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THE MOLECULAR SURFACE ENERGY
of
BINARY MIXTURES

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THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES

by

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THE MOLECULAR SURFACE ENERGY OF BINARY MIXTURES.

Among the purely physical properties of materials, to which the chemist has been compelled to pay an increasing amount of attention, in recent years, surface tension undoubtedly occupies the first place.¹

Innumerable papers have been published on the surface tension of pure liquids and related functions. Van Der Wall² has two equations connecting surface tension and temperature which involve the critical constants. Fergusson³ developed a formulae $S = S_0 (1 - bt)^n$ connecting surface tension with temperature. Macleod⁴ has shown $S = C(D - d)^4$ whereas Ramsay and Shield⁵ give the molecular surface energy $\frac{S_1(MV_1)^{2/3} - S_2(MV_2)^{2/3}}{t_2 - t_1} = K$. Harrison E. Patton⁶ deduced a relationship between surface tension and Electro Chemistry while E. S. Edwards⁷ discusses the relationship between osmotic pressure, solution tension, surface tension, and the elastic coefficient of the ether.

Irwin Langmuir⁸, in his paper "The Constitution of Liquids, with special reference to surface tension phenomena", claims that, with organic liquids, the surface layer of the atoms is the principal factor in determining the surface tension, or rather the surface energy of liquids.

1. "Surface tension and Surface energy" Willows and E. Helsehek.
2. Physical Chemistry 13 (716)
3. Phil. Mag. 1916. 31 (37)
4. Trans. Farad Soc. 1923, 19(38)
5. Physical Chemistry, Lewis, Vol. 1
6. Trans. Am. Electro. Chem. Soc. 19 (360)
7. Engr. 105. 1915 (290)
8. Met. Chem. Engr. 15 (468)

J. Livingston, R. Morgan and Mary A. Griggs⁹ have published a paper dealing with the properties of mixed liquids and the law of mixtures. They explain their experimental surface tension results by Denison's¹⁰ equation, that is, by plotting the deviation of observed value from calculated value (from the law of mixtures) against concentration. The maximum point of difference represents a compound, identical with the composition of the mixture. In the cases where they found a compound it was of a 50-50 mixture of the two compounds.

The object of this research is to obtain evidence from surface tension supporting the theory of solvation. The theory purports that when one substance is immiscible in another there is a union between the two substances which will be evident in the physical properties.

The substances chosen were sulphur dioxide and benzene. The density and surface tension of benzene has been measured several times and the values so consistent that the values of Samuel Sudgen¹¹ were used. The density and surface tension of sulphur dioxide were measured from -60° to 100° and of four mixtures of sulphur dioxide and benzene from their freezing point to 80°C .

9. J. Am. Chem. Soc. 39 (1917) (2261)

10. Trans Faraday Soc. 8, (20), (35), 1913

11. "Variation of Surface Tension with temperature and some related functions". J. Chemical Soc. 1924. Vol 125, January

APPARATUS AND METHOD

The method used for the determination of surface tension was a modification of one developed by T. W. Richards¹².

Capillary tubes (found to have radii of .11255 cm and .02376 cm) were fused together to form a "U" tube. They were standardized by measuring the length of a column of mercury at different positions along the tube with a micrometer microscope and then weighing the mercury. From this the radius could be calculated. Several tubes were investigated, but only those in which the bore was uniform to 1 in 2000 were used. A hole about .5 cm diameter was blown in the base of each capillary to allow for the rise or fall of liquid in the capillary. The "U" tube was fused vertically in an outside tube just large enough to hold it. Its diameter was about 2.5 cms. and length about 15 cms.



Fig 1.

After being cleaned with aqua regia and washed twenty times with distilled water the tube was rinsed out with the pure water and then filled with it so that the liquid in the fine capillary stood near the centre of the tube. It was then evacuated and placed in the constant temperature bath. This consisted of a 1500 cc. Dewar flask provided with a pump stirrer which circulated the water every two minutes, and an electrical thermometer. A standard platinum resistance thermometer was used to read

temperature. The difference between the levels of the liquid in the two arms of the "U" tube was read by a cathetometer.

The equation used to calculate surface tension and also the tube's constant was $S = Kh_d$. developed by T. W. Richards¹² in which K. is the constant for the tube, d the density of the mixture corrected for the vapor, $h = h_1 - h_2 - \frac{r_1^2 - r_2^2}{3} - .01288 \frac{r_1^2}{h_1} - \frac{r_2^2}{h_2}$ where h_1 r_1 and h_2 r_2 are the heights and radius of the smaller and larger capillary tubes. The last term was negligible, so for this experiment $h = h_1 - h_2 - .0295$.

The results obtained for tube I were:

Difference in height between two miniscuses 4.875 cm.

Correstion for curvature of miniscus .0295

True value of h 4.8455

Surface Tension of water 72.80¹²

Density of water at 20° .99982¹²

Then K the constant for the tube equals $\frac{S}{h_c d}$

$$\text{equals } \frac{72.80}{4.8455 \times .99982} = 15.0266$$

This first tube was used for mixtures I & 3¹ and pure SO₂. A second was made and standardized in the same way K being 18.482. This was used for mixtures 2 & 4.

To test the exactness of tube I it was partly filled with pure benzene. The benzene was frozen, the tube evacuated, and then put into the constant temperature bath at 20°C and the difference in level read by the cathetometer.

Result:

average value for h 2.217 cm.

correction for curvature of meniscus .0295

True h 2.1875

$S = Kh\delta$

$= 12.0266 \times 2.1875 \times .8787$

$= 28.87$

The value for density of benzene (Samuel Sudgen¹³) is .8788 but being corrected for vapor = .8787 and that for surface tension is 28.88. It is thus shown that this method gave correct values for surface tension.

The measurement of the surface tension of sulphur dioxide and mixtures of sulphure dioxide and benzene was carried out by sealing the liquid under consideration in the tube and reading the differences in height at various temperatures ranging from its freezing point to 80°C.

The tube was placed in different parts of the Dewar flask and the Dewar was rotated to see if there were any optical defects due to the glass, but none could be found. The heights read in a constant temperature without the Dewar flask gave the same value for surface tension showing the Dewar flask didn't introduce any optical defects.

In taking the readings the bulb was held at the temperature required until the readings became constant. This was usually about 30 minutes. The bulb was frequently shaken to keep the walls above the miniscus wet

13. Variation of Surface Tension with temperature and some Related functions. Journal of The Chemical Society 1924, Vol 125, January

so as to get a clear meniscus. This is very important at lower temperatures to prevent the high viscosity causing a lag in the liquid coming to its right level.

The Dewar flask was filled with water from 0° to 80° and with ether below 0°. To obtain the low temperatures solid carbon dioxide was used with a little alcohol to dissolve the water, thus preventing ice forming in the bath.

Two methods were employed for the measurement of densities.

