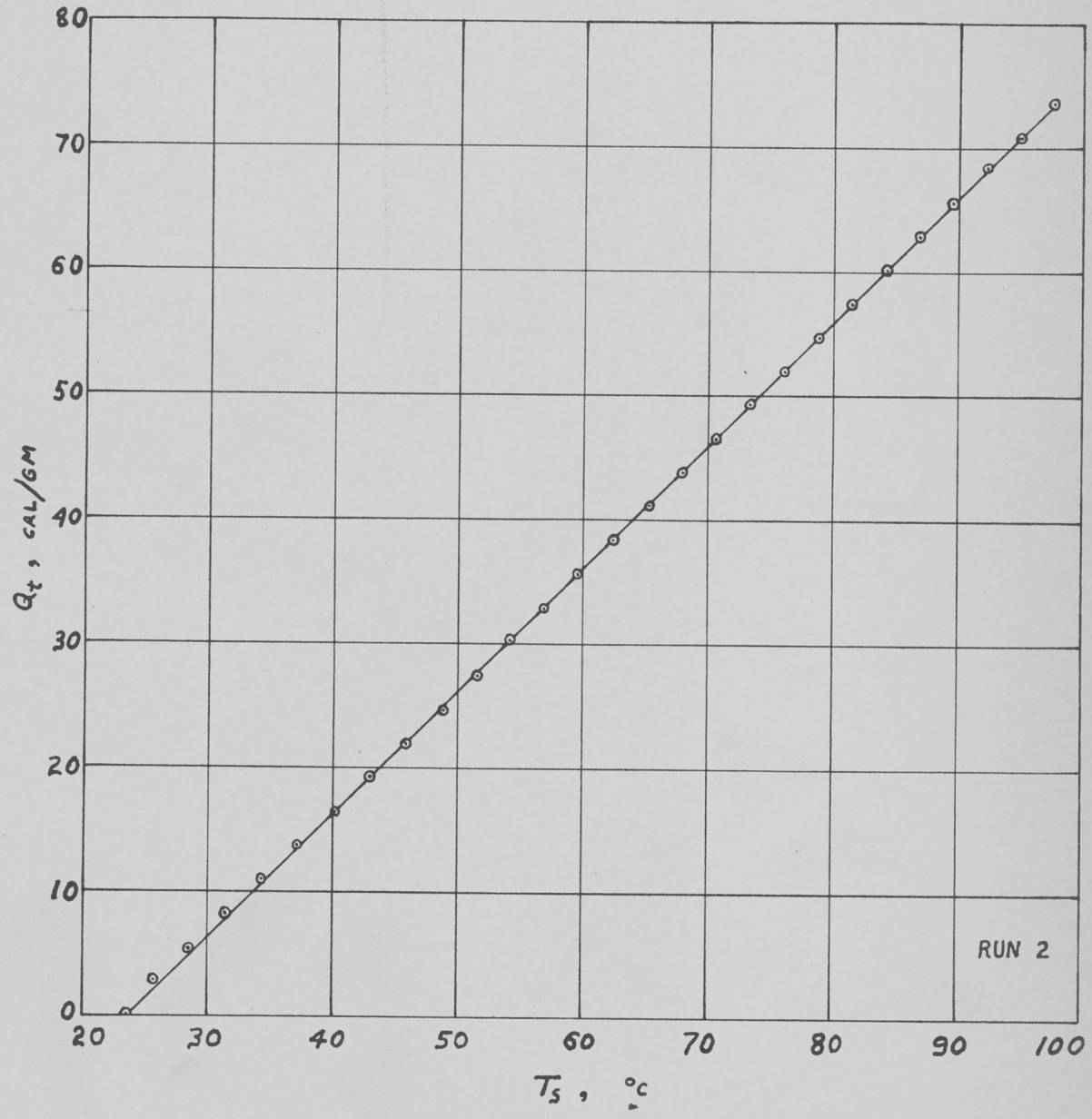


FIGURE 7

Q_t VERSUS T_s — 1.218 % DYE

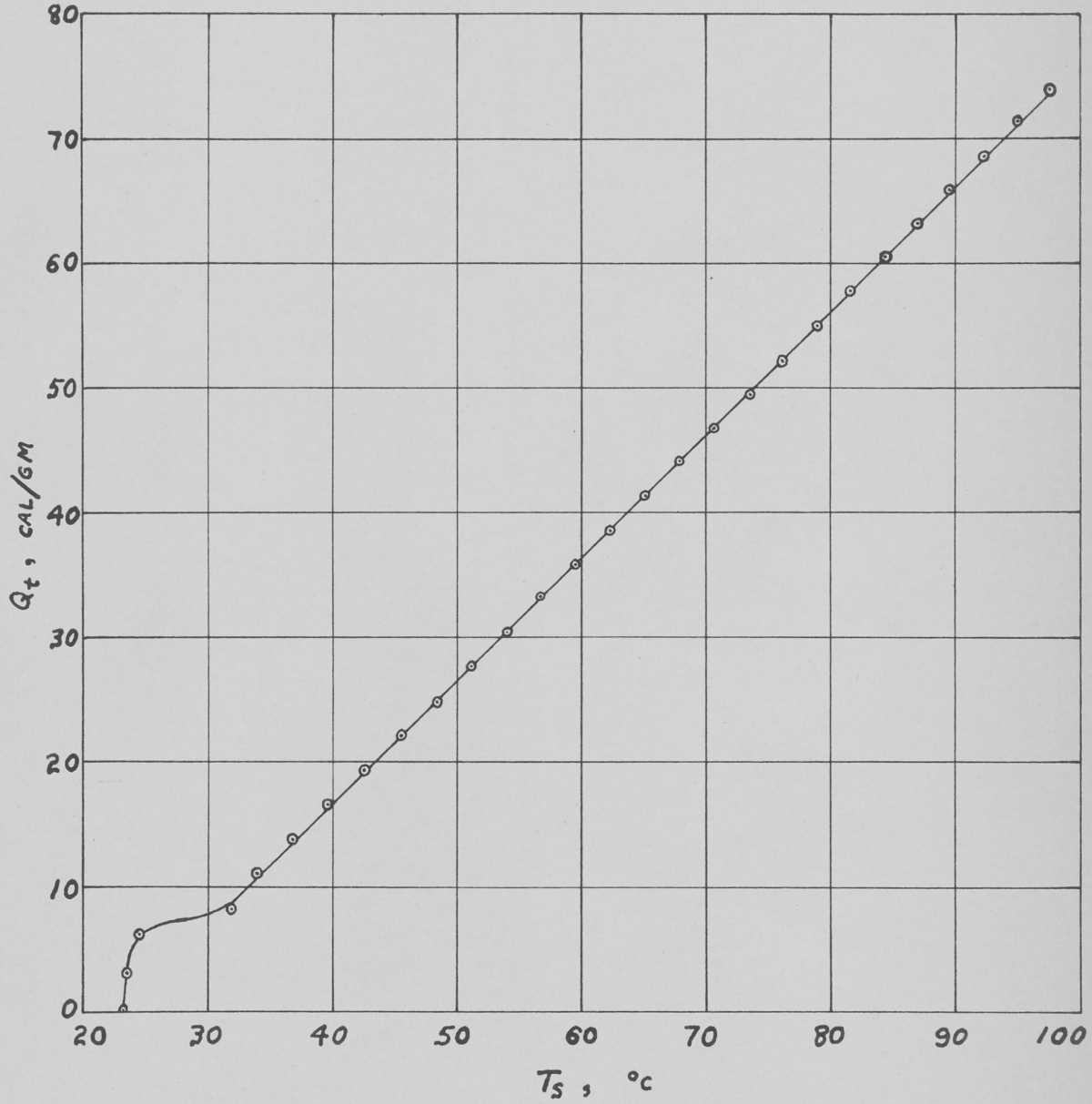


FIGURE 8

Q_t VERSUS T_s — 1.615 % DYE

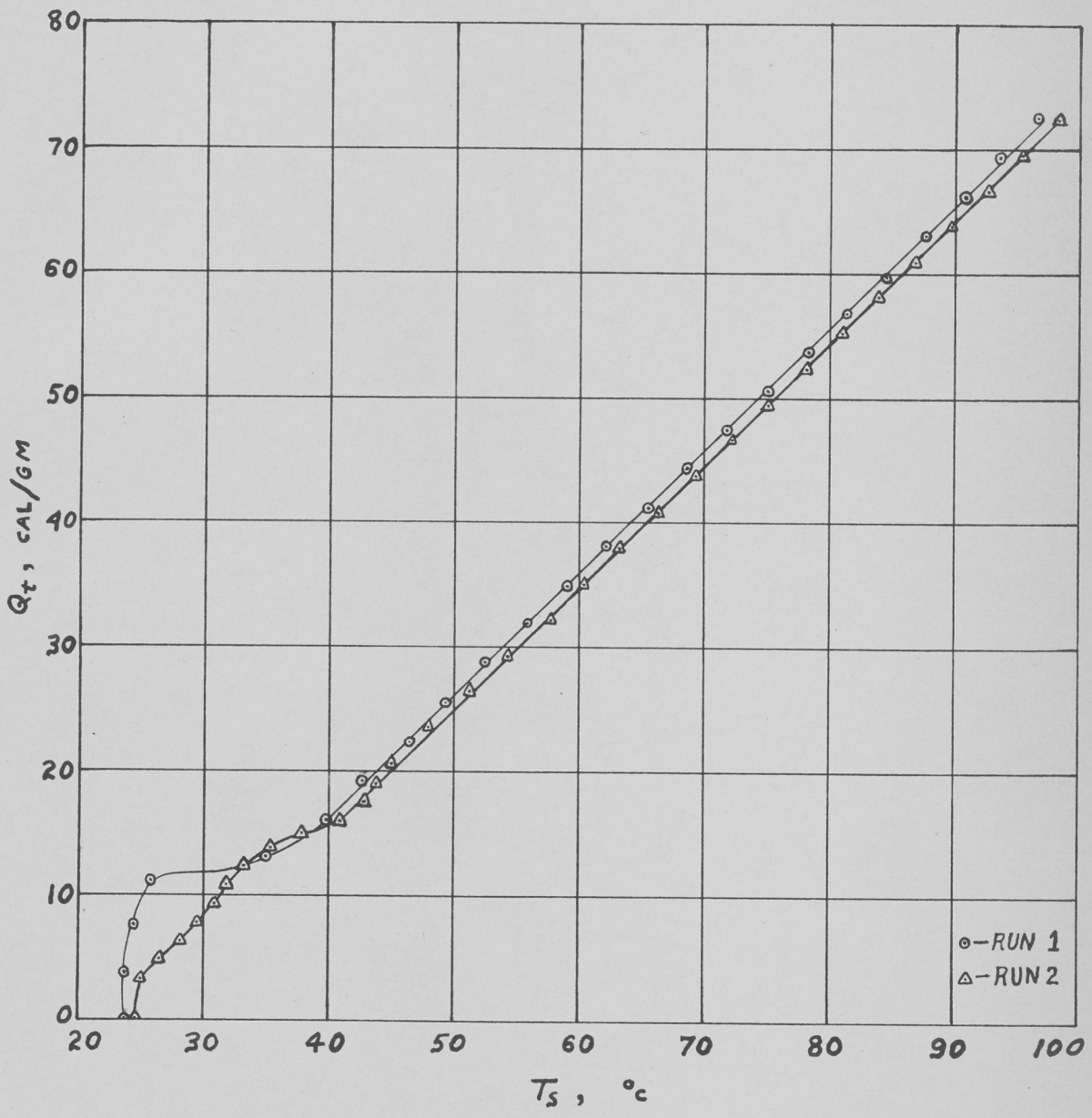


FIGURE 9

Q_t VERSUS T_s — 2.003 % DYE

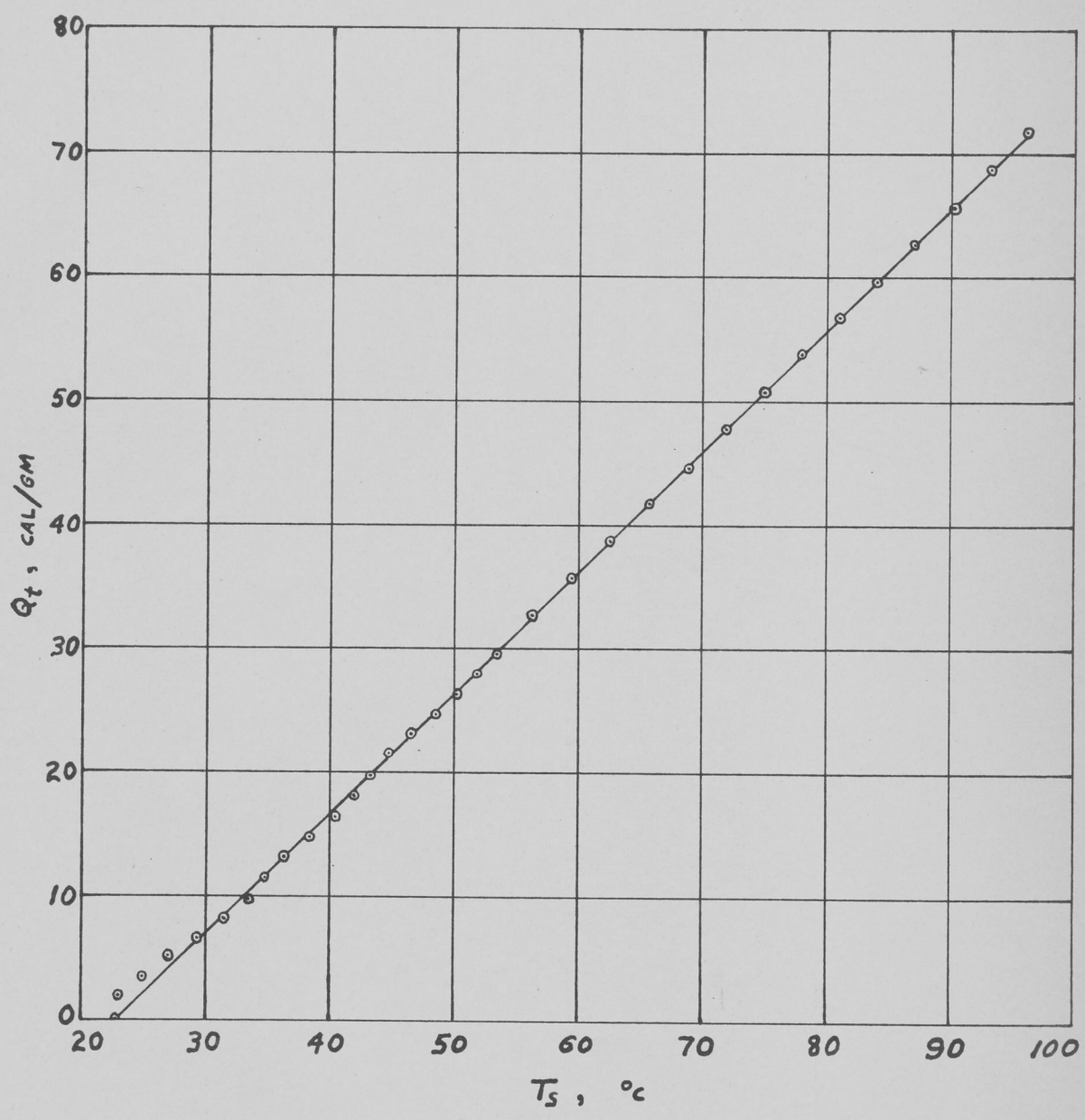


FIGURE 10

Q_t VERSUS T_s – 2.248 % DYE

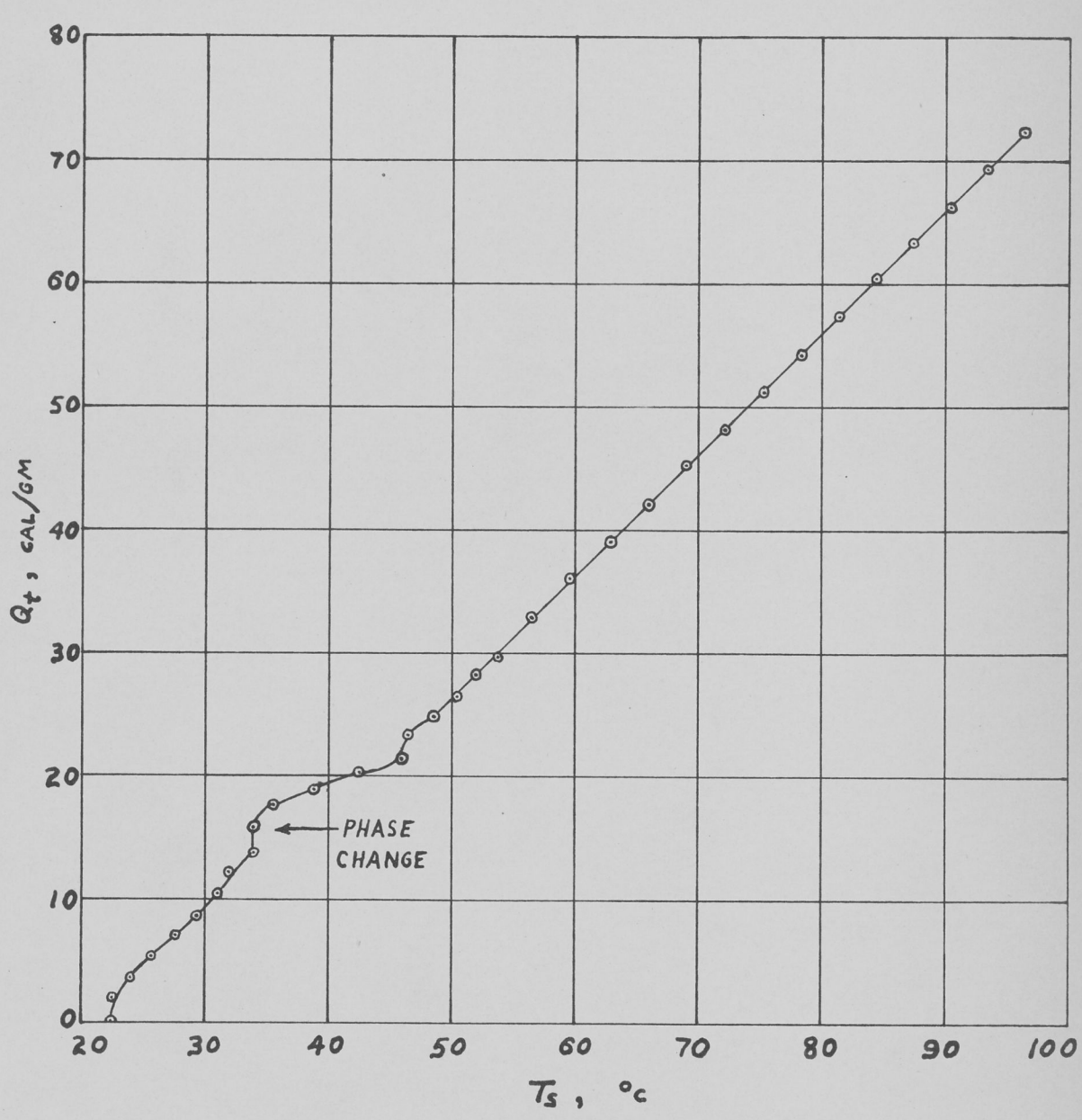


FIGURE 11

Q_t VERSUS T_s — 2.501 % DYE

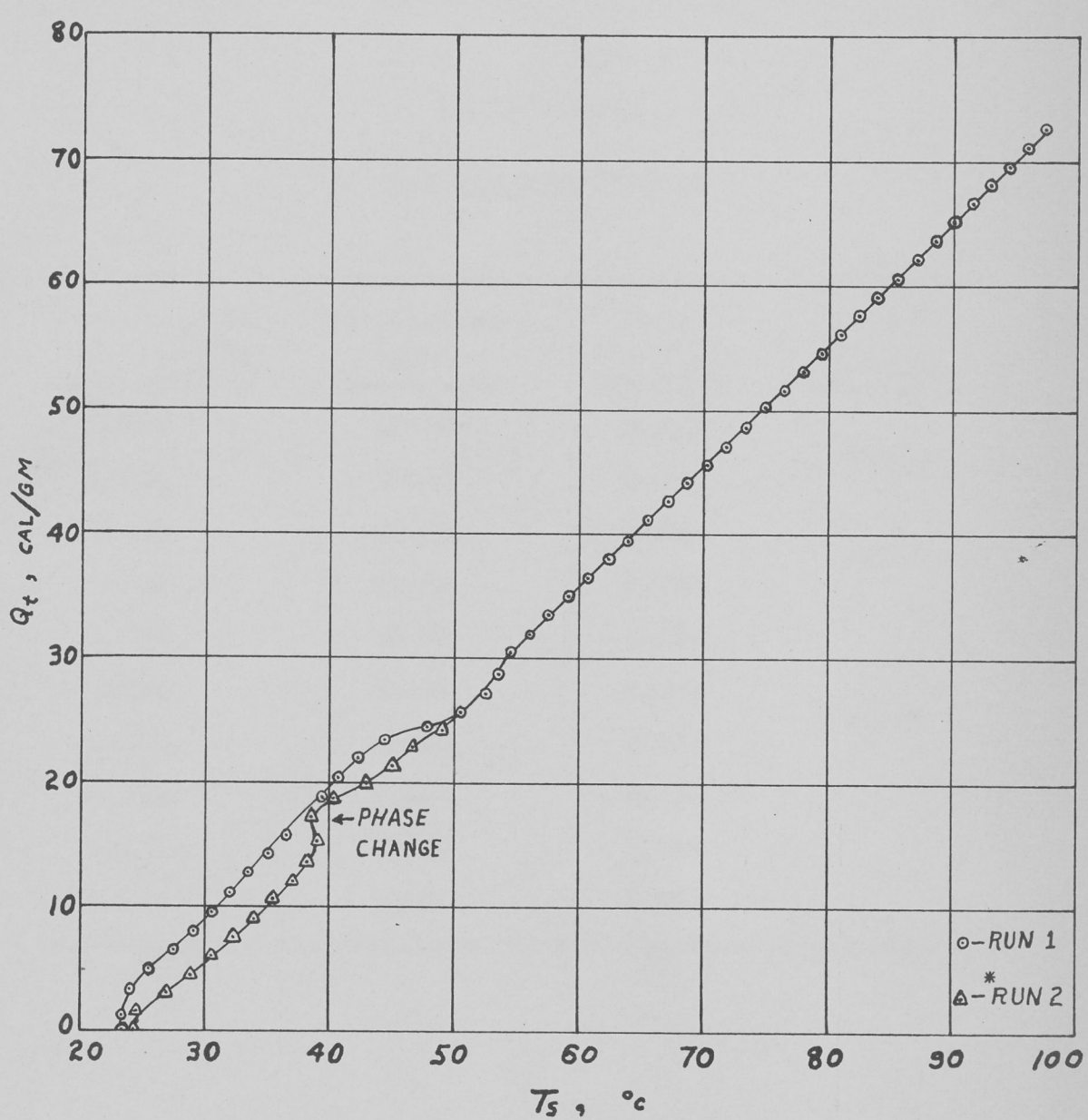


FIGURE 12

Q_t VERSUS T_s – 2.762 % DYE

*RATE OF HEAT INPUT CUT TO ONE-HALF

TABLE VIII

HEAT CAPACITY RESULTS

