THE REFINING AND HYDROGENATION OF FISH OILS.

A thesis presented to
The Faculty of Graduate Studies and Research
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Master of Engineering.

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by

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CONTENTS

FOREWORD

The Refining and the hydrogenation of fish oils in the preparation of solid fats for general industrial purposes have been in general use for a comparatively short time.

So an attempt was made to determine the most satisfactory conditions for the refining of fish oils and to investigate the rate of hydrogenation of these oils in the presence of nickel catalyst. The author studied also the variation of iodine value with hydrogen absorption, the mecanism followed by the hydrogenation, as given by an interpretation of the results, and the order of the reaction.

The oil used for this investigation was seal oil probably because this oil, being relatively little known in the industrial applications, possesses however many properties capable to render it very useful for different purposes.

The hydrogenation was carried out at atmospheric pressure in an apparatus of the closed type.

The thesis proper contains a review of the general properties of fats and a short historical account of the main workers in the field of hydrogenation. Following this is a complete description of the apparatus used and experimental procedure involved in the investigation together with a description of the results obtained with tables and graphs. The interpretation of these results and graphs is fully discussed in the section headed "Discussion", and the conclusions are summarized under a separate heading.

Full details of experimental methods and data are given in the appendices, for convenience.

The investigation was made under the direction of Dr.J.B.Phillips, and the apparatus was constructed and the experiments carried out by the author himself.

INTRODUCTION

Properties of Fats:

The vegetable and animal fats and oils are included in a great group of esters, known as glycerides. Besides the principal constituent glycerides, all oils contain small amounts of "unsaponifiable matter," existing as such or as esters, and phosphatides. The colour is due to characteristic pigments, such as carotin, xanthophyll, or chlorophyll.

The principal acids combined with glycerol in the natural fats are stearic, $C_{17}H_{35}COOH$, palmitic , $C_{17}H_{31}COOH$, oleic , $C_{17}H_{33}COOH$, and butyric, C_3H_7COOH. One molecule of glycerol combines with three molecules of acid to form a fat. The three acid molecules may be alike or different. The most commonly occuring glycerides are represented by the following general structure:

$$\begin{array}{l} CH_2\text{- O-CO-R} \\ | \\ CH\ \text{- O-CO-R} \\ | \\ CH_2\text{- O-CO-R} \end{array}$$

Where R is the acid radicle. The natural fats are mixtures of these esters with smaller quantities of glycerol esters of other acids and with mixed esters, that is esters in which two or three different acids are in combination with the same glycerol residue.

Fats may be hydrolyzed by boiling with diluted acids or alkalies or by heating with steam. The products formed are glycerol and the free fatty acids or, if boiled with alkalies, glycerol and the salts of fatty acids, that is, soaps.

Hydrolysis by an alkali is referred toas saponification:

$$\begin{array}{l} CH_2\text{-}O\text{-}CO\text{-}R \\ CH\text{-}O\text{-}CO\text{-}R \\ CH_2\text{-}O\text{-}CO\text{-}R \end{array} + 3NaOH = \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + 3RCOO\,Na$$

Since all natural sources of fats yield mixed esters, the soaps ordinarily manufactured are not pure salts. They are mixtures of the salts of several acids in which more or less water, glycerol, and alkali are incorporated. Different soaps are made by varying the relative proportions of different fats, by using different bases, by incorporating different amounts of glycerol, and so on. Hard soaps and soap powders are made by saponifying solid fats with sodium hydroxide. Potassium salts are softer than the corresponding sodium derivatives, and soaps derived from oils are softer than those obtained from solid fats.

The free fatty acids are prepared in large quantities by hydrolysing the fats with superheated steam. Stearic acid freed by pressure from the softer acids is mixed with a little paraffin to render it less brittle and is used in the manufacture of candles.

Some of the vegetable and animal oils consist in part of unsaturated esters, which are capable of combining with hydrogen gas in the presence of a catalyzer (usually finely divided nickel) to form solid or semi-solid fats. This is the principle by which oils are hardened by catalytic hydrogenation. Most of the lard substitutes now on the market are made in this way. Considerable quantities of fish oil, whale oil, and inedible fats are hydrogenated, previous to being converted into soap. The raw material is there by deprived of objectionable odors that

would otherwise injure the finished product.

Linseed oil, poppy oil and a few other vegetable oils consist very largely of unsaturated compounds , that can combine with the oxygen of the air to form solid film . This is the principle by which linseed oil and the hydrocarbon, turpentine, harden when paint "dries". On account of this property, linseed oil is a valuable component of varnishes and paints. It is called a "drying" oil. The oxidation product is a firm, smooth, solid substance. Boiled linseed oil is simply linseed oil to which a lead or manganese salt has been added to serve as a catalyzer for the "drying" process, which is really not drying at all, but oxidation. Linoleum is made from boiled linseed oil and ground cork.

Fats allowed to remain exposed to the air, develop an objectionable odour, and are said to have gone rancid. Rancidity is the result, usually, of chemical changes brought about by the action of oxygen on the fat, but in many cases is due apparently, to the action of enzymes. Rancidity brought about by oxygen is aided by the action of light, heat, and certain metals which act as catalysts. Rancidity due to enzymes action may proceed in the absence of both air and light. Products of rancidity are aldehydes, ketones, lactones, alcohols, oxy and hydroxy acids, carbondioxide and moisture. Reactions are yet but little understood.

Classification of Fats:

Distinction between oils and fats is merely physical. Oils are those oleaginous substances that are fluid at ordinary temperature, while those solid, at ordinary temperature are fats.

It is known that unsaturated glycerides are liquid while saturated, are solid. Therefore, since the Iodine number is a measure of unsaturation, it appears that the most convenient method of classification of fats is given by arranging them according to the magnitude of the iodine value. As stated by Lewkowitsch[1]:

" This principle leads, without unduly forcing it, to a natural subdivision into liquid fats and solid fats, the former being differentiated from the latter by the considerably higher iodine value. Hence an arrangement based on the magnitude of the iodine value would include the older system of classification according to consistency. Inasmuch as the magnitude of the iodine value stands in close relationship to the absorption of oxygen, or in other words, to the drying power, classification on the iodine value would also include the older subdivision into drying and non-drying oils."

According to this, fats in general may be conveniently classified as follows:

1- Fatty oils:

a) Vegetable oils
   1) Drying oils
   2) Semi-drying oils
   3) Non-drying oils

B) Animal oils
   1) marine animal oils
      a) Fish oils
      b) liver oils
      c) Blubber oils
   2) Terrestrial animal oils
      a) Semi-drying
      b) Non-drying

II Solid fats:

A) Vegetable fats

B) Animal fats

1) Drying fats

2)Semi-drying fats

3) Non-drying fats

a) Body fats

b) Milk fats

HYDROGENATION:

Hydrogenation may be said to cover those cases whereby hydrogen is directly added to unsaturated linkages in organic substances, producing another substance having different properties.

Although some of the reactions occur spontaneously to a very limited extent, the great majority are carried out through the medium of heterogeneous catalysis, and hence such reactions are called catalytic hydrogenation.

In the production of solid fats, we have essentially the catalytic addition of hydrogen gas to the unsaturated linkages of the acid radicles of oils, to yield hardened products. The change consists in the conversion of unsaturated glycerides, such as olein and linolein to synthetic stearin.

The velocity of a chemical reaction frequently is accelerated by the presence of a foreigh substance which remains unchanged when the reaction is complete. For example, cane sugar is inverted very slowly by pure water alone, but when a trace of acid is added, the rate of inversion is greatly increased. A substance which accelerates a chemical reaction and is not consumed by it is termed a catalyst, and the process is known as catalysis.

Theterm heterogeneous catalysis is applied to those systems in which the components are not in the same phase. For example, the hydrogenation of an oil in the presence of pure metallic nickel as catalyst is an heterogeneous catalysis, because the oil is in the liquid phase, the hydrogen in the gaseous phase and the catalyst in the solid phase.

As an illustration of the mechanism of hydrogenation of oils, let us consider oleic acid. It combines with hydrogen, in the

presence of metallic nickel as a catalyst, to form stearic acid. Thus,

$$C_{18}H_{34}O_2 + H_2 \overset{Ni}{=} C_{18}H_{36}O_2$$

282 units of oleic acid combine with 2 units of hydrogen, yielding 284 units of stearic acid, by weight.

In general, many changes in the constitution and in the nature of the oil accompany the hydrogenation. The most commonly encountered physical and chemical changes are:

a) Increase in melting-point.

b) Decrease in Iodine Value.

c) Decrease in Refractive Index.

d) Increase in specific gravity.

Other changes effected in the nature of the material are:

a) Improvement in odour and taste.

b) Brightening of the colour.

c) Elimination of rancidity.

d) Rendered chemically stable.

e) Commercial value greatly enhanced.

Industrially, hydrogenation or hardening of oil consists in bringing hydrogen gas in contact with the heated oil in the presence of a nickel catalyst, of amount 0.1-1.0%. The hydrogenation may or may not be carried out under elevated pressure. The temperatures permitted are from 120-210°C, the range 160-180°C being the most widely used.

It is very important that the hydrogen used be as pure and dry as possible, and that the oil be free from impurities that may provide interference with the oil. The greater majority of processes

in use to-day employ electrolytic hydrogen. Great care must be taken in the preparation of the catalyst since the success of the method is largely dependent upon the condition of the metal. The catalyst is susceptible to various poisons, particularly chlorine, sulfur, arsenic, and phosphorus, and their compounds.