1. The measurement of densities of sulphur dioxide and mixtures of sulphur dioxide and benzene below -10°.

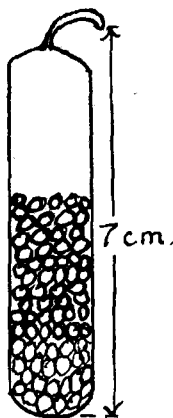


Fig 2

A quartz bulb (Fig. 2) filled with shot was cleaned, dried and suspended by a silk thread from the scale pan of a balance. It was weighed in dry air the weight being corrected for the buoyancy of the bulb and weights the expression $W \left(1 + \frac{\text{density of dry air}}{\text{density of bulb}} - \frac{\text{density of dry air}}{\text{density of brass}} \right)$. It was next weighed in pure distilled water the weight being corrected for the buoyancy of the weights.

Calculations:

Weight of bulb in dry air 31.0194 grams

corrected for buoyancy of bulb and weights

$$31.0194 \left(1 + \frac{.001205}{31.0191} - \frac{.001205}{8.4826} \right) - \frac{.001205}{8.5} = 31.0250 \text{ grams}$$

Weight of bulb in pure water 22.5398 grams

corrected for buoyancy of weights

$$22.5398 \times 1 - \frac{.001205}{8.5} = 22.5305 \text{ grams}$$

Difference 8.4945 grams

$$\text{Volume of bulb} = \frac{8.4945}{.998235} = 8.5095 \text{ c.c.}$$

To measure the density of sulphur dioxide or of a mixture of sulphur dioxide and benzene a tube (Figure 3) was placed in the constant temp-

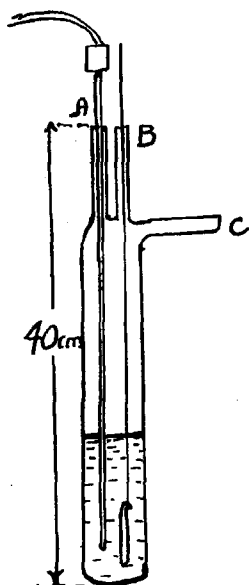


Fig 3

erature bath. One outlet (a) was for the platinum thermometer, one (b) for the thread and quartz bulb and the third (c) was to allow for a stream of dry air to pass through thus preventing the entry of moisture. The balance to which the silk thread was attached was placed over the Dewar and bulb was weighed in the liquid at temperature from -10° to its freezing point. By subtracting the found weight corrected for buoyancy of weights from 31.0250 and dividing by 8.5095 the density of the solution was found. It is interesting to note that this density apparatus was more sensitive to temperature than the platinum thermometer.

Method 2. To determine the density of:

(a) Sulphur dioxide from -10 to 110°C .

(b) Mixtures of sulphur dioxide and benzene from -10 to 80°

(a) A bulb about .5 cc. was blown on the end of a uniform bore calibrated capillary tube whose radius was found to be .02821 cm. The size of the bulb up to a certain scratch was found by weighing the bulb counterpoised by a similar one, filling it with distilled mercury so that at a definite temperature it would just be at the scratch and again weighing the bulb.

Weight of mercury

8.2907 grams

Temperature 23.5°C .

Density of mercury at 23.5°C .

13.53763

Volume of the bulb up to scratch $\frac{8.2907}{13.53763} = .615247$ cc.

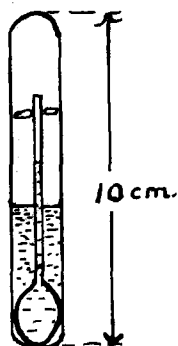


Fig. 4.

This tube had three glass knobs fused on the side, near the top, so that when it was in the outside tube it would stand vertical (Figure 4). The inside tube rested on the bottom of the outside and was not sealed to it. The tube was vacuated, partly filled with sulphur dioxide and sealed off. Liquid from the outer tube was distilled into the inner tube by keeping the bottom cool and warming the sides. When the bulb and

a little of the capillary were filled the tube was placed in the constant temperature bath and the height of the liquid above the scratch measured. It was then heated 10° and the height again measured. The capillary tube was long enough for two rises of 10° . From these heights the volume

was obtained and by finding the absolute density by Method I at any one temperature the higher densities were found by successive use of the equation density = $\frac{\text{weight}}{\text{volume}}$.

(b) Method (a) had to be modified for the mixtures of benzene and sulphur dioxide to assure a uniform mixture throughout.

A bulb of about 1 c.c. was blown on a uniform bore capillary tube whose diameter had been found. The volume up to the scratch was found as in method (a). The tube (Figure 5) was evacuated, filled with the mixture and sealed off. The heights were read at different temperatures and the volume was calculated. By finding the density at any temperature by Method I the densities for the other temperatures can be calculated in the same manner as method 2 (a).

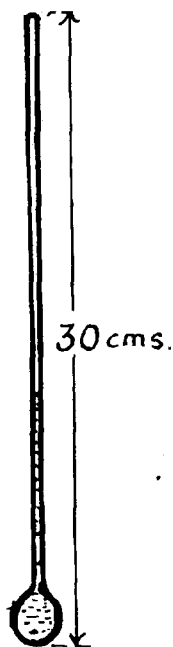


Fig.5.

PREPARATION OF MATERIALS

The pure water used to standardize the surface tension apparatus and quartz density bulb was prepared by distilling the laboratory distilled water with sulphuric acid and potassium permanganate to remove the organic matter, distilling it with sodium hydroxide to remove some of the carbon dioxide and then twice freezing the water under vacuum to remove the carbon dioxide.

The benzene was washed several times with sulphuric acid to remove the thiophene; with sodium hydroxide to remove the sulphuric acid, and

with distilled water. It was then refluxed over metallic sodium and distilled.

Sulphur dioxide was passed through six washbottles filled with sulphuric acid to remove any sulphur trioxide and through three phosphorous pentoxide tubes to dry it. It was then caught in a tube with a spiral

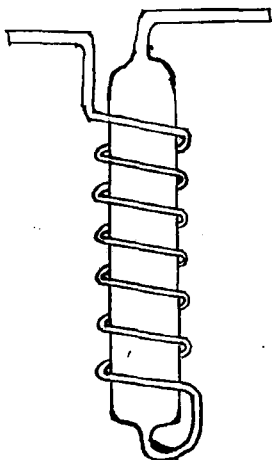


Fig. 6.

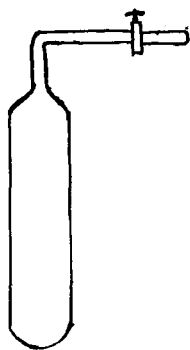


Fig. 7.

around the outside (Figure 6). Salt, calcium chloride and ice were used for cooling the sulphur dioxide tube to collect the sulphur dioxide. The mixtures of sulphur dioxide and benzene were made up by weighing the reservoir tube (Figure 7)

counterpoised with a similar one. It was then evacuated, benzene sucked in and weighed again.