Dye Concentration of Solution, % by weight	Temperature Range, °C	Heat Capacity, cal/gm-°C	Heat Capacity (Average), cal/gm-°C
1.001	24-99	0.990	0.994
1.001	24-97	0.997	
1.218	25-100	0.989	0.990
1.218	24-97	0.990	
1.615	32-97	0.990	
2.003	43-97	0.986	0.983
2.003	44-98	0.980	
2.248	23-96	0.979	
2.501	49-96	0.986	
2.762	55-97	0.980	

TABLE IX

PHASE CHANGE RESULTS

Dye Concentration of Solution, % by weight	Temperature at Visual Indication of Phase Change, °C	Temperature at Thermal Indication of Phase Change, °C
2.762	37-38	38.5
2.501	31-32	34.0
2.248	26-27	-

CHAPTER VII

DISCUSSION OF RESULTS

A linear* relationship for the plot of Q_t versus T_s was obtained for 1.001 per cent and 1.218 per cent dye solutions, as shown in Figures 4, 5, 6, and 7. In the case of the 1.615 per cent dye solution, it was noted that the linear relationship did not hold below 32°C, shown in Figure 8. The 2.003 per cent dye solution, in Figure 9, also showed the deviation from a linear relationship except in this case the break-away was at 44°C instead of 32°C. Another interesting point was brought out by making two experimental runs on the 2.003 per cent dye solution. The plotted results of the two runs gave two different types of curves in the region below the break-away from the linear relationship.

The fact that the results were not reproducible in the low temperature region pointed to the possibility of poor agitation of the dye solution in the calorimeter. If good mixing were not maintained, it would be possible to read a point temperature that differed appreciably from the bulk temperature of the dye solution. This explanation is supported by the fact that the viscosity of the dye solution

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*All straight line graphs were drawn by visual approximation.

increases rapidly as the dye concentration increases and the temperature decreases. It was noted that a two per cent dye solution acts like a thick syrup whereas a one per cent dye solution is thin and water-like. A possible remedy for the poor mixing was to increase the speed of the stirrer. However, this was not feasible because the stirrer vibrated too much at higher speeds.

It was decided to cut the rate of energy supply to the dye solution to allow time for more uniform mixing to occur. An experimental run was made on the 2.248 per cent dye solution with the heating rate cut from about 30 cal/sec to 18 cal/sec. A linear relationship was given by the plot of Q_t versus T_s, Figure 10.