Previous Works on the Subject:

Toward the latter part of the nineteenth century Sabatier and Senderens discovered that reduced nickel will bring about the combination of hydrogen with ethylene, or acetylene, with the formation of ethane, as shown by the equations

$$C_2H_4 + H_2 = C_2H_6$$
$$C_2H_2 + 2H_2 = C_2H_6$$

Sabatier[2] also succeed in converting oleic acid to stearic acid in the gaseous phase using a nickel catalyst. His works, in collaboration with Senderens, turned the attention of scientists to hydrogenation of fatty acids in the gaseous phase. These two workers are responsible in great part that hydrogenation of organic substances with metal catalyst is recognized as a major branch of chemical technique.

The first industrial application of hydrogenation to oil in the liquid phase is due to Norman[3], in 1903.

In 1908, Fokin[4] concluded from a study of hydrogen absorption in the case of linoleic acid, that the shape of the curve depends upon:

a) The velocity of diffusion of the gas through the oil.

b) The condition of the catalyst surface.

c) The presence of catalyst poisons.

In 1914, Ipatiev[5], after a study on the effect of temperature on the hydrogenation of fatty acids, found that the temperature of hydro-

genation depends upon the type of catalyst used.

But the most important works on the effect of temperature on the hydrogenation of fatty oils are due to Maxted[6], in 1921. He found that the optimum working temperature depends on the nature of catalyst and on the oil to be treated. He also showed that relatively high temperatures have an adverse influence on the products and rate of reaction but this influence is counterbalanced by the fact that certain poisons have a less toxic effect at high temperature. Finally, Maxted is also responsible for the desigh of much apparatus in use in industrial hydrogenation today.

A great contribution on the preparation of nickel catalyst and the reactivation of the spent catalyst was given by Lush[7], in about 1921.

In the presence of a catalyst the action of hydrogen on the glycerides of an oil is said to be selective, the more unsaturated ones being hydrogenated first, the remaining ones following in the order of their unsaturation. This subject of selectivity was fully discussed by Richardson, Knuth, and Milligan[8] in 1925.

In 1927, Williams[9] found that the selectivity of hydrogenation varies from oil to oil, and depends upon the temperature of operation and the proportion of double linkages in the oil.

An apparent proof of this selectivity is given by the fact that rate curves proceed in definite steps. Such curves were obtained by Meigen and Bartels[10], in 1914, for the hydrogenation of cottonseed oil, by Armstrong and Hilditch[11], in 1920, for the hydrogenation of pure organic compounds, and by Brocklesby and Charnley[12], in 1933, for the hydrogenation of Pilchard oil.

FISH OILS:

The development of fish oils in Canada is relatively new, but the results of the different studies undertaken by the workers of the Fisheries Research Board of Canada have proved the great number of industrial applications of these oils and permitted to expect a great future in this field.

One of the best contributions was given by Brocklesby who occupied himself chiefly with the development of industrial chemistry of fish oils. His work is well summarized in the book[13] on the subject which he published, in collaboration with Denstedt, in 1933. He also carried out a very complete investigation of pilchard oil,[14] studying successively, with other collaborators, the properties, the decolourization, and the hydrogenation of this highly unsaturated fish oil.

Much has been added in recent years to the knowledge of fish oils by the volume entitled: Chemistry and Technology of Marine Animal Oils, which was issued by the Fisheries Research Board of Canada.

The oil used in carrying out the investigations belongs to the class known as the marine animal oils, Seal oil being a blubber oil.

Marine mammals such as the Seal, whale, or porpoise, possess a layer of fatty tissue beneath the skin, known as blubber, which is the source of considerable quantities of useful technical fatty oils. Certain species such as the sperm whale, dolphin, porpoise, etc., also have deposits of fats in the head cavity, and occasionally in the jaw.

Modern research on the component glycerides of marine animal fats is not lacking but, in this field, the large number of component

acids present, and the highly unsaturated nature of many of these, has prevented the application of the methods which can be used only when the major constituent acids of a fat are three or four in number, and when unsaturation is practically confined to acids of the C_{18} series (usually oleic and linoleic).

The great majority of fish oils and of ordinary whale, seal, and similar oils only contain about 15-20% of saturated fatty acids, and consequently most of them possess no detectable quantity of fully saturated components.

Seal Oil:

Seal blubber oil has been used for various purposes for at least as long as whale oil, but no very definite analysis of its composition appears to have been made, with the exception of some data given in 1935 by Williams and Makhrov.[15] These authors suggest that the percentage of the various component acids (wt. per cent) is somewhat as follows:

Saturated (mainly palmitic):..... 18%
Liquid mono-ethenoid (presumably hexadecenoic and oleic)..... 61%
Solid mono-ethenoid (gadoleic, etc.,)..... 7%
Highly unsaturated acids (C_{20} and C_{22}) 14%

The semi-quantitative analytical data of Tsujimoto[16], in 1916, and of Bauer and Neth[17], in 1924, support the view that seal oil and ordinary whale oil are similar in fatty acid composition.

EXPERIMENTAL PROCEDURE

Refining

A) Alkali Refining:

Fish oils are frequently encountered having a free fatty acid content above that permitted in medicinal oils or in oils for animal feeding; such oils usually possess an undesirable colour and flavour.

Many procedures have been suggested for the removal of the free fatty acids and colour; one of the commonest of these methods is that of alkali refining.

In that process, the soap formed through union of the alkali with the fatty acids has certain adsorbent properties and carries down with it a certain amount of colouring matter, finely dispersed tissue material and finally, a small portion of the oil itself.

The amount of alkali used depends upon the free fatty acid content in the oil and the strength of caustic soda solution depends upon both the colour and the free fatty acid content of the oil. The darker the oil and the higher the free fatty acid content , the stronger must the solution be.

Difficulties are often encountered in removing the soap and an attempt has been made by Louis-C. Dugal and A.J. Wood,[18] to determine the most satisfactory conditions for the soap clearing of Cod-liver oil and Seal oil.

It was the method followed by the author, with equally good results. The essential details of the method are as follows:

The precipitation of the soap is carried out by the addition of 15 per cent sodium hydroxide (weight 1 volume) to the violently agitated oil. The best results are obtained when twice the theoretical amount of sodium hydroxide needed for exact neutralization of free fatty acids is used. The alkali is added to the oil maintained at 70°F in the form of a fine jet.

After addition of the alkali, rapid agitation of the oil is continued for fifteen minutes. At the end of this time, the temperature is raised slowly to 115-120°F (43-46°C). During the heating, the speed of agitation is reduced to the point where the soap is just maintained in suspension.

When agglutination occurs, that is, when the mixture shows a clear oil carrying floculent black specks in it, agitation and heating are stopped and the soap is permitted to settle. To facilitate the separation of the soap or foot, a small amount of sodium silicate may be added. The time required for this settling varies with the caracter of the soap, but is usually in the vicinity of half an hour.

After the separation of the oil and soap is complete the clear oil is decanted, and washed with boiling distilled water until no more traces of alkali remain in it.

The oil is then filtered and a filter aid such as Bentonite is very helpful in order to remove any water that remains in suspension and causes a certain turbidity in the oil.

B) Bleaching:

The bleaching is ordinarily effected by Fuller's earth but other earth such as highly activated decolorizing earth or

activated carbons may be used with equally good results.

The adsorbent used is added to the hot oil, stirred in , and the mixture filtered with small amount of filter aid such as filter-cel.

Since the bleaching and the conditions of operation (amount of earth, temperature, time of mixing) depend upon the type of earth used, an attempt was made in order to determine the best earth to be used and the most satisfactory conditions for the oil in hand, that is, Seal oil.

The method used is as follows:

1) Determination of best decolorizing earth.

The different earth used in this experiment were Fuller's-earth, nuchar, Celite, Diatomaceous earth and infusorial earth. All this material was obtained from the McGill supply.

Five samples of 100 c.c. of oil previously treated with alkali were prepared. To each sample, 3 grams of one of the different earth were added, and the mixtures stirred in during 15 minutes at 100°C. After the end of this time, the mixtures were allowed to cool and filtered by suction. The resulting samples of oil were then compared together and the one treated by Fuller's earth was found to be the best.

2) Amount of Fuller's earth.

The experiment was carried out in exactly the same way; but instead of using same amounts of different earth, Fuller's earth was taken in different concentrations, that is, 1,2,3,4, and 5 grams.

The most economical amount of Fuller's earth was found to be: 3 grams of earth for 100 c.c. of oil.

3) Temperature.

The same experiment was carried out using 3 grams of Fuller's earth for 100 c.c. of oil at the following temperatures: 22, 50, 75, 100, 150, and 200°C. 100°C was found to be the most economical temperature.

4) Time of mixing.

For this experiment 3 grams of Fuller's earth for 100 c.c. of oil were again employed, and the mixtures at 100°C were stirred in during 5, 10, 15, 20, 25 and 30 minutes.

The most economical time of agitation was found to be 20 minutes.

HYDROGENATION

A) Apparatus

The apparatus in which the oil samples were hydrogenated is of the closed type as illustrated in figure 1. It consists essentially of a gasometer, A, a reaction flask, B, immersed in an oil bath, C, and a motor, D, which provides the agitation to the reaction flask.

The gasometer consists of two large glass tubes, 1 and 2, being stoppered at one end. The open end of the smaller tube, 1, is inserted in the open end of the other tube which is half filled with water. When the volume of the gas in the tube decreases, the level of water in this tube increases. Then the decreasing volume can easily be calculated knowing the increasing of the level of water from the graduations on the tube and the inner diameter of the same tube.