The benzene was frozen and the tube connected to a "T" tube with a stopcock on one arm and the sulphur dioxide tube connected to the third. Thick rubber suction tubing was used to connect the glass together but the ends of glass were touching, thus preventing contamination of the liquid by rubber.

The "T" tube and the tube with frozen benzene were evacuated, the stopcock on the "T" tube shut off and the sulphur dioxide distilled into the benzene. The tube was then disconnected and weighed. To check the composition of the mixture the liquid in the surface tension apparatus was weighed and

titrated for sulphur dioxide against a standard sodium hydroxide solution.

The surface tension and density apparatus were filled by attaching them to the "T" tube evacuating the air and allowing the mixture to flow into it. They were then sealed off thus being free from air.

RESULTS

The results of the experiments are given in the following tables. Tables 1, 2, 3, 4, 5, 6 and 7 give the temperature, the density and density corrected for vapor, corrected height, surface tension and molecular surface energy $S(MV)^{2/3}$.

Sulphur dioxide

Temperature	Density	Density corrected for vapor	Corrected h	Surface Tension	Molecular Surface Energy
-50	1.5589		1.470	34.42	409.62
-40	1.5349	1.5349	1.415	32.57	
-30	1.5106	1.5096	1.365	30.97	
-20	1.4859	1.4842	1.316	29.36	361.00
-10	1.4611	1.4583	1.265	27.79	
0	1.4348	1.4306	1.215	25.93	
10	1.4116	1.4057	1.135	24.08	308.08
20	1.3845	1.3754	1.070	22.12	
30	1.3570	1.3443	1.000	20.21	
40	1.3290	1.3118	.9205	18.38	242.25
50	1.3007	1.2687	.8505	16.61	
60	1.2653	1.2318	.7855	14.52	

Temperature	Density	Density corrected for vapor	Corrected h	Surface Tension	Molecular Surface Energy
70	1.2337	1.1930	.7155	12.74	181.15
80	1.1959	1.1443	.6355	10.93	
90	1.1575	1.0935	.5605	9.21	
100	1.1163	1.0380	.4855	7.57	118.17

Table II Benzene¹³

135	---	.8857	---	29.72	588.92
20	---	.8787	---	28.88	573.73
32.5	---	.8653	---	27.30	
39	---	.8581	---	26.36	553.12
54.8	---	.8400	---	24.28	
61	---	.8330	---	23.61	461.48
72	---	.8207	---	22.15	
90	---	.8006	---	20.13	
120	---	.7616	---	16.42	359.58
210	---	.6011	---	6.45	165.39
280	---	.2305	---	0.36	17.49

Table III

Composition of Mixtures

<u>Percent by weight</u>		<u>Molar percent</u>	
Benzene	Sulphur dioxide	Benzene	Sulphur dioxide
Mixture 1. 77.7	22.3	74.1	25.9
3. 46.01	53.99	41.2	58.8

13. Journal of Chemical Society, 1924 Vol. 125, January

	Benzene	Sulphur dioxide	Benzene	Sulphur dioxide
Mixture 2.	62.69	37.31	58.0	42.0
4.	22.07	77.93	18.9	81.1

Table IV Mixture 1.

Temperature	Density	Density corrected for vapor	Corrected h	Surface Tension	Molecular Surface Energy
-10	.9926	.9917	2.136	31.83	571.06
0	.9799	.9787	2.051	30.16	545.81
10	.9662	.9635	1.976	28.61	523.85
20	.9543	.9510	1.901	27.16	502.70
30	.9418	.9375	1.826	25.72	480.34
40	.9293	.9237	1.751	24.30	458.11
50	.9167	.9092	1.676	22.90	437.99
60	.9045	.8942	1.601	21.57	415.41
70	.8920	.8795	1.526	20.08	394.11
80	.8795	.8630	1.446	18.75	371.49

Table V Mixture 3.

-30	1.1191	1.1186	1.620	33.50	530.38
-20	1.1044	1.1035	1.545	31.45	502.28
-10	1.0897	1.0882	1.470	29.52	476.78
0	1.0741	1.0718	1.405	27.84	453.40
10	1.0585	1.0549	1.335	26.04	428.55
20	1.0475	1.0425	1.270	24.42	405.19
30	1.0374	1.0304	1.205	22.90	382.93

Temperature	Density	Density corrected for vapor	Corrected h	Surface Tension	Molecular Surface Energy
40	1.0269	1.0172	1.140	21.39	360.73
50	1.0135	1.0003	1.070	19.79	337.45
60	1.0017	.9928	1.000	18.26	315.13
70	.9853	.9620	.9355	16.84	294.67
80	.9773	.9478	.8755	15.33	271.08

Table VI Mixture 2.

-30	1.0761	1.0758	2.090	33.79	560.90
-20	1.0625	1.0619	2.010	32.08	537.32
-10	1.0491	1.0481	1.930	30.40	515.94
0	1.0358	1.0343	1.850	28.76	489.03
10	1.0221	1.0195	1.770	26.95	462.84
20	1.0084	1.0045	1.695	25.59	443.58
30	.9945	.9893	1.620	24.09	421.43
40	.9808	.9734	1.545	22.53	397.80
50	.9678	.9579	1.470	21.21	377.80
60	.9548	.9409	1.390	19.73	355.01
70	.9388	.9220	1.320	18.29	332.57
80	.9235	.9023	1.250	16.95	311.62

Table VII Mixture 4

-60	1.2969	---	1.615	38.720	537.60
-50	1.2812	---	1.555	36.83	515.52
-40	1.2630	---	1.495	34.91	493.28

Temperature	Density	Density corrected for vapor	Corrected h	Surface Tension	Molecular Surface Energy
-30	1.2468	---	1.440	33.19	473.11
-20	1.2313	1.2300	1.380	31.38	451.35
-10	1.2149	1.2127	1.320	29.53	428.71
0	1.1962	1.1929	1.250	27.57	404.69
10	1.1784	1.1734	1.185	25.78	381.58
20	1.1604	1.1534	1.120	23.88	358.57
30	1.1415	1.1316	1.055	22.06	335.53
40	1.1229	1.1095	.990	20.31	312.83
50	1.1037	1.0854	.925	18.56	290.23
60	1.0838	1.0608	.855	16.76	266.08
70	1.0623	1.0303	.785	14.95	241.95
80	1.0403	1.0000	.715	13.23	218.33

Table VIII Freezing Point

Benzene	8°
Sulphur dioxide	72.8°
Mixture 1	13.6°
3	41.0°
2	26.5°
4	61.1°

Table IX Ramsays & Shields "K"

Temperature	Sulphur dioxide	Benzene	Mixture			
			1	2	3	4
-30	1.65	---	---	---	---	2.15
-20	1.71	---	---	2.68	2.20	---
-10	1.77	---	2.06	2.44	2.00	2.33
10	1.94	2.13	2.08	2.42	2.06	2.31
30	2.14	2.13	2.12	2.32	2.13	2.29
50	2.08	2.14	2.12	2.10	2.11	2.33
70	2.07	2.13	2.12	2.10	2.10	2.39

DISCUSSION OF RESULTS.