The smaller heating rate was also used in the experimental runs on the 2.501 per cent and 2.762 per cent dye solutions. The Q_t versus T_s plots gave linear relationships except in the region of the phase change indication. The phase change was indicated in Figure 11 by the addition of energy at a constant solution temperature. In Figure 12, it was indicated by an actual decrease in solution temperature while energy was added. This is explained by the fact that the dye solution might become slightly superheated before the transition occurs.

From examination of the heat capacity results in Table VIII, it was noted that the heat capacity is practically

unaffected by changing the dye concentration. In going from a 1.001 per cent to a 2.762 per cent dye solution, the heat capacity changes from 0.994 to 0.980 cal/gm-^{o}C, which is only a 1.4 per cent difference. As shown in Table VIII, a check was made on three solutions, and the results were reproduced to within 0.7 per cent or better.

Table IX relates the thermally indicated phase change and the visual change from a non-spontaneously to a spontaneously doubly refracting solution. It should be pointed out that the visual observation was subject to error because the visual change occurs very slowly and is not sharp. Also, the phase change indications were observed as the dye solutions were heated, but the visual observations were made as the dye solutions were cooled, introducing the possibility of a hysteresis error.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

As a result of this investigation it is concluded that:

1) The dye concentration has very little effect on the heat capacity of aqueous solutions of Milling Yellow NGS dye in the concentration range from one to two per cent dye by weight.
2) Strong evidence points toward the existence of a phase change that is associated with the change of the more concentrated solutions from a non-spontaneously to a spontaneously doubly refracting state.

Due to the small thermal change accompanying the indicated phase change, it is recommended that a further study of the phase change be carried out with more sensitive calorimetric equipment.

NOTATION

E - voltage drop across heater, volts

I - current through heater, amp

Q - energy added to dye solution, cal/gm

Q_c - energy added to calorimeter, cal

Q_N - net energy added to calorimeter system, cal

Q_s - energy added to dye solution, cal

Q_t - total energy added to dye solution in t minutes, cal/gm

q_A - rate of heat added to calorimeter system, cal/sec

q_L - rate of heat loss from calorimeter system, cal/sec

q_N - net rate of heat added to calorimeter system, cal/sec

T_c - calorimeter temperature, ^oC

T_R - room temperature, ^oC

T_s - dye solution temperature, ^oC

ΔT - $(T_c - T_R)$, ^oC

ΔT_c - calorimeter temperature change, ^oC

Δt - time interval, min

$U \times A$ - overall heat transfer coefficient and area product for calorimeter, cal/sec-^oC

W - weight of dye solution, gm

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BIBLIOGRAPHY

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APPENDIX

APPENDIX

DETERMINATION OF U x A

The data for the determination of the U x A values for the calorimeter are tabulated in Table X.

A linear relationship was obtained from a plot of U x A versus ΔT, Figure 13. The line was extrapolated to obtain values of U x A for low values of ΔT.

TABLE X

U x A RESULTS

Experimental Data				Derived Data	
Room Temperature, °C	Calorimeter Temperature, °C	Heater Current, amp	Heater Voltage, volt	ΔT, °C	U x A, cal/sec-°C
24.35	70.00	0.170	16.5	45.65	0.0147
24.35	80.20	0.190	19.0	55.85	0.0154
24.35	85.00	0.200	20.0	60.65	0.0158
24.35	90.10	0.210	21.0	65.75	0.0160
24.35	95.00	0.220	22.0	70.65	0.0164
24.35	98.00	0.225	22.5	73.65	0.0165
24.40	74.75	0.180	18.0	50.35	0.0154
24.40	80.55	0.190	19.0	56.15	0.0154
24.40	85.20	0.200	20.0	60.80	0.0157
24.40	90.30	0.210	21.0	65.90	0.0160
24.40	70.95	0.170	17.0	46.55	0.0148