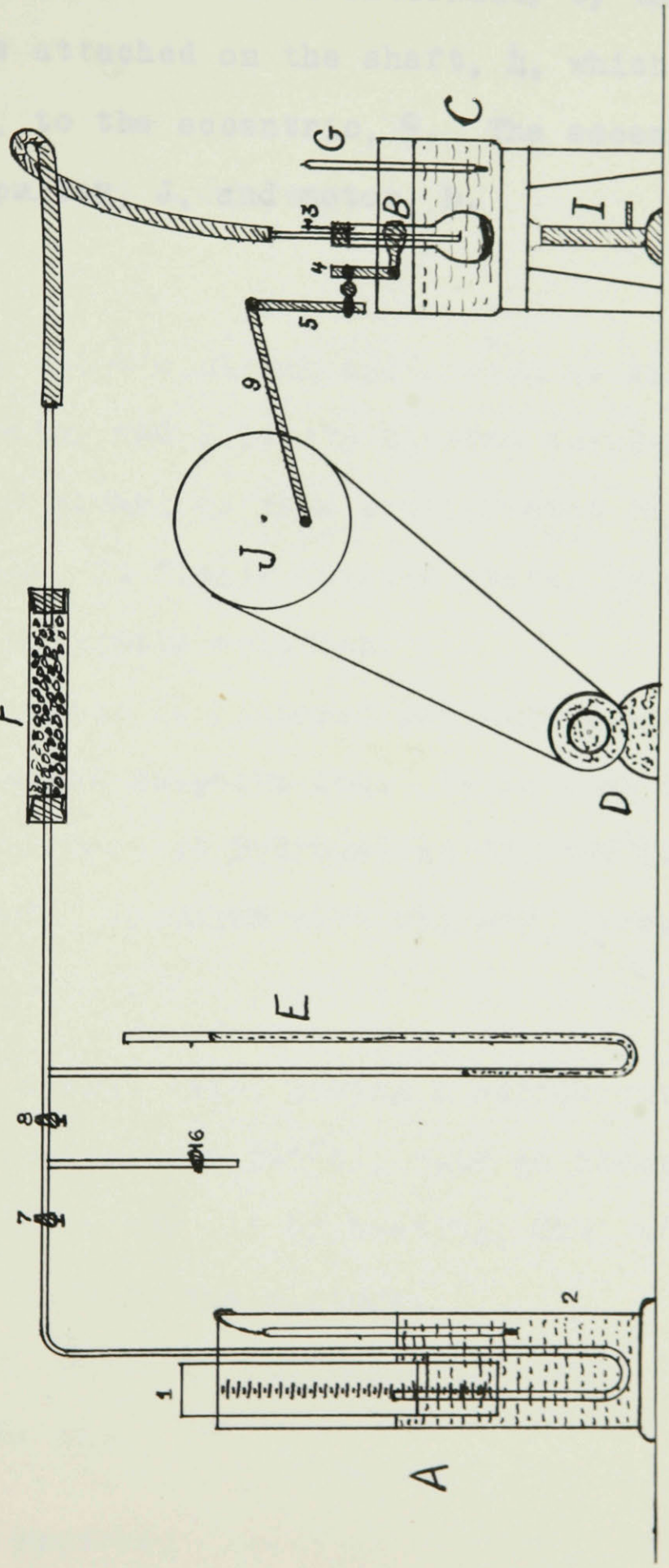
The gas-delivery tube leading from the gasometer to the reaction flask, is provided with a water-pressure gauge, E, which indicates the excess of pressure over atmospheric pressure in the gasometer.

Since the hydrogen is measured over water, it is necessary to insert the calcium chloride tube, F, into the gas circuit to remove any moisture carried along with the gas in its passage from the gasometer to the reaction flask.

Connection between the reaction flask and the glass delivery tube is made with a convenient length of heavy rubber tubing.

The stopper of the reaction flask, a 300 c.c. Kjeldahl flask, is fitted with the hydrogen inlet tube and with an outlet tube carrying a glass stopcock,3.

-FIGURE 1-
HYDROGENATION APPARATUS



To maintain the reaction temperature at the desired value, the flask containing the reaction mixture is immersed in the oil bath, C, the temperature of which is indicated by the thermometer, G. The oil bath is heated externally by the gas burner,I.

The flask is attached on the shaft, 4, which is connected by the member, 5, to the eccentric, 9. The eccentric is driven by the reducing pulley, J, and motor, D.

B) Materials:

1) Catalyst:

Nickel Catalysts are generally prepared by three methods:

1) The Dry Process.

2) The Wet Process.

3) The Decomposition Process.

The Dry Process:

A soluble nickel salt, such as nickel sulphate, is dissolved in water and a finely divided carrier is added to the solution. The nickel is then precipitated on the carrier as nickel carbonate, in finely divided state, by adding a slight excess of sodium carbonate solution.

The precipitate is filtered and washed with water until free from sulphate and sulphite ion. It is then dried at 105°C and reduced in a current of Hydrogen at 325-350°C. The active catalyst so produced, is mixed with oil and stored until required.

The Wet Process:

A nickel salt, having a sufficiently low temperature of decomposition (240-260°C), such as nickel formate, may be reduced directly in the oil by heating, and, at the same time, bubbling hydrogen through the mixture.

The salt should be sufficiently finely divided to form a suspension in the oil.

The Decomposition Process:

Certain easily decomposable organic nickel salts, especially the formate and acetate, yield finely divided nickel when decomposed thermally in the dry state

at 240-260°C and with an atmosphere of hydrogen in the flask.

The decomposition process is certainly the most convenient and rapid method of obtaining a catalyst. The apparatus required is that in which the hydrogenation itself is later carried on, thus cutting the manipulation to a minimum.

In our case, the catalyst used was not prepared by the author, in order to save time, but obtained directly from the McGill supply.

The material from the store was very finely divided nickel and it was reduced with hydrogen in the reaction flask immediatly before each hydrogenation at [redacted] a temperature of 310-350°C. To prevent deactivation of the catalyst during the introduction of the oil, the reduced catalyst was cooled down in hydrogen. The proportion of catalyst used was 1 per cent.

2) Oil:

The refined Seal oil used in the hydrogenation experiments was prepared from a commercial sample of raw oil.

Approximately 1000 c.c. of raw oil were treated with alkali in order to remove the free fatty acids, and a certain amount of colour. The process followed is described on page 12.

The filtered oil was then treated with 100 grams of anhydrous sodium sulphate, the mixture thoroughly shaken and set aside for several hours.

The dry oil recovered from the sodium sulphate mixture by filtration was there upon carefully mixed with Fuller's Earth and the mixture treated as described on page 23.

The resulting sample was a very light and clear oil, and some of its properties are recorded on taole I.

- TABLE I . - Properties of refined Seal oil.

Iodine value (Wijs)	141.1
Free fatty acids	0.0
Saponification value	175.4

C) Experimental:

In hydrogenating a sample of oil, the oil-bath was first brought to the temperature of hydrogenation (180°C), the oil in the bath being agitated by substituting a flask similar to the reaction flask. When the required temperature had been reached, the reaction flask containing the newly-reduced catalyst and the oil was attached to the delivery tube and fastened by means of a clamp to a stand near the oil bath. The gasometer was then closed off by means of stopcock, 7, (fig. 1) and the system washed out with hydrogen by opening stopcocks, 8,and 3, and introducing the gas in, 6. After the pressure of the hydrogen gas in the system had been adjusted to atmospheric pressure, the stopcocks,8 and 3, were closed and the gasometer was likewise washed out and filled with hydrogen by opening stopcock, 7. Then stopcock, 6, was closed and, 8, opened.

To begin the hydrogenation the shaker was stopped and the substitute flask quickly replaced by the reaction flask. The time of the experiment was taken from the moment of immersion of the reaction flask in the hot oil. Similarly the end of a hydrogenation run, was taken at the time at which the flask

was withdrawn. In experiments where the hydrogenation was not continued until the oil was near its saturation point, the reaction flask on withdrawal was immediately plunged into a beaker of cold water in order to prevent any further absorption of gas.

EXPERIMENTAL RESULTS

Refining:

1) Alkali Refining:

Before the oil was treated with alkali, it was a dark brown oil with free fatty acids content of about 3.0%.

After the treatment, it was found that the free fatty acids were completely removed and that there was a marked improvement in color of the oil being pale yellow. However a certain turbidity remained in the oil.

2) Bleaching:

a) Best decolorizing earth.

By this experiment it was found that Fuller's earth was certainly the best decolorizing earth for Seal oil. Good results were also obtained with Celite, Infusorial earth and Diatomaceous earth.

It may be noted that the turbidity remaining in the oil after it has been treated with alkali is completely removed by using these earth. However, Nuchar seems to be no good as a bleaching agent for Seal oil. With this adsorbent, the mixture is very difficult to filter and a certain amount of turbidity remains in the oil which becomes green colored.

b) Conditions of operation.

It was found that the most economical method of operation for the bleaching of Seal oil with Fuller's earth is to use 3 per cent (weight / volume) of earth and stir in during 20 minutes at 100°C. At the end of this time, the mixture is filtered with a small amount of a filter aid such as filter-cel.

Hydrogenation: 1) Rate of Hydrogen Absorption:

The results recorded in table II show the rate of Hydrogenation of 4.59 grams (5.0 c.c.) of refined seal oil in the presence of .0450 grams of catalyst (1 per cent Ni to oil) which had been reduced for ½ hour at 325°C.