The experimental results have been plotted so that the effect of the mixture can be better visualized.

Graph 1, 2 and 3 in which density, surface tension, and molecular surface energy are plotted against temperature are straight lines showing the relationships linear.

In the density - molar concentration curve Graph 4 the values of density for the mixtures are below a straight line joining the two pure substances, that is the molecular volumes of the mixtures are higher than the calculated value. The addition of benzene to sulphur dioxide causes the benzene to take up some of the residual valency of sulphur dioxide and a loose compound of the two is formed, thereby increasing the molecular volume. The lower the temperature the steeper the curves showing the lower the temperature the greater the compound formed.

In Graph 5 (molar concentration vs. surface tension) the curves tend towards a straight line at higher temperatures as one would expect from the law of mixtures. At lower temperatures there is a maximum indicating compound formation.

In molar surface energy vs. molar concentration curve (Graph 6) we have again indications at lower temperatures of compound formation.

In Graph 7, K the molecular surface energy per degree, has been plotted against temperature for the experimental values and also for the calculated by the Law of Mixtures' value. The experimental value was calculated over a 20° range and then divided by 20 as in that way a smoother

curve was obtained. From the sulphur dioxide curve the value of K is low increasing with temperature which shows the sulphur dioxide is associated and breaks up as the temperature increases reaching a constant value at about 20°C. The values for the mixtures start at high values and decrease as the temperature increases. There are three possibilities to account for this.

1. Association and Dissociation.

It is quite conceivable that the addition of benzene to sulphur dioxide might affect the association of the sulphur dioxide but it would lower the value of K or bring it back to a constant value. It could not cause it to increase to the values obtained. Association therefore had not caused the difference. Because of the two substances used, dissociation is out of the question.

2. Physical influence of one compound on the other.

If the difference between the two curves was due to the physical influence of one constituent on the other it should increase with temperature but the opposite was found to be the case. Therefore physical influence of one compound on the other has not accounted for the difference.

3. Chemical Combination.

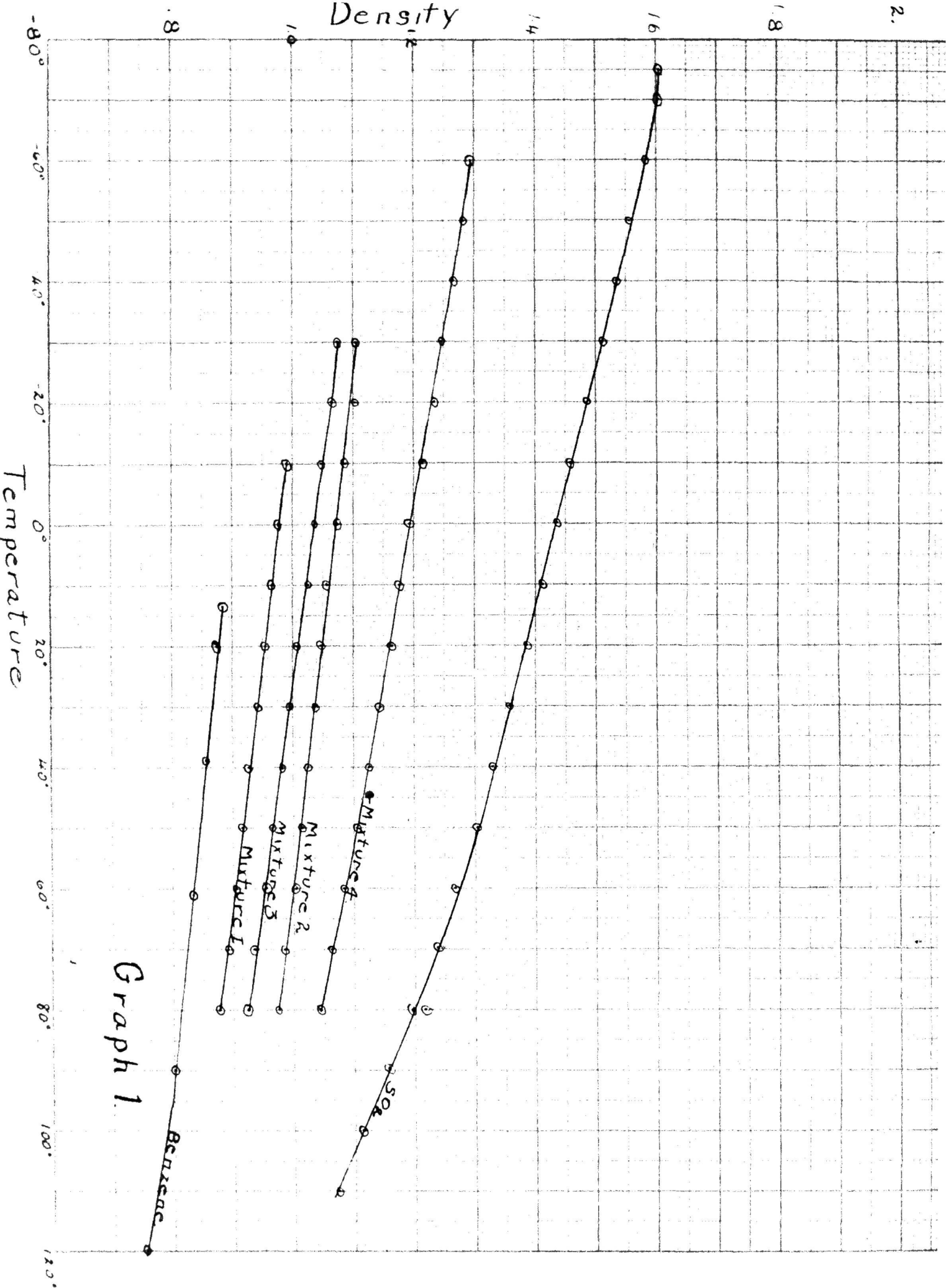
Chemical combination between the sulphur dioxide and benzene seems to account for the behavior. This is evident from the fact that at the lower temperature the molecular surface energy is considerably higher than the calculated value and union of sulphur dioxide and benzene is thereby shown. As the temperature increases the difference between the calcul-