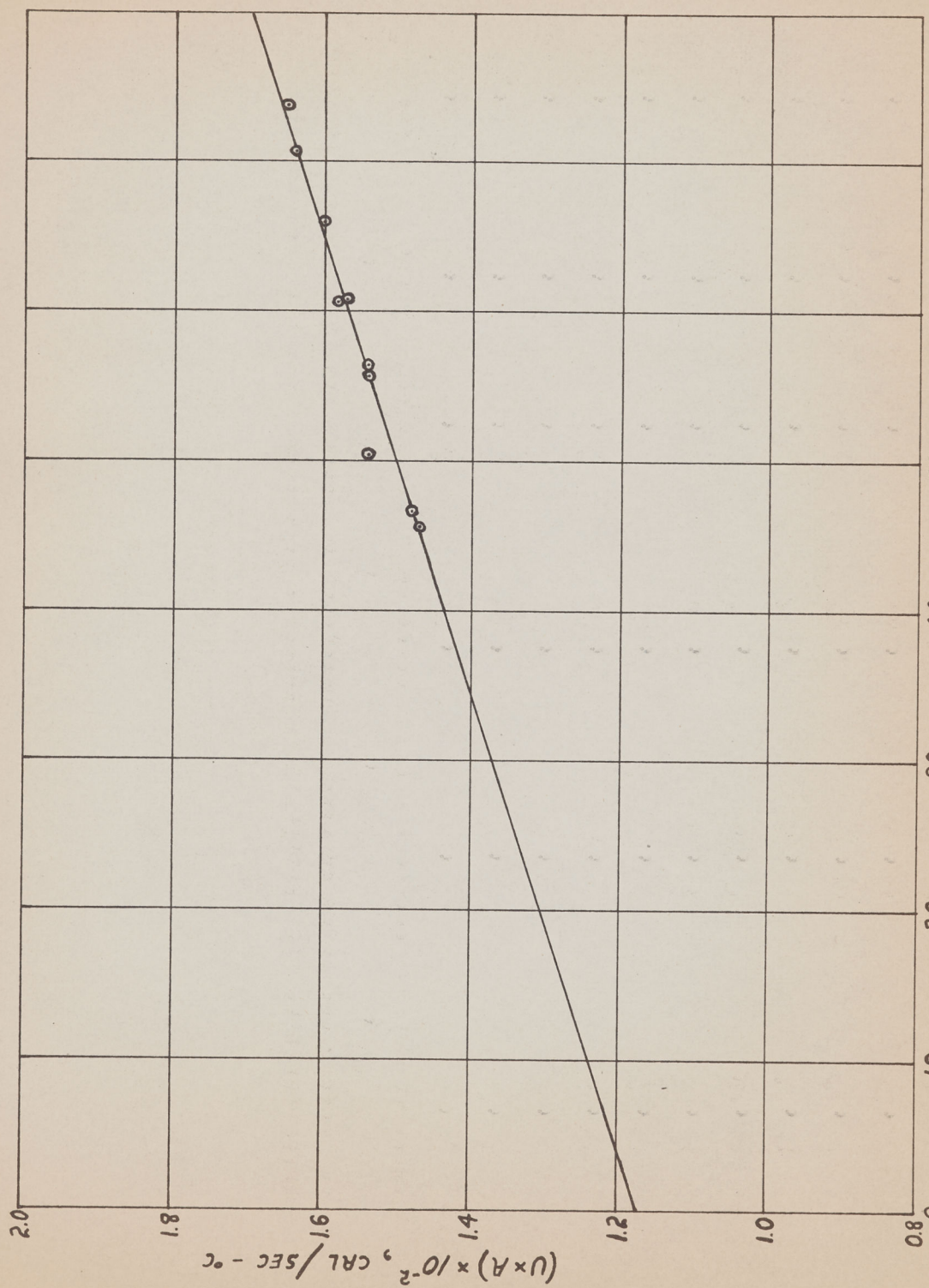


FIGURE 13

U×A VERSUS ΔT

CALORIMETER HEAT CAPACITY DETERMINATION

Tabulated in Table XI are typical data that were taken for the purpose of determining the heat capacity of the calorimeter. The entire set of data may be found on pages 21270-21275 of the Original Record of Research, Department of Chemical Engineering, University of Tennessee.

The heat capacity of the c alorimeter was found to be 110.8 $\pm$ 2.4 cal/^{o}C.

TABLE XI

EXPERIMENTAL DATA

Water sample - 584.1 gm
Room temperature - 24.50°C

Water Temperature, °C	Heater Current, amp	Heater Voltage, volt	Time, min
24.50	1.20	113.0	0
26.90	1.20	113.0	1
29.50	1.18	112.0	2
32.40	1.19	112.5	3
35.20	1.19	112.5	4
38.10	1.18	112.0	5
40.90	1.18	111.5	6
43.70	1.18	111.5	7
46.50	1.19	112.0	8
49.30	1.19	112.0	9
52.10	1.19	112.5	10
54.80	1.19	112.5	11
57.10	1.19	112.5	12
60.20	1.18	112.0	13
62.80	1.17	111.0	14
65.50	1.17	111.0	15
68.20	1.17	111.0	16
70.80	1.17	111.0	17
73.50	1.18	112.0	18
76.10	1.18	112.0	19
78.80	1.18	112.0	20
81.40	1.18	112.0	21
84.00	1.18	112.0	22
86.60	1.18	112.0	23
89.20	1.17	111.5	24
91.80	1.17	111.5	25
94.40	1.17	111.5	26
97.00	1.17	111.5	27

EXPERIMENTAL DATA

A typical set of the experimental data used in the determination of the heat capacities of the dye solutions is tabulated in Table XII. The entire volume of experimental data may be found on pages 13313-13317, 21276-21280, 21293-21294, and 21296-21298 of the Original Record of Research, Department of Chemical Engineering, University of Tennessee.

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TABLE XII

EXPERIMENTAL DATA

Dye concentration - 1.218% by weight
Dye sample - 611.2 gm
Room temperature - 26.36°C

Dye Solution Temperature, °C	Heater Current, amp	Heater Voltage, volt	Time, min
24.20	1.20	114.5	0
26.40	1.20	114.5	1
29.20	1.20	114.5	2
32.00	1.20	114.5	3
35.80	1.20	114.5	4
37.70	1.20	114.5	5
40.60	1.20	114.5	6
43.40	1.20	114.5	7
46.20	1.20	114.5	8
49.10	1.20	114.5	9
51.90	1.20	114.5	10
54.60	1.20	114.5	11
57.30	1.20	114.5	12
60.00	1.20	114.5	13
62.70	1.20	114.5	14
65.40	1.20	114.5	15
68.20	1.20	114.5	16
70.80	1.20	114.5	17
73.50	1.20	114.5	18
76.20	1.20	114.5	19
78.90	1.20	114.5	20
81.50	1.20	114.5	21
84.30	1.20	114.5	22
87.00	1.20	114.5	23
89.60	1.20	114.5	24
92.20	1.20	114.5	25
94.80	1.20	114.5	26
97.50	1.20	114.5	27
100.00	1.20	114.5	28