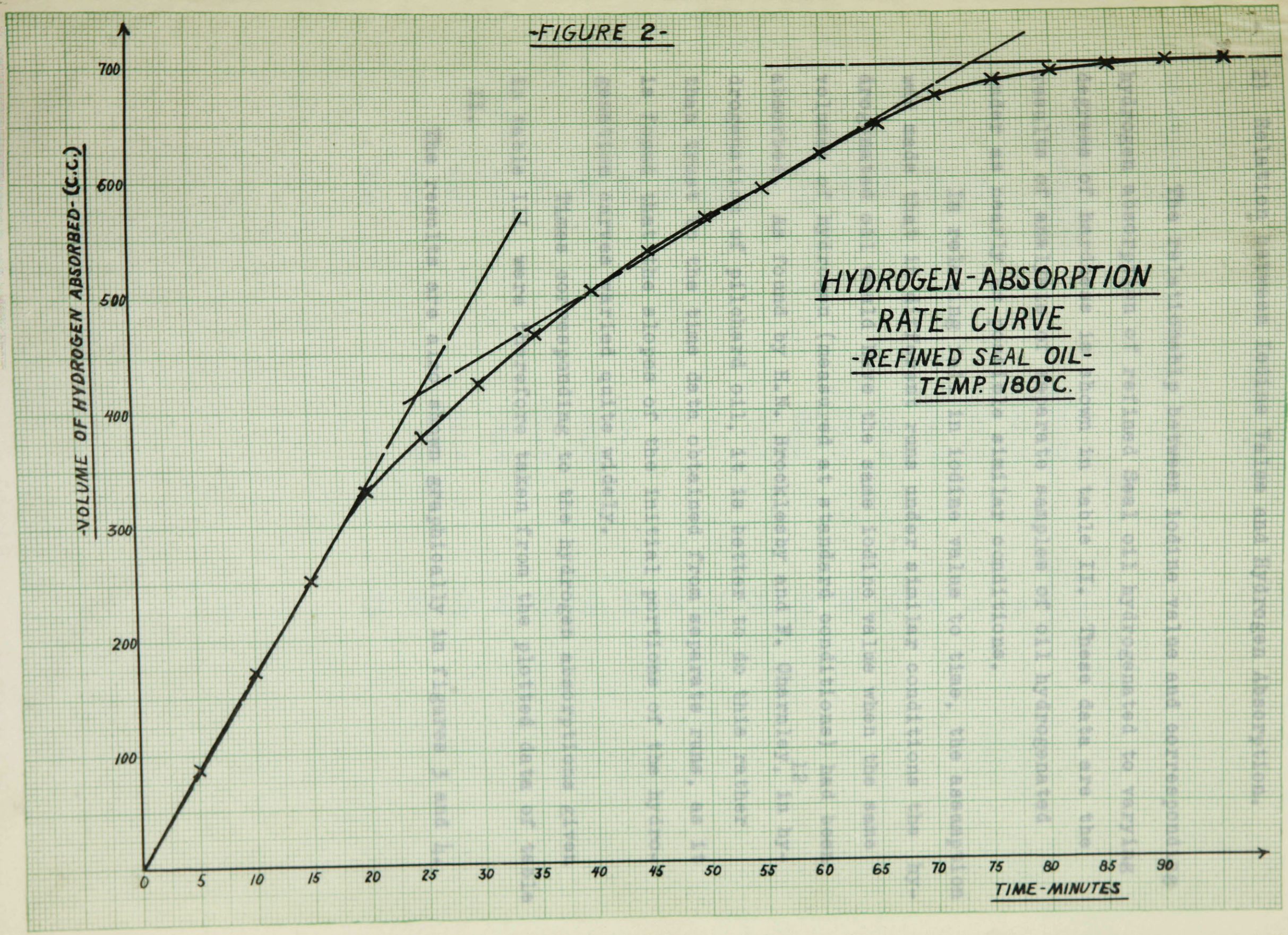
During the experiment the temperature of the gasometer remained very nearly constant varying only from 24.1 to 24.3°C; the pressure varied from 772.3 to 772.9 mm. and the temperature of the oil bath from 179 to 182°C. The volumes recorded in the table denote volumes of hydrogen absorbed up to time t, and were corrected for the variation in pressure caused by the gasometer, and then reduced to standard conditions.

The results of the experiment are shown graphically in figure 2.

TABLE II - Rate of Hydrogen Absorbed.

TIME	VOLUME OF H_2 ABSORBED			
t (mins.)	Gasometer Readings	ΔH	c.c. of H_2	c.c. of H_2 Stand. cond.
0	2.3	0	0	0
5	4.4	2.1	94.5	87
10	6.4	4.1	184.8	172
15	8.3	6.0	270.	252
20	10.1	7.8	355	332
25	11.3	9.0	405	378
30	12.4	10.1	454	424
35	13.4	11.1	500	467
40	14.3	12.0	540	504
45	15.1	12.8	576	538
50	15.8	13.5	607	567
55	16.4	14.1	634	591
60	17.1	14.8	666	622
65	17.7	15.4	693	646
70	18.3	16.0	720	672
75	18.6	16.3	734	685
80	18.8	16.5	743	694
85	18.9	16.6	747	698
90	19.0	16.7	752	702
95	19.0	16.7	752	702

-FIGURE 2-



2) Relation between Iodine Value and Hydrogen Absorption.

The relationship between iodine value and corresponding hydrogen absorption of refined Seal oil hydrogenated to varying degrees of hardness is shown in table II. These data are the results of analysis of separate samples of oil hydrogenated under as nearly as possible similar conditions.

In relating fall in iodine value to time, the assumption was made that in different runs under similar conditions the hydrogenated oil would have the same iodine value when the same volumes of hydrogen (measured at standard conditions) had been absorbed. As found by H.N. Brocklesby and F. Charnley,[12] in hydrogenation of pilchard oil, it is better to do this rather than trust to the time data obtained from separate runs, as it is found that the slopes of the initial portions of the hydrogenation curves varied quite widely.

Times corresponding to the hydrogen absorptions given in table III were therefore taken from the plotted data of table II.

The results are also shown graphically in figures 3 and 4.

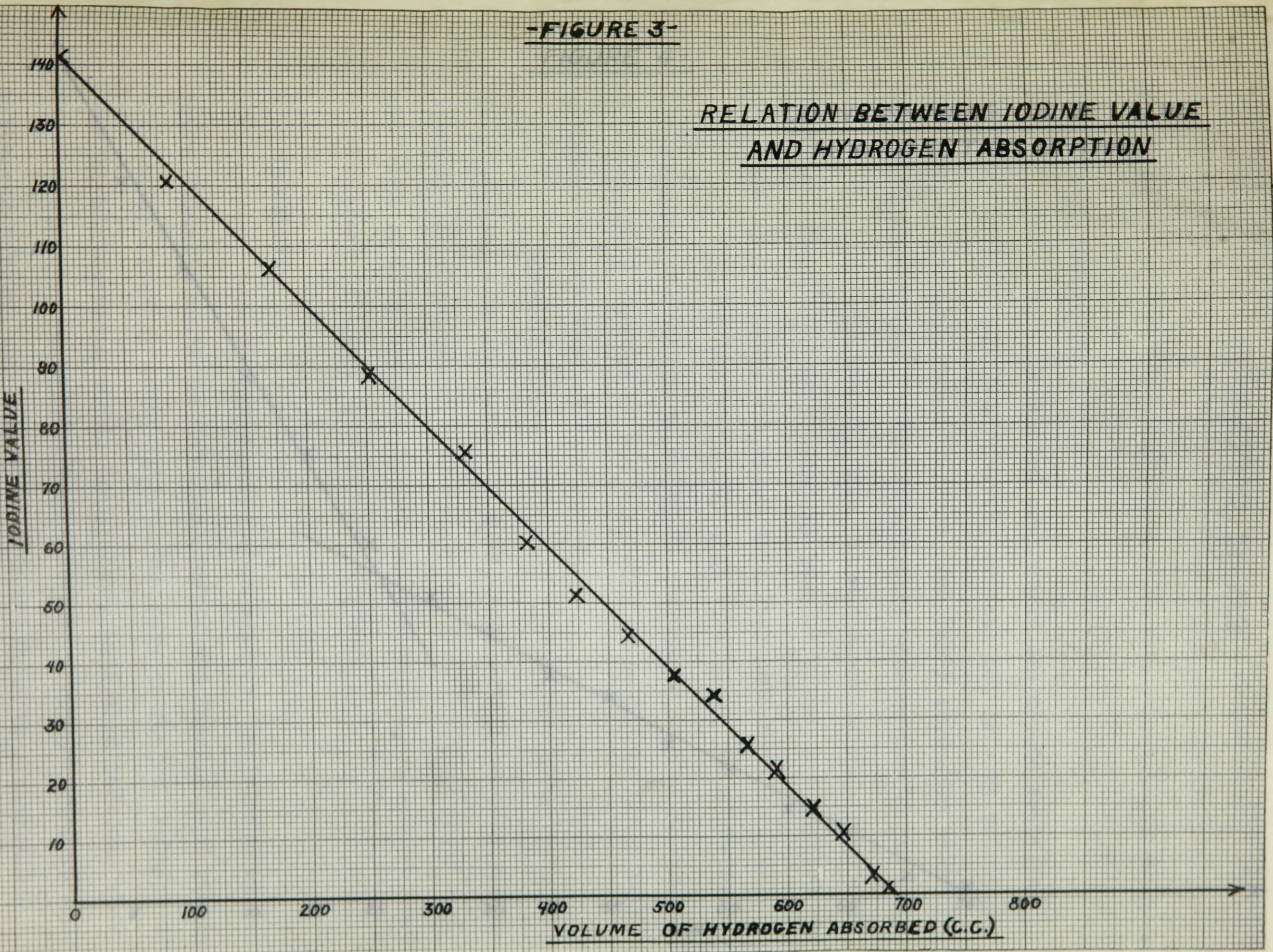
TABLE III

Relation between iodine value and hydrogen absorption.