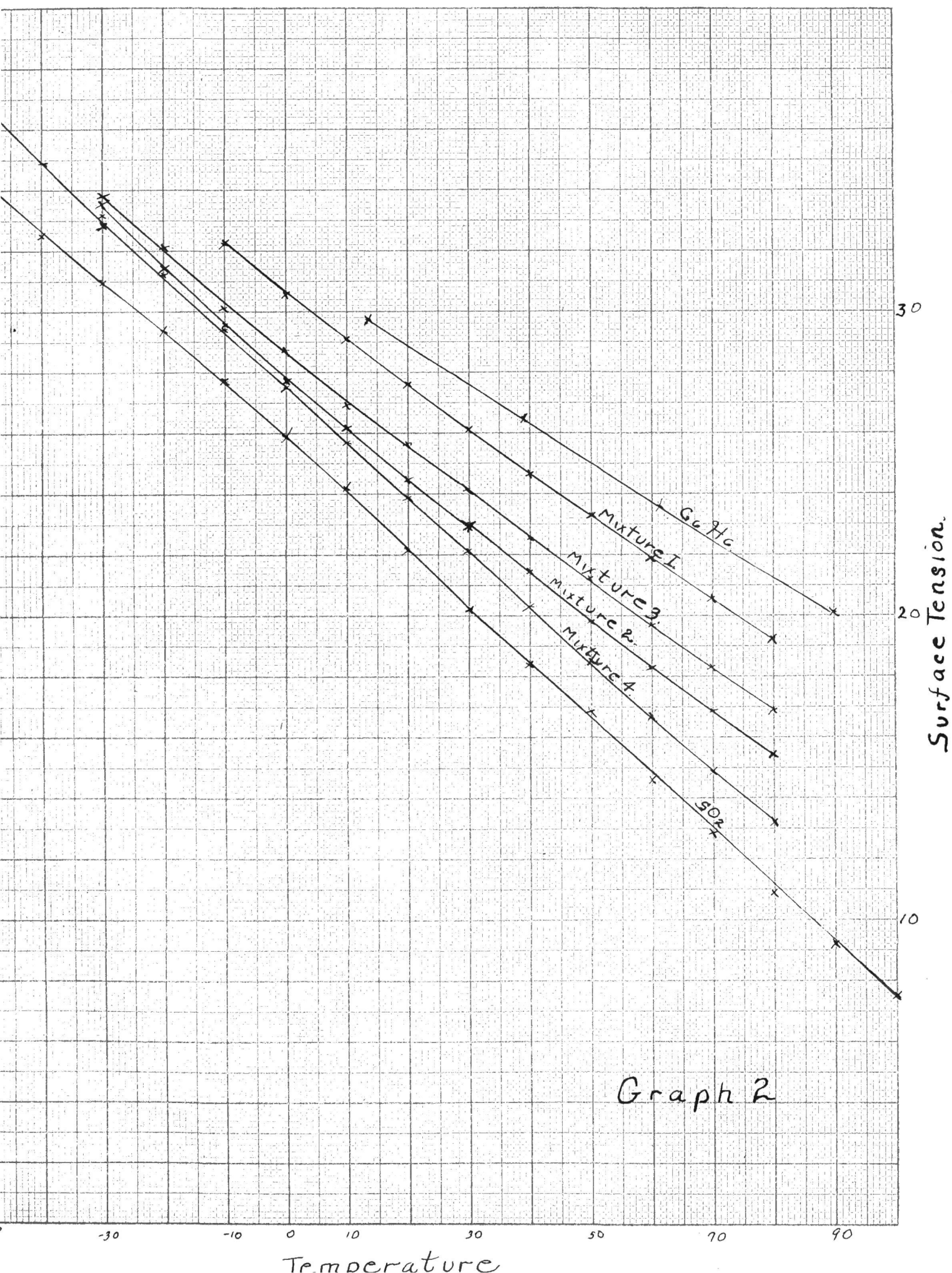
ated and found decreases and the compound breaks up as we would expect. The compound formed is very unstable as can be seen from the freezing point curve (Graph 8) which has only one eutectic which from thermodynamics would indicate no compound. This is the case since the force tending to make the benzene crystallize out is stronger than the force holding the sulphur dioxide and benzene, thus there is no effect on the freezing point curve. From the study of the molecular surface energy per degree (K) curves for the calculated and measured values an unstable chemical compound between sulphur dioxide and benzene has been shown.

SUMMARY

1. The density and surface tension of sulphur dioxide were measured from $-60 - 100^{\circ}$.
2. The density and surface tension of four mixtures of sulphur dioxide and benzene were measured from their freezing point to 80°
3. The relationship of density, surface tension and molecular surface energy with temperature was linear.
4. Evidence has been obtained supporting the theory of solvation in solution.

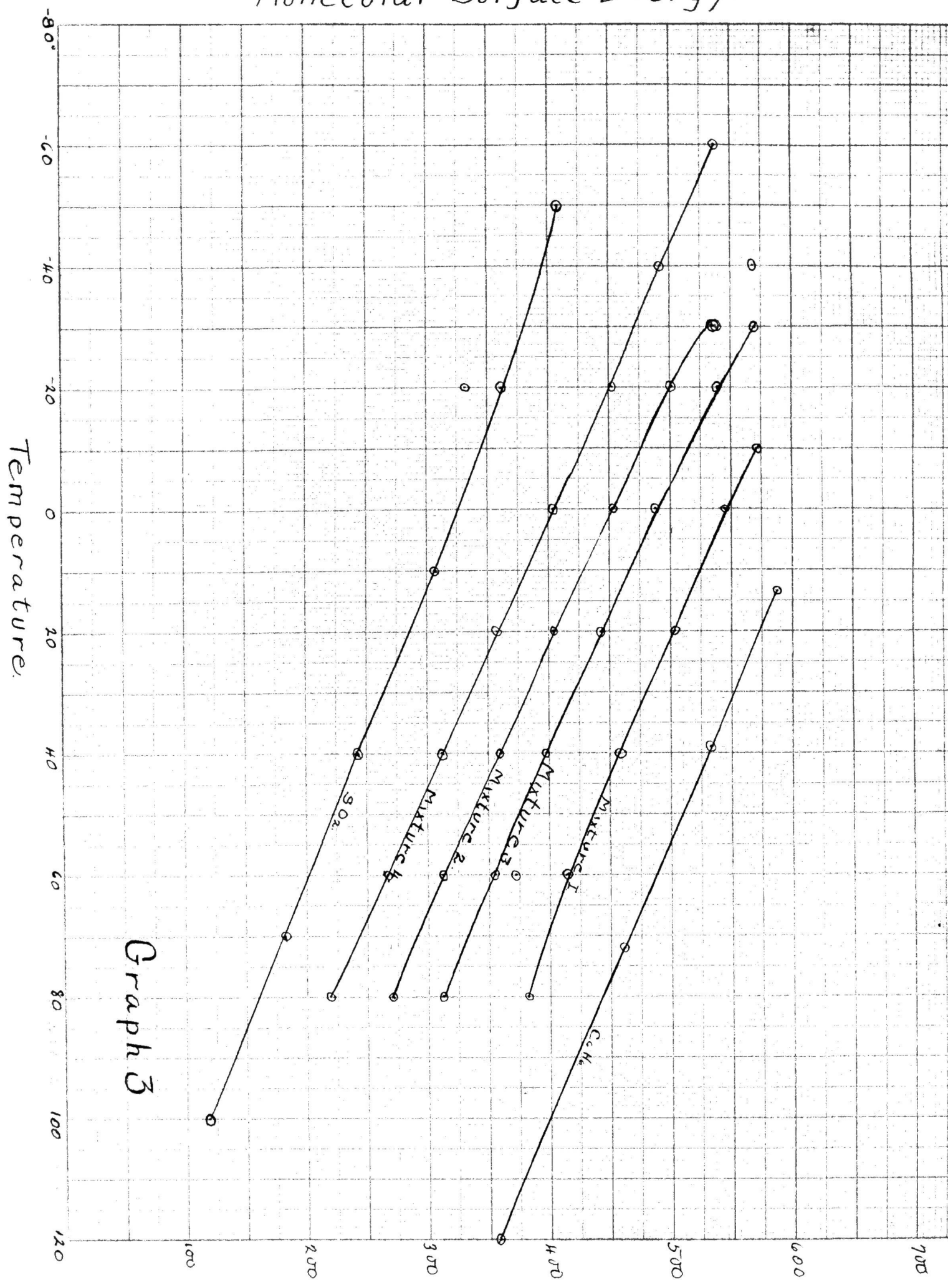
I wish to thank Dr. W. F. Seyer for his valuable assistance during these experiments.