SAMPLE CALCULATIONS

Part I: Calculation of U x A

1. Calorimeter temperature = 70.00°C, Table X
2. Room temperature = 24.35°C, Table X
3. ΔT = (Item 1) - (Item 2)
   = 70.00 - 24.35 = 45.65°C
4. Heater current = 0.17 amp, Table X
5. Heater voltage = 16.5 volts, Table X
6. Rate of heat loss from calorimeter = rate of heat generation by heater
   = (Item 4)(Item 5)(conversion factor)
   = (0.17)(16.5)(1/4.186) = 0.670 cal/sec
7. $U \times A = \frac{(\text{Item 6})}{(\text{Item 3})} = \frac{0.670}{45.65} = 0.0147$ cal/sec-°C

Part II: Calculation of Calorimeter Heat Capacity

1. Heater current = 1.20 amp, Table XI
2. Heater voltage = 113.0 volts, Table XI
3. Rate of heat input to calorimeter = (Item 1)(Item 2) x (conversion factor)
   = (1.20)(113.0)(1/4.186) = 32.39 cal/sec
4. Calorimeter temperature = 26.90°C, Table XI
5. Room temperature = 24.50°C, Table XI

6. ΔT = (Item 4) - (Item 5)

   = 26.90 - 24.50 = 2.40°C

7. U x A = 0.0119 cal/sec-°C, Figure 13

8. Rate of heat loss from calorimeter = (Item 6)(Item 7)

   = (2.40)(0.0119) = 0.03 cal/sec

9. Net rate of heat input to calorimeter system

   = (Item 3) - (Item 8)

   = 32.39 - 0.03 = 32.36 cal/sec

10. $\dfrac{\int_o^t (\text{Item 9})\, dt}{t - o}$ where t = time of the experimental run

Since the net rate of heat input to the calorimeter fluctuated very little throughout the experimental run, the above expression is approximated by calculating the arithmetic mean for all the values of Item 9.

Item 10 = 31.04 cal/sec

11. Length of run = 27 min, Table XI

    = 1620 sec

12. Total energy added to calorimeter system

    = (Item 10)(Item 11)

    = (31.04)(1620) = 50,280 cal

13. Weight of water sample used = 584.1 gm, Table XI

14. Temperature at start of run = 24.50°C, Table XI

15. Temperature at end of run = 97.00°C, Table XI

16. Total calorimeter temperature change = (Item 15) - (Item 14)

= 97.00 - 24.50 = 72.50°C

17. Energy added to water = (Item 13)(Item 16) x (Heat capacity of water)

= (584.1)(72.50)(1.00) = 42,350 cal

18. Energy added to calorimeter = (Item 12) - (Item 17)

= 50,280 - 42,350 = 7,930 cal

19. Calorimeter heat capacity = $\frac{\text{(Item 18)}}{\text{(Item 16)}}$

= $\frac{7,930}{72.50}$ = 109.4 cal/°C

Part III: Calculation of the Heat Capacities of the Dye Solutions

1. I = 1.20 amp, Table XII
2. E = 114.5 volts, Table XII
3. q_A = E I x (conversion factor)

   = (114.5)(1.20)(1/4.186) = 32.82 cal/sec
4. T_C = 29.20°C, Table XII
5. T_R = 26.36°C, Table XII
6. $\Delta T = T_C - T_R$

   = 29.20 - 26.36 = 2.84°C
7. U x A = 0.0120 cal/sec-°C
8. q_L = (U x A)(ΔT)

   = (0.0120)(2.84) = 0.03 cal/sec

9. $q_N = q_A - q_L$

   $= 32.82 - 0.03 = 32.79$ cal/sec

10. Δt = 1 min = 60 sec, Table XII

11. $Q_N = (q_N)(\Delta t)$

    $= (32.79)(60) = 1967$ cal

12. ΔT_c = calorimeter temperature change per minute

    $= 29.20 - 26.40$, Table XII

    $= 2.80^{\circ}C$

13. Calorimeter heat capacity = 110.8 cal/°C

14. $Q_c = (\Delta T_c)$(Item 13)

    $= (2.80)(110.8) = 310$ cal

15. $Q_s = Q_N - Q_c$

    $= 1967 - 310 = 1657$ cal

16. W = 611.2 gm, Table XII

17. $Q = \frac{Q_s}{W}$

    $= \frac{1657}{611.2} = 2.711$ cal/gm

18. $Q_{t-1} = 2.822$ cal/gm

19. $Q_t = Q + Q_{t-1}$

    $= 2.711 + 2.822 = 5.533$ cal/gm

20. $T_s = 29.20^{\circ}C$, Table XII

Plots were made of Q_t versus T_s. A linear relationship resulted. The slope of the line is equal to the heat capacity of the dye solution.

21. Heat capacity of solution = slope of line

$$= \frac{\text{change in } Q_t}{\text{corresponding change in } T_s}$$

$$= \frac{(70.0 - 5.6)}{(95.1 - 30.0)} = 0.989 \text{ cal/gm-}^{\circ}\text{C}$$

22. Solution - 1.218 per cent dye by weight, Table XII