Hydrogen Absorption	Iodine Value	Time
0	141.1	0
87	120.8	5
172	106.3	10
252	88.2	15
332	75.4	20
378	60.1	25
424	51.3	30
467	44.4	35
504	37.8	40
538	34.1	45
567	25.8	50
591	21.6	55
622	14.5	60
646	10.6	65
672	3.0	70
685	1.0	75

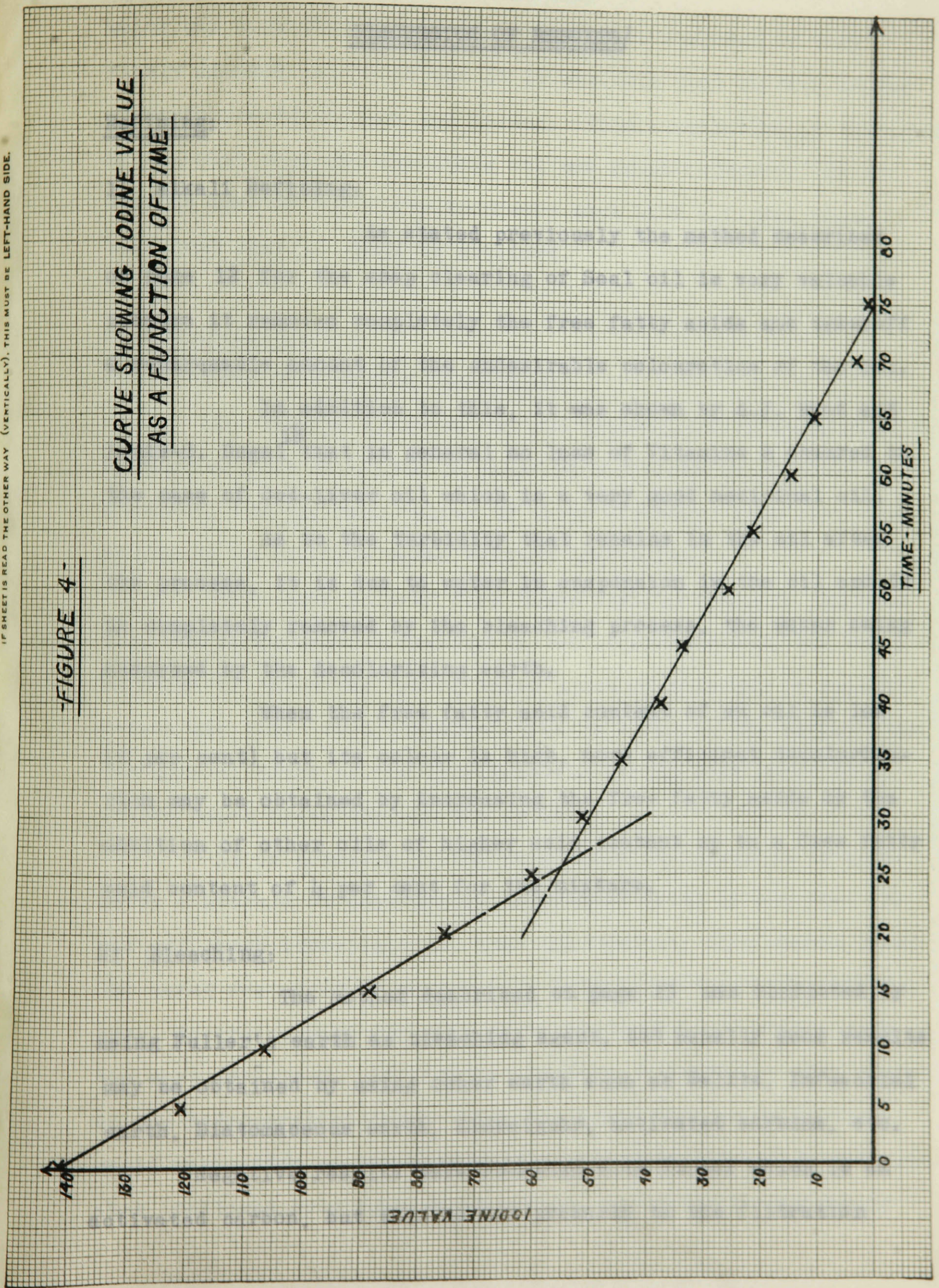
-FIGURE 3-

RELATION BETWEEN IODINE VALUE AND HYDROGEN ABSORPTION



-FIGURE 4-

CURVE SHOWING IODINE VALUE AS A FUNCTION OF TIME



DISCUSSION OF RESULTS/

Refining:

1) Alkali Refining:

As stated previously the method described on page 12 for the soap clearing of Seal oil is very valuable because it removes completely the free fatty acids and takes off a remarquable amount of the undesirable colouration of the oil.

In addition to this, it was shown by A.J. Wood and Louis-C. Dugal[18] that in general no loss of Vitamine A occured in the case of Cod-Liver oil which is a very good medicinal oil.

As to the turbidity that remains in the oil after the process, it is due to water in suspension in the oil and it is completely removed by the bleaching process, the water being absorbed by the decolorizing earth.

When the free fatty acid content of an oil is low (2 per cent) but its colour is high, more efficient decolorization may be obtained by increasing the free fatty acids by the addition of other oils of higher acid content up to a free fatty acid content of 4 per cent for the mixture.

2) Bleaching:

The method described on page 23 was conducted by using Fuller's earth as bleaching agent, but equally good results may be obtained by using other earth such as Celite, Infusorial earth, Diatomaceous earth, Kieselguhr, activated carbons, etc.

Negative results were obtained with Nuchar which is an activated carbon, but this is due probably to the filtration

which was conducted by suction. Nuchar is composed of very finely divided particles and it is possible that certain amount of earth passed through the filter. This explanation is confirmed by the fact that the resulting oil was green coloured. It is evident that if the filtrations were made with a filter press, different results would be obtained.

B) Hydrogenation:

1) Rate of Hydrogen absorption.

The results obtained for the experiments on hydrogenation of Seal oil, as tabulated in page 25 and shown graphically in figure 2, are the mean values of three different runs conducted as nearly as possible under similar conditions.

The curve plotted from these results seems to indicate that the hydrogenation occured in two separate steps, the break in slope of the curve having taken place at a volume of approximately 420 c.c. This stepwise curve is shown by the broken line, the general trend of the hydrogenation having been shown by a smooth curve drawn through the points.

It is possible in the case where the material is made up of a mixture of unsaturated compounds, which is the case for the oil under investigation, that the reaction will choose first the least resistant or most easily hydrogenated unsaturated centres, following with the next least resistant, and ending with the most resistant. If this is the case, a gradation will appear in the hydrogenation curve; that is, there will be an initial rapid saturation as the most easily saturated linkage is hydrogenated, followed by a less rapid period, as the next most easily

saturated bond is hydrogenated, and so on until complete saturation is reached. Thus the saturation curve of any given oil should show, according to this supposition, a definite number of steps or periods, depending on the composition of the particular oil.

The hydrogen absorption rate curve, it will be noticed, bears a general resemblance to the unimolecular type. That it approaches this type is partially borne out by the values of the ordinary unimolecular constant, K_1 given in table IV for the time-volume data. But it appears to be equally good grounds for the view that the curve represents the summation of a series of linear-type reactions similar to the linear-rate curves obtained by Armstrong and Hilditch[11] for the hydrogenation of pure organic compounds and later by H. N. Brocklesby and F. Charnley[12] for the hydrogenation of Pilchard oil. As will be seen from a comparison of the constants for a linear relation recorded under K and the values of K_1, the linear relation constants show better agreement during the first twenty minutes than do the unimolecular constants. There is also some indications that the second stage of the reaction approaches linearity.

The values under K_2 are the bimolecular constants calculated with respect to the volume of hydrogen absorbed. From these values it is evident that hydrogenation is not a bimolecular reaction or a reaction of the second order.

So neither the unimolecular nor the linear type curves satisfactorily fit the data of table II, but as has been pointed out, it is quite possible that the rate curve represents the total effect of a series of linear or approximately linear-rate

reactions rather than unimolecular reactions. Other evidence tends to support this view. As was previously stated, there are good grounds for believing that the sudden decrease in the reaction rate at a volume of approximately 420 c.c. corresponds to a stage in the hydrogenation at which unsaturated glycerides containing more than one double bond in the fatty-acid residue have largely, if not entirely, disappeared.

2) Relation between Iodine Value and Hydrogen absorption.

Within the limits of experimental error, the fall in iodine value is directly proportional to hydrogen absorption (figure 3). This is quite conform to the theory because the iodine value, being a direct measure of the unsaturated linkages present in the oil, should fall with hydrogen absorption at a constant rate during the course of hydrogenation.

The curve in figure 4, it will be observed, shows a pronounced linearity over the two regions of hydrogenation, indicating, as did the hydrogen-absorption curve, that the hydrogenation of the unsaturated glycerides in this oil under the conditions stated takes place mainly in two stages. The characteristic bend in this curve is apparently intimately related to the degree of unsaturation and carbon content of the glycerides undergoing hydrogenation. A further discussion of this question cannot, therefore, be undertaken until complete data on the composition of the oil have been obtained.

The values under K_1^1 and K_2^1 (table IV) are the unimolecular and bimolecular constant calculated from the Iodine values. It is quite evident that the curve in figure 4 does not fit the bimolecular type. But from an inspection of the values of K_1^1, it

seems that the unimolecular constants calculated from the iodine values show better agreement, especially during the first twenty minutes, than do the unimolecular constants K_2 calculated from the volumes of hydrogen absorbed. This fact cannot be explained, but it is quite sure that the values of K_1 are obtained with more accuracy than the values of K_1'. The volume of Hydrogen absorbed is directly calculated while the iodine value is obtained after many procedures.