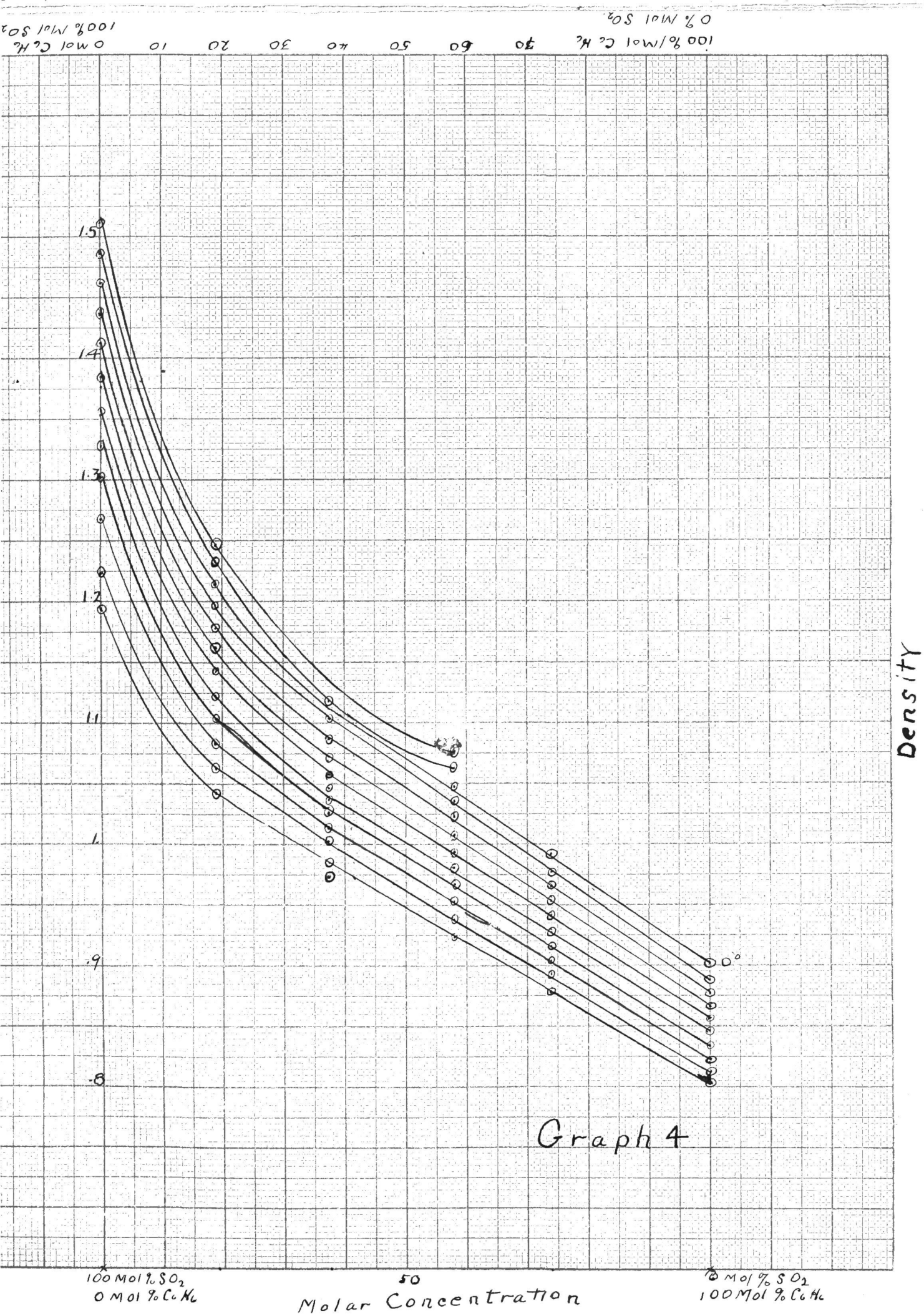


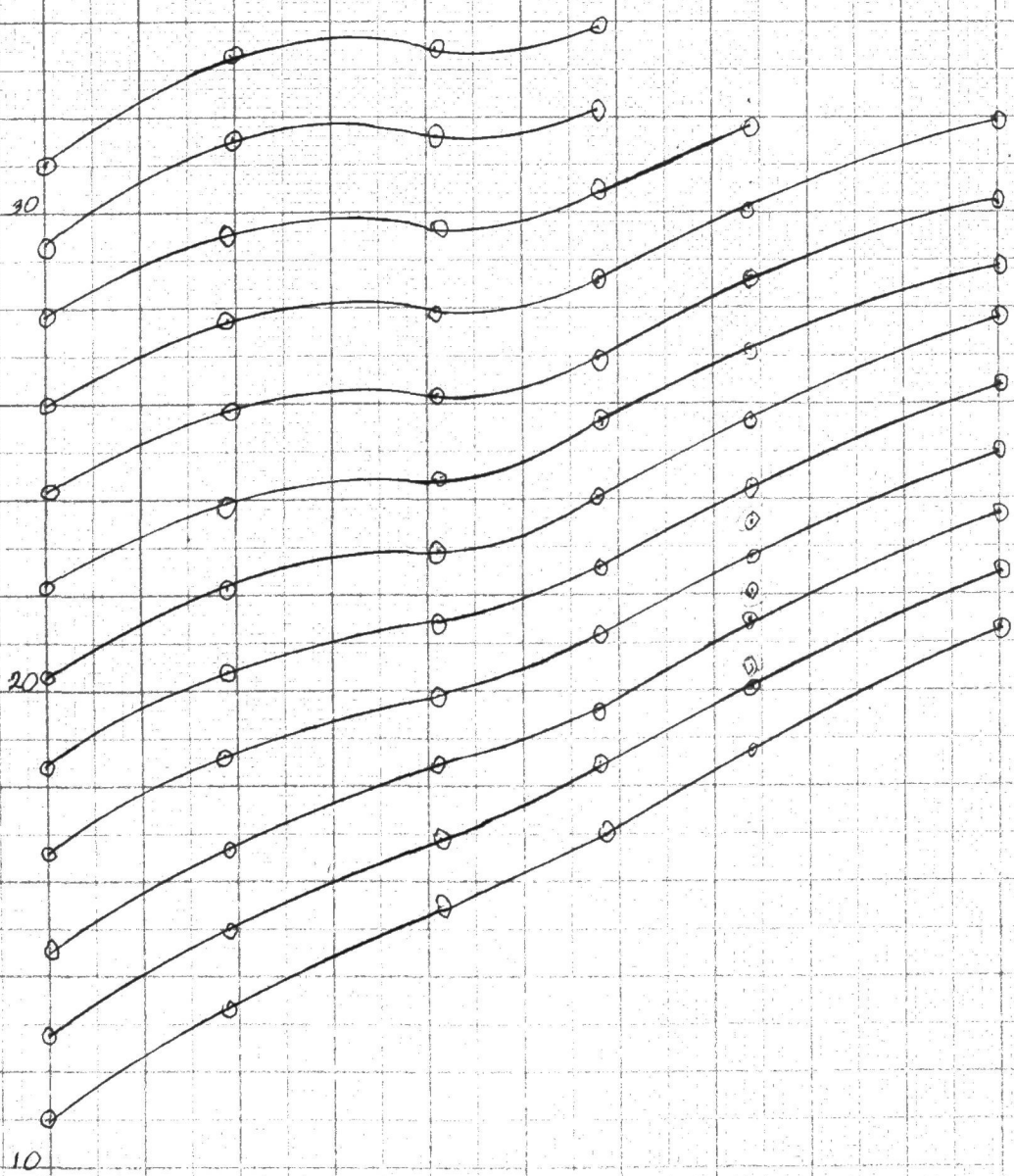


Graph 2

Molecular Surface Energy







Surface Tension

