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PHYSICAL PROPERTIES OF NICKEL CARBONYL

by
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ABSTRACT

The vapor pressure of nickel carbonyl was determined with material obtained by laboratory preparation with carbon monoxide and nickel powder and by purifying commercial nickel carbonyl. The observed vapor pressure data were used in the derivation of the following equations which express the vapor pressure, P, of liquid nickel carbonyl and the sublimation pressure, P_s, of the solid, respectively, as a function of the absolute temperature, T:

$$\log P = 7.8843 - 1578/T$$
$$\log P_s = 10.1897 - 2173/T$$

The average heat of vaporization is calculated to be 7.22 ± 0.01 kcal per mole and the molecular heat of sublimation of nickel carbonyl is 9.94 ± 0.11 kcal. Extrapolation to 760 mm Hg gives a boiling point of 42.2°C.

The melting point of purified nickel carbonyl occurred at -17.2°C. The sensitivity of the melting point to the effect of impurities was demonstrated with commercial nickel carbonyl which melted at -19.4°C before purification, at -18.3°C after distillations at 0°C, and at -17.2°C after sublimation at -25°C. The vapor pressure of liquid nickel carbonyl at 0°C is of little value in evaluation of the purity of the material.

1. Introduction

The thermal decomposition of nickel carbonyl vapors has been employed for over fifty years in the commercial production of metallic nickel by the Mond process. This reversible reaction is also used for the application of a thin metallic film of nickel on other surfaces. An investigation of this decomposition reaction has been undertaken with emphasis on the mechanism of the reaction, rates of decomposition, and the equilibrium states of the system.

As a preliminary step preceding the investigation of the equilibrium and kinetic aspects of the thermal decomposition of nickel carbonyl, the physical properties of nickel carbonyl should be established in order to assign some standards for the evaluation of the purity of the material. For this purpose, measurements have been made to determine the temperature dependency of the vapor pressure of liquid and solid nickel carbonyl. In addition, determinations of the melting point and boiling point of this compound have been made to aid in the establishment of purity criteria. The results of similar measurements have been reported by Mittasch,[1] Anderson,[2] and others, but the discordancy in these reported values indicates that the nickel carbonyl employed in some of these earlier investigations may not have been completely purified.

2. Review of the Literature

Nickel carbonyl, prepared for the first time by Mond, Langer, and Quincke,[3] is formed by the direct combination of the metal with carbon monoxide. Although nickel carbonyl may be obtained from the reaction between nickel salts and carbon monoxide in the presence of various combinations of reagents, none of the wet methods can compete with the dry synthesis as a method of preparation.

In the direct combination method for the laboratory synthesis of nickel carbonyl, much of the success of the procedure depends upon the previous treatment and the condition of the metallic nickel. Finely divided nickel may be obtained by reduction in hydrogen of nickel oxide[4] at 400°C, of nickel oxalate[5] or of nickel nitrate[6] at 290-300°C, and of nickel formate[7] at 190-200°C. The lower the temperature, in general, at which the nickel compound is reduced, the more active is the form of the nickel powder obtained. The least trace of oxygen poisons the nickel so that it ceases to react readily. The hydrogen obtained from commercial sources is usually freed from traces of oxygen and moisture prior to the reduction of the nickel salt.

Carbon monoxide is generally prepared for laboratory work by the dehydration of oxalic or formic acid.[8] Air-free formic acid is dropped on concentrated or fuming sulfuric acid. The evolved carbon monoxide is purified by passage through caustic potash and over a suitable

desiccant. Complete removal of oxygen is assured by the addition of sodium pyrogallate to the caustic potash solution.

Passage of carbon monoxide over the finely divided metallic nickel at room temperature forms nickel carbonyl which is swept from the reaction vessel and condensed in a receiver surrounded by a cold bath. If the nickel is very finely divided, the exothermic heat of reaction is sufficient to maintain the required temperature, which is about 30°C to 100°C, depending upon the method used in preparing the nickel.

Measurements of the vapor pressure of nickel carbonyl have been made by Mittasch,[1] Dewar and Jones,[9] Anderson,[2] and Suginuma and Satozaki.[10] The dissociation of nickel carbonyl first becomes apparent at 36°C (Mond and Nasini),[11] so the values obtained above this temperature represent, not the vapor pressure, but the equilibrium pressure of the system. The values obtained for the vapor pressure of nickel carbonyl in these earlier investigations show some discordancy, which may be attributed to the experimental method of measurement, purity of the nickel carbonyl, accuracy of the temperature and pressure measurements, or partial decomposition of the nickel carbonyl to form carbon monoxide.

The Clausius-Clapeyron relationship between the vapor pressure of nickel carbonyl and the temperature may be represented by Equation (1), according to Anderson,[2] or by Equation