TABLE IV

Reaction Velocity Constants.

Time (mins.)	Vol.H_2 Absorbed	Iodine Number	Linear K	Unimolecular K_1	Unimolecular K_1^1	Bimolecular K_2	Bimolecular K_2^1
5	87	120.8	17.4	11.6	13.6	40.1	23.8
10	172	106.3	17.2	12.2	12.3	46.4	23.2
15	252	88.2	16.8	12.9	13.6	53.2	28.4
20	332	75.4	16.6	13.9	13.7	64.0	30.9
25	378	60.1	15.1	13.4	14.8	66.5	38.2
30	424	51.3	14.1	13.4	14.7	72.4	41.3
35	467	44.4	13.4	13.6	14.4	80.9	44.1
40	504	37.8	12.6	13.7	14.3	90.5	48.4
45	538	34.1	12.0	14.0	13.7	104.0	49.4
50	567	25.8	11.3	14.3	14.7	119.5	63.4
55	591	21.6	10.7	14.6	14.8	139.2	71.4
60	622	14.5	10.4	15.8	16.4	185	103.1
65	646	10.6	9.9	16.9	17.3	253	134.1
70	672	3.0	9.6	19.5	23.9	456	466
75	685	1.0	9.2	21.6	28.7	766	1324
80	694	....	8.7	24.3	....	....	.....
85	698	....	8.2	26.5	....	....	....

CONCLUSIONS

A) An effective and economical method can be carried out for the Refining of Seal oil.

B) This method proceeds into two general steps:

1) The alkali refining by which all the free fatty acids and a great amount of colour is removed.

2) The bleaching with an activated earth, such as Fuller's earth, to complete the decolouration of the oil.

C) Seal oil can be hydrogenated under atmospheric pressure at about 180° C., in a simple apparatus of the closed type providing thorough mixture of the oil and catalyst.

D) Hydrogenation of Seal oil is a stepwise reaction. The rate curve exhibits a definite break and shows two distinct branches.

E) Neither the unimolecular nor the linear type curves satisfactorily fit the hydrogen absorption rate curve, but there are good grounds for believing that the rate curve represents the total effect of a series of linear or approximately linear-rate reactions rather than unimolecular reactions.

F) Within the limits of experimental error, the fall in iodine value is directly proportional to hydrogen absorption.

-APPENDIX A -

Analytical Methods[19]

Saponification Number:

By Saponification Number is meant the number of milligrams of potassium hydroxide required to saponify one gram of the oil. It must not be confounded with Saponification equivalent which is the number of grams of oil which would be saponified by a litre of normal alkali.

Saponification number - Acid Number = Ester Number, that is the number of milligrams of alkali actually used in the saponification of the glyceryl esters.

Preparation of Reagents:

a) 0.5 N Hydrochloric acid solution.

b) Alcoholic Potassium Hydroxide solution: Dissolve 40 grams of " potash by alcohol" in one litre of alcohol which has been purified as follows: 1½ grams of silver nitrate, dissolved in 3 cubic centimeter of water, is added to one litre of alcohol and the mixture thoroughly shaken; 3 grams of potassium hydroxide is dissolved in 15 cubic centimeter of warm alcohol and after cooling, added to the alcoholic silver nitrate and thoroughly shaken, best in a tall bottle or cylinder. The silver oxide is allowed to settle, the clear liquid siphoned off and distilled.

Standardization of 0.5 N Hydrochloric acid solution:

Pure sodium carbonate is prepared by heating sodium bicarbonate for a period of one hour, during which time the temperature is allowed to rise from 270 to 300 degree centigrade. It is then cooled in a dessicator.

One gram of the sample of sodium carbonate is weighed out and dissolved in 80 cubic centimeter of distilled water, two drops of methyl orange solution being added as an indicator. The resulting solution is titrated with the hydrochloric acid to be standardized and from this data the normality of the hydrochloric acid solution calculated. This determination is done in triplicate.

Sample Calculation:

Weight of Sodium Carbonate:

A = 1.0167

B = 1.1321

C = 1.1804

Hydrochloric Acid:

A = 39.30 c.c.

B = 43.85 c.c.

C = 45.72 c.c.

$$\text{Factor} = \frac{\frac{36.46}{106}}{2} = 0.6887$$

Hence weight of HCl necessary for :

A = .6887 x 1.0167

B = .6887 x 1.1321

C = .6887 x 1.1804

1 c.c. N HCl is equivalent to 0.0365 gram HCl

•) Normality of HCl:

$$A = \frac{.6887 \times 1.0167}{39.30 \times .0365} = 0.4887 \text{ N}$$

$$B = \frac{.6887 \times 1.1321}{43.85 \times .0365} = 0.4878 \text{ N}$$

$$C = \frac{.6887 \times 1.1804}{45.72 \times .0365} = 0.4878 \text{ N}$$

Mean Normality: 0.4881 N

Standardization of Alcoholic Potassium Hydroxide Solution:

This solution is standardized by comparison with the standard hydrochloric acid solution.

Sample calculation:

HCl (0.4881 N)	Alcoholic KOH sol.
20.00 c.c.	17.25 c.c.
20.00 c.c.	17.30 c.c.

•) Mean titration of HCl by KOH = 17.26 c.c.

•) Normality = $\frac{0.4881 \times 20.00}{17.26}$ = 0.5656 N

Method of Determination :

Weigh 1.2 to 2.0 grams of the oil into a 200 c.c. Erlenmeyer flask. This is best done by weighing 5 to 10 grams of the oil in a small beaker together with a small pipette or medicine dropper. The required amount of oil is transferred by means of the dropper to the flask, taking care not to get any on the neck, the dropper replaced and the whole reweighed. Add carefully from a pipette or burette 25 c.c. of the alcoholic solution of potassium hydroxide, close the flask with a cork carrying a straight glass tube several

feet long, and heat on a boiling water bath for 30 minutes or until completely saponified. When saponification is completed, as shown by a clear solution free from fat globules, cool the flask, add one c.c. of phenolphthalein solution and titrate the excess of alkali with half-normal hydrochloric acid. Two determinations are made at the same time and in similar flasks, the pipette or burette being allowed to drain for the same time in each case.

Sample Calculation:

Sample: Raw Seal oil.

A: Weight of oil: 1.9573 grams

25.00 c.c. KOH require 15.35 c.c. HCl (0.4881 N)

25.00 c.c. KOH are equivalent to 28.40 c.c. HCl (0.4881 N)

c.c. HCl sol. corresponding to KOH taken by oil:

$$28.40 - 15.35 = 13.05 \text{ c.c.}$$

1 c.c. HCl (0.4881 N) = 27.38 mgrs. KOH

Mgrs. KOH taken by oil = $27.38 \times 13.05 = 357.3$

For 1.00 gram of oil = $\frac{357.3}{1.9573} = 182.5$ mgrs. KOH

B: Weight of oil: 1.9703

25.00 c.c. KOH require 15.37 c.c. HCl (0.4881 N)

25.00 c.c. KOH are equivalent to 28.40 c.c. HCl (0.4881 N)

c.c. HCl (solution corresponding to KOH taken by oil:

$$28.40 - 15.37 = 13.03 \text{ c.c.}$$

1 c.c. HCl (0.4881 N) = 27.38 mgrs. KOH

Mgrs. KOH talen by oil = $27.38 \times 13.03 = 356.8$

For 1.00 gram of oil = $\frac{356.8}{1.9703} = 181.1$ mgrs. KOH

Mean Saponification Number: 181.8

Iodine Number:

By Iodine Number, or Iodine Value, is meant the number of grams of iodine absorbed by one hundred grams of the oil.

The iodine is absorbed by the unsaturated linkages of the oil, two atoms of iodine is taken up at each double bond. By measuring the quantity of iodine absorbed at any time, the degree of unsaturation of the oil may be determined at that time. Thus during the course of hydrogenation, the Iodine Number decreases as the unsaturation decreases.

Wijs Method:[20]

a) Wijs Iodine Solution:

The solution is prepared by dissolving 13.0 grams of resublimed iodine in one litre of glacial acetic acid, subsequently passing in washed and dried chlorine gas until the original titration of the solution is not quite doubled. The most convenient way to do this is to dissolve the iodine in the acetic acid by warming and set aside a small portion of this solution while chlorine is passed into the remainder until the halogen content is double. Ordinarily it will be found that by passing the chlorine into the main part of the solution until the caracteristic color of free iodine has just been discharged there will be a slight excess of chlorine which is corrected by the addition of the necessary amount of the unchlorinated portion until all the free chlorine has been removed. A slight excess of iodine does little or no harm, but excess of chlorine must be avoided.

The solution is preserved in glass-stoppered amber bottles and sealed with paraffin until ready for use. The date on which

the solution was prepared is marked on the bottle and no solution that is more than thirty days old should be used if accuracy is desired.

The glacial acetic acid used for the preparation of the solution should be 99.0 to 99.5% strength. For glacial acetic acids of somewhat lower strength, freezing and centrifuging or draining is recommended as a means of purification.

b) 0.1 N Sodium Thiosulphate Solution:

The solution is prepared by dissolving 25 grams of the recrystallized salt in recently boiled distilled water and diluting the same to one litre at the temperature at which the titrations are to be made.

c) Starch Paste:

One gram of starch is mixed with 20 c.c. of cold distilled water, the whole being added to 500 c.c. of boiling distilled water and boiled for ten minutes. The solution thus formed is cooled and preserved in glass-stoppered bottle.

d) 15% Potassium Iodine solution:

150 grams of Potassium iodide is dissolved in distille water and made up to one litre.

e) 0.1 N Potassium bichromate solution:

4.9033 grams of potassium bichromate are dissolved in distilled water, the volume being made up to one litre at the temperature at which the titrations are to be made.