Graph 5

100 Mol % SO_2

50
50

Molar Concentration

100% Mol C_6H_6

Molecular Surface Energy

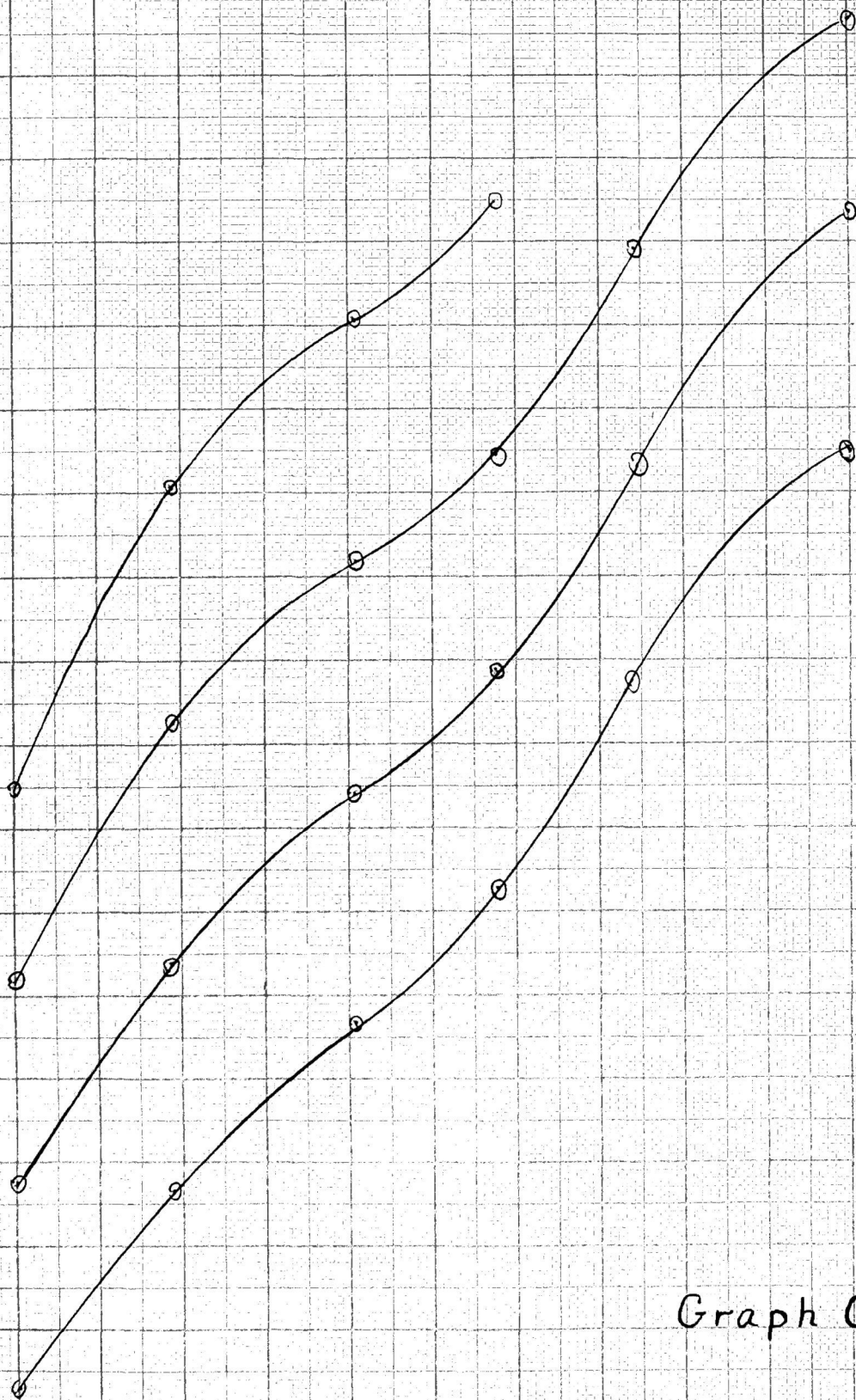
Graph G.