Standardization of the Potassium Bichromate Solution:

0.1 N Potassium bichromate solution contains 4.9033 grams per litre. The bichromate may be regarded as pure, and hence the solution does not need standardizing.

However the standardization may be effected by this way: 0.2500 grams of iron wire is weighed out and added to 30 c.c. hydrochloric acid of specific gravity 1.12 that has just been brought to boiling. Concentrated stannous chloride solution ($SnCl_2$ crystals dissolved in concentrated HCl and then twice the volume of distilled water added little by little) is added from a dropper until the solution becomes colourless, and then one drop in excess. The solution is then diluted with 150 c.c. distilled water and 30 c.c. of a 5 per cent mercuric chloride solution are added. The solution is allowed to stand for three minutes and titrated with the potassium bichromate, arriving at the end point with the aid of potassium ferricyanide solution as an outside indicator. The indicator reacts with the ferrous ion to give a light brown colouration. Thus the end point is reached by removing a drop of the solution being titrated and adding it to the indicator solution on the spot plate, the end point being taken as the point where the resulting blue colour just fades out.

The determination is done in triplicate, and results should check to 0.002 . From the net volume of the bichromate solution used, its normality is readily calculated.

Standardization of the Sodium Thiosulphate Solution:

The approximately deci-normal solution of sodium thiosulphate is standardized by adding to 40.00 c.c. of the potassium bichromate solution, 10.00 c.c. of the solution of potassium iodide and 5 c.c. of strong hydrochloric acid.

The resulting solution is diluted with 100 c.c. distilled

water, and the sodium thiosulphate solution allowed to flow slowly into the flask. When the yellow colour due to the iodine becomes faint, a few drops of a freshly prepared starch solution are added, and with constant agitation, the addition of the thiosulphate solution is continued until the blue colour just disappears.

Simple calculation then gives the normality of the solution.

Sample calculation:

Sample	$K_2Cr_2O_7$ (0.1009 N)	$Na_2S_2O_3$
A	40.00 c.c.	35.55
B	40.00 c.c.	35.45

Hence mean value = 35.50 c.c. $Na_2S_2O_3$

Normality of $Na_2S_2O_3$ solution = $\frac{40.00}{35.50}$ x 0.1009 = 0.1135 N

Determination of Iodine Number:

Weigh accurately about 0.5 grams of the melted and filtered sample into a clean dry 450 c.c. iodine absorption bottle containing 20 c.c. carbon tetrachloride, which acts as a solvent for the oil. Add 250 c.c. of the iodine solution prepared as above from a pipette or glass-stoppered burette, taking care that none of the solution touches the neck of the bottle and allowing it to drain for a definite time. The excess iodine should be about 50-60% of the amount added, that is, 100-150% of the amount absorbed. Moisten the stopper with the potassium iodide solution to prevent loss of iodine and chlorine by volatilisation, guarding against an amount sufficient to run down inside the bottle. Then shake gently and allow the bottle to stand in a dark place for thirty minutes at a uniform temperature . In similar

bottles two blank determinations are carried out in exactly the same manner and measuring the same quantity of reagents.

At the end of thirty minutes, the bottle is removed, 20.0 c.c. of the potassium iodide solution and 100 c.c. distilled water are added. The whole solution is now titrated immediately with the standard sodium thiosulphate solution, which may be run in rapidly until the yellow colour has almost disappeared. Then a few drops of the starch solution are added and the titration continued until the disappearance of the blue color. Toward the end of the titration, the bottle is stoppered and shaken vigorously in order to react with any iodine that may be dissolved in the carbon tetrachloride.

The number of cubic centimeter of the standard sodium thiosulphate solution required by the blanks, less the amount used in the determination, gives the thiosulphate equivalent of the iodine absorbed by the sample. From this, calculation is made to centigrams of iodine absorbed by one gram of the sample, or more simply, percent iodine absorbed.

Notes: It is best to measure out the various quantities of the iodine solution required for duplicate determinations and for the blanks within a short interval of time, since on account of the very high coefficient of expansion of acetic acid, the strength of the solution is materially altered by slight changes in temperature.

When the titrated solution is allowed to stand it frequently becomes blue again, due probably to the splitting off of iodine from the compound formed, the reaction being to some extend a reversible one. The first end point should be the one taken.

Sample calculation:

Sample: Refined Seal Oil.

Weigh of sample: A = .4984

B = .5018

Sample:	c.c. $Na_2S_2O_3$(0.1135 N)	c.c. $Na_2S_2O_3$(net)
Blank	81.4	
A	32.1	49.3
B	32.6	48.8

1 c.c. $Na_2S_2O_3$(0.1135 N) is equivalent to 0.0144 gram iodine

Hence, factor = 0.0144

Amount iodine absorbed by 100 grams oil:

Sample A: $\frac{49.3 \times 0.0144}{0.4984} \times 100 = 142.2$

Sample B: $\frac{48.8 \times 0.0144}{.5018} \times 100 = 140.0$

Therefore mean iodine Number = 141.1

Free Fatty Acids:

Reagents:

a) 0.1 N NaOH solution: 4.0 grams of NaOH are dissolved in distilled water, the volume being made up to one litre at the temperature at which the titrations are to be made.

b) 95 per cent alcohol.

Standardization of the NaOH Solution:

The NaOH solution is standardized by comparison, using methylorange as indicator, with a standard hydrochloric acid solution prepared as indicated in the method of determination of Saponification Number.

Sample Calculation:

HCl (0.1123 N)	NaOH solution
25.00 c.c.	26.75 c.c.
25.00 c.c.	26.80 c.c.
25.00 c.c.	26.80 c.c.

Mean titration of 25.00 c.c. of 0.1123 N HCl by NaOH = 26.78

$$\text{Normality} = \frac{0.1123 \times 25}{26.78} = 0.1050 \text{ N}$$

Method of Determination:

To 10-20 grams of the oil weighed into an Erlenmeyer flask are added 50 c.c. of 95 per cent alcohol which has been previously neutralized to phenolphthalein with tenth normal sodium hydroxide solution. The whole is then heated on the water bath nearly to boiling and titrated with tenth normal NaOH solution and phenolphthalein.

It is necessary to shake thoroughly after each addition of alkali to secure complete extraction of the fatty acid from the immiscible oily layer.

If the solution is dark-colored, Alkali Blue 6B may be used in place of phenolphthalein.

The result may be expressed as Percentage of Oleic acid (1 c.c. 0.1 N alkali = 0.0282 gram of Oleic acid) or as the milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of oil (Acid Number)

Sample Calculation:

Sample: Raw Seal Oil.

Weight of oil: A = 13.9725 grams

B = 10.6597 grams

c.c. NaOH (0.1050 N)

A = 13.80

B = 10.60

1 c.c. NaOH (0.1050 N) is equivalent to 0.0296 grams of Oleic Acid

Therefore % of Oleic Acid:

$$A = \frac{0.0296 \times 13.80}{13.9725} \times 100 = 2.924$$

$$B = \frac{0.0296 \times 10.6}{10.6595} \times 100 = 2.941$$

Mean value: 2.932% of Oleic Acid.

1 c.c. NaOH (0.1050 N) is equivalent to 5.89 milligrams of KOH

Hence, Acid Number:

$$A = \frac{5.89 \times 13.8}{13.9725} = 5.82$$

$$B = \frac{5.89 \times 10.6}{10.6597} = 5.86$$

Mean value: 5.84 = Acid Number.

-APPENDIX B -

Calculation of Rate Constants:

The determination of the specific rate constant not only serves to describe the type of reaction mechanism and to indicate the order of reaction, but it makes possible a calculation of the amount of material which will react in a given time, or the time required for any specified portion of the material to react.

1- Linear Reaction:

A linear reaction is one in which the rate of reaction is constant, that is the concentration of the reacting substance is directly proportional to the time.

Hence, $K = c/t$

where K = Linear constant

c = Concentration of the substance that has reacted during the time t.

Sample calculation:

After 10 minutes 172.2 c.c. of Hydrogen has been absorbed by the oil.

Therefore $K = \frac{172.2}{10} = 17.22$

2- First-Order Reaction:

In a unimolecular reaction only one molecule reacts at a time. Such a molecule may decompose into simpler molecules, or it may rearrange to give a different molecule.

A first-order reaction is one in which the rate of reaction is directly proportional to the concentration of the reacting

substance. Expressing this relation mathematically:

$$-\frac{dc}{dt} = kc$$

Integrating between the limits, concentration c_1 at time t_1 and c_2 at a later time t_2 and rearranging:

$$k = \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2}$$

This equation may be modified to give the following equation:

$$K_1 = \frac{1}{t} \log \frac{c_o}{c}$$

where K_1 = Unimolecular constant

c_o = Concentration at the beginning of the reaction when the time is zero.

c = Concentration after time t has elapsed.

Sample calculation:

a) By using the volume of Hydrogen absorbed.

After 10 minutes 172.2 c.c. of Hydrogen has been absorbed by the oil which is able to absorbe 702 c.c.

Therefore $c_o = 702$ and $c = 702 - 172.2 = 529.8$

Hence $K_1' = \frac{1}{10} \log \frac{702}{529.8} = .0122$

b) By using the Iodine Number:

The Iodine Number, being a direct measure of the number of unsaturated linkages present, is thus proportional to the concentration of the unsaturated linkages, and may be substituted for the concentration by assuming a new velocity constant K_1'.

At the beginning, Iodine Number = 141.1

After 10 minutes, Iodine Number = 106.3

Hence $K_1' = \frac{1}{10} \log \frac{141.1}{106.3} = .0123$

3) Second-Order Reaction:

When two molecules, either of the same of different species, react, the reaction is bimolecular. When the rate of the reaction depends on the concentration of two molecules, the reaction is one of the second order.

If a = The initial molar concentration of the reacting substance.

x = The amount of the substance reacting in the interval of time t.

Then the velocity of the reaction is expressed by the equation:

$$\frac{dx}{dt} = K_2(a-x)^2$$

Integrating: $\frac{1}{a-x} = K_2 t + C$

Evaluating the integration constant C by setting x = o when t = o :

$$K_2 = \frac{1}{t} \frac{x}{a(a-x)}$$

Where K_2 = Bimolecular constant

Sample calculation:

a) By using the volume of Hydrogen absorbed:

After 10 minutes 172.2 c.c. of Hydrogen has been absorbed by the oil which is able to absorbe 702 c.c.

Hence $x = 172.2$ $a = 702$ $(a-x) = 529.8$

Therefore $K_2 = \frac{1}{10} \frac{172.2}{702 \times 529.8} = 4.64 \times 10^{-5}$

b) By using the Iodine Number:

At the beginning Iodine Number = 141.1

After 10 minutes Iodine Number = 106.3

Therefore: $x = 141.1 - 106.3 = 34.8$, $a = 141.1$, $(a-x) = 106.3$

Hence: $K_2^1 = \frac{1}{10} \frac{34.8}{141.1 \times 106.3} = 2.32 \times 10^{-4}$

Rate Constant Determinations:

1) Linear Rate Constant: $K = \frac{c}{t}$

Time t	Volume H_2 c	Linear constant K
5	87	17.4
10	172	17.2
15	252	16.8
20	332	16.6
25	378	15.1
30	424	14.1
35	467	13.4
40	504	12.6
45	538	12.0
50	567	11.3
55	591	10.7
60	622	10.4
65	646	9.9
70	672	9.6
75	685	9.2
80	694	8.7
85	698	8.2
90	702	7.8

2) Unimolecular Rate Constant:

$$K_1 = \frac{1}{t} \log \frac{c_o}{c}$$

a) Calculated by using the volume of Hydrogen absorbed:

$$c_o = 702$$

time t	Volume of H_2 x	c_o-x c	Unim. Const. K_1
5	87	615	.0116
10	172	530	.0122
15	252	450	.0129
20	332	370	.0139
25	378	324	.0134
30	424	278	.0134
35	467	235	.0136
40	504	198	.0137
45	538	164	.0140
50	567	135	.0143
55	591	111	.0146
60	622	80	.0158
65	646	56	.0169
70	672	30	.0195
75	685	17	.0216
80	694	8	.0243
85	698	4	.0265

b) Calculated by using the Iodine Number:

$$c_o = 141.1$$

time t	Iodine Number [redacted] c	Unimol. Const. K_1^1
5	120.8	.0136
10	106.3	.0123
15	88.2	.0136
20	75.4	.0137
25	60.1	.0148
30	51.3	.0147
35	44.4	.0144
40	37.8	.0143
45	34.1	.0137
50	25.8	.0147
55	21.6	.0148
60	14.5	.0164
65	10.6	.0173
70	3.0	.0239
75	1.0	.0287

3) Bimolecular Rate Constant:

$$K_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

a)Calculated by using the volume of Hydrogen absorbed:

a= 702

Time t	Volume of H_2 x	a-x	Bimol. const. $K_2 \times 10^5$
5	87	615	4.01
10	172	530	4.64
15	252	450	5.32
20	332	370	6.40
25	378	324	6.65
30	424	278	7.24
35	467	235	8.09
40	504	198	9.05
45	538	164	10.40
50	567	135	11.95
55	591	111	13.92
60	622	80	18.50
65	646	56	25.30
70	672	30	45.60
75	685	17	76.60
80	694	8	157.20
85	698	4	293.00

b) Calculated by using the Iodine Number:

$$a = 141.1$$

Time t	Iodine Number (a-x)	a-(a-x). x	Bimol. Const. $K_2 \times 10^4$
5	120.8	20.3	2.38
10	106.3	34.8	2.32
15	88.2	52.9	2.84
20	75.4	65.7	3.09
25	60.1	81.0	3.82
30	51.3	89.8	4.13
35	44.4	96.7	4.41
40	37.8	103.3	4.84
45	34.1	107.0	4.94
50	25.8	115.3	6.34
55	21.6	119.5	7.14
60	14.5	126.6	10.31
65	10.6	130.5	13.41
70	3.0	138.1	46.60
75	1.0	140.1	132.40

Iodine Number determinations:

a) Run I

Normality of Thiosulphate solution: 0.1135 N

Factor: 0.0144

Time	Weight	Blank	Thiosulphate	Net Thiosulphate	I.N.	Mean I.N.
5	0.4952	81.4	40.0	41.4	120.2	121.9
	0.5114	81.4	37.5	43.9	123.6	
10	0.5124	81.6	42.9	38.7	108.8	108.1
	0.4875	81.6	45.2	36.4	107.4	
15	0.4782	81.6	50.9	30.7	92.4	91.6
	0.5082	81.6	49.5	32.1	90.9	
20	0.4576	81.8	59.0	22.8	71.8	73.0
	0.5134	81.8	55.4	26.4	74.2	
25	0.4882	81.8	60.9	20.9	61.6	60.7
	0.4982	81.8	61.1	20.7	59.8	
30	0.5008	81.8	63.8	18.0	51.7	50.7
	0.4784	81.8	65.3	16.5	49.7	
35	0.4674	60.4	46.8	13.6	41.9	43.7
	0.4998	60.4	44.6	15.8	45.6	
40	0.4894	60.4	48.0	12.4	36.5	35.9
	0.5282	60.4	47.4	13.0	35.4	
45	0.4982	60.4	48.7	11.7	33.8	33.2
	0.5416	60.4	48.1	12.3	32.7	
50	0.4876	60.6	52.6	8.0	23.6	24.2
	0.4677	60.6	52.5	8.1	24.9	
55	0.4734	60.6	53.4	7.2	21.9	22.5
	0.4985	60.6	52.6	8.0	23.1	

Time	Weight	Blank	Thiosulphate	Net Thiosulphate	I.N.	Mean I.N.
60	0.5321	60.6	54.7	5.9	16.0	15.4
	0.5013	60.6	55.5	5.1	14.7	
65	0.5282	58.1	54.7	3.4	9.26	9.89
	0.4932	58.1	54.5	3.6	10.52	
70	0.5234	58.1	56.6	1.5	4.13	3.62
	0.5084	58.1	57.0	1.1	3.12	
75	0.5113	58.1	57.7	0.4	1.13	1.00
	0.4918	58.1	57.8	0.3	0.88	

b) Run II

Normality of Thiosulphate solution: 0.1020 N

Factor : 0.01292

Time	Weight	Blank	Thiosulphate	Net thiosulphate	I.N.	Mean I.N.
5	0.4813	58.0	13.1	44.9	120.8	119.8
	0.5014	58.0	12.0	46.0	118.8	
10	0.4728	58.0	19.5	38.5	105.2	104.6
	0.5134	58.0	16.7	41.3	104.0	
15	0.4933	58.0	25.7	32.3	84.6	85.6
	0.5148	58.0	23.5	34.5	86.6	
20	0.5124	57.9	27.6	30.3	76.5	77.7
	0.4994	57.9	27.4	30.5	78.9	
25	0.5283	57.9	33.2	24.7	60.5	59.5
	0.4876	57.9	35.8	22.1	58.6	
30	0.4916	57.9	37.7	20.2	53.1	52.0
	0.4894	57.9	38.6	19.3	51.0	
35	0.4728	57.9	41.6	16.3	44.6	45.0
	0.5232	57.9	39.5	18.4	45.4	
40	0.4934	61.4	46.8	14.6	38.3	39.8
	0.5184	61.4	44.8	16.6	41.4	
45	0.5281	61.4	46.3	15.1	37.0	35.1
	0.5082	61.4	48.3	13.1	33.3	
50	0.5347	61.6	49.8	11.8	28.6	27.4
	0.4786	61.6	51.9	9.7	26.2	

Time	Weight	Blank	Thiosulphate	Net thiosulphate	I.N.	Mean I.N.
55	0.5184	61.6	53.7	7.9	19.7	20.8
	0.4834	61.6	53.4	8.2	21.9	
60	0.5004	61.6	56.8	4.8	12.4	13.5
	0.5283	61.6	55.6	6.0	14.7	
65	0.4834	61.7	57.3	4.4	11.8	11.2
	0.5192	61.7	57.5	4.2	10.5	
70	0.4782	61.7	60.6	1.1	3.0	2.3
	0.5284	61.7	61.0	0.7	1.7	
75	0.4934	61.7	61.2	0.5	1.3	0.9
	0.4834	61.7	61.5	0.2	0.5	

c) Mean Iodine Number for Runs I and II

Time	Run I	Run II	Iodine Number
5	121.9	119.8	120.8
10	108.1	104.6	106.3
15	91.6	85.6	88.2
20	73.0	77.7	75.4
25	60.7	59.5	60.1
30	50.7	52.0	51.3
35	43.7	45.0	44.4
40	35.9	39.8	37.8
45	33.2	35.1	34.1
50	24.2	27.4	25.8
55	22.5	20.8	21.6
60	15.4	13.5	14.5
65	9.89	11.2	10.6
70	3.62	2.3	3.0
75	1.00	0.9	1.0

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