100% Mol. SO_2

50

100% Mol C_6H_6

Concentration



Mixture 2

Mixture 1

Mixture 4

Mixture 3

Benzene

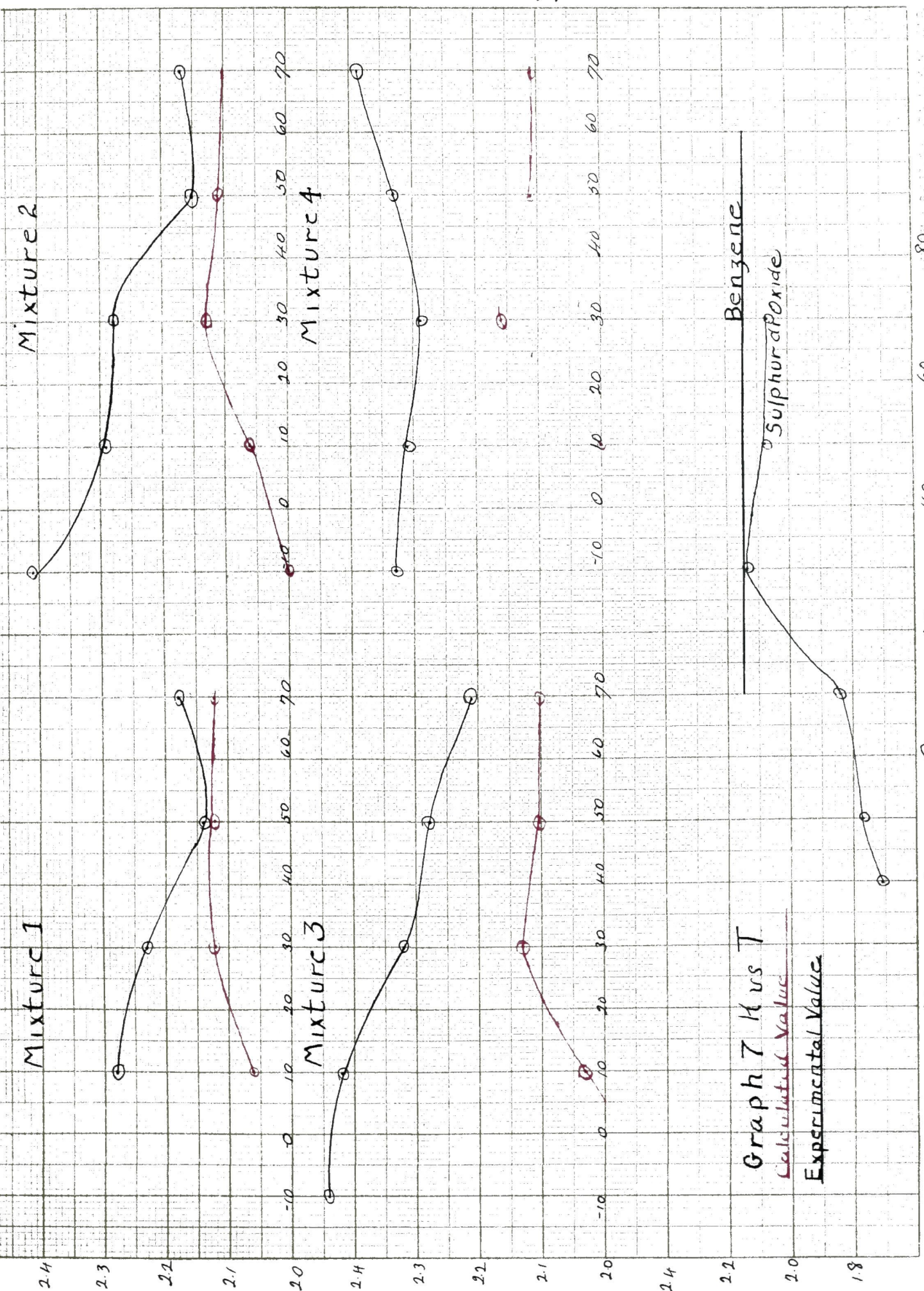
Sulphur dioxide

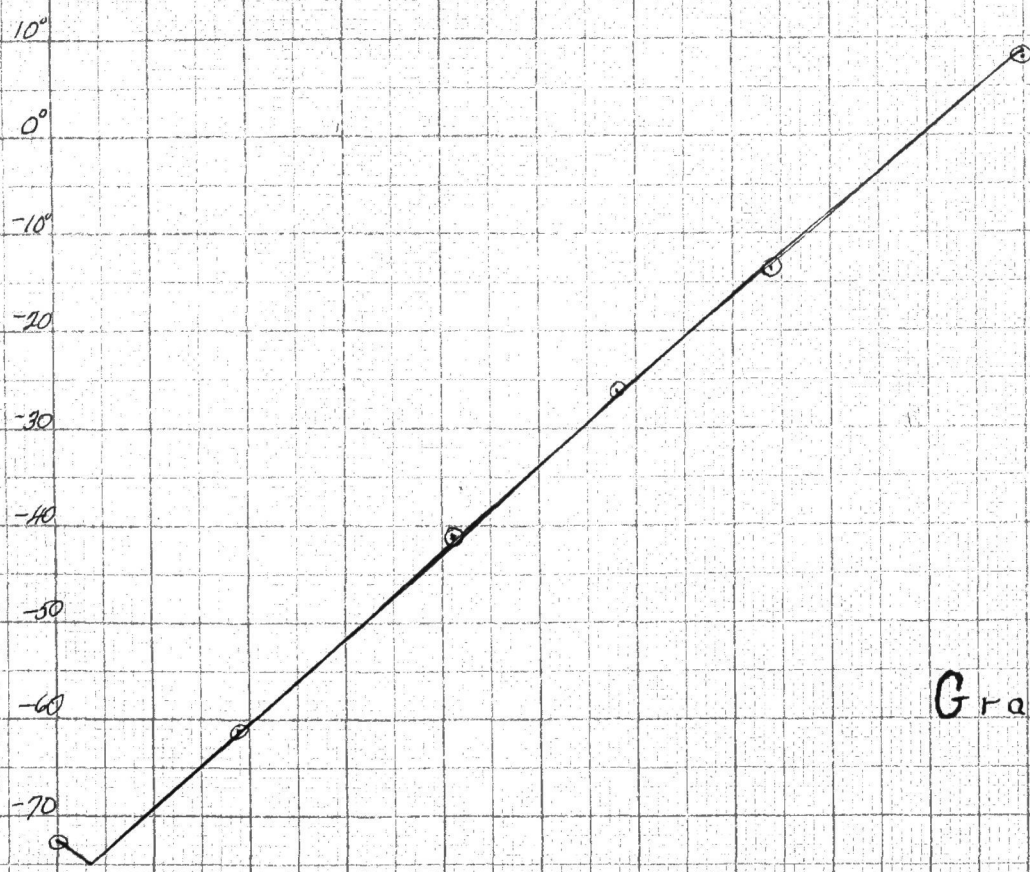
Graph 7 K vs T

Calculated Value

Experimental Value

Temperature





Graph 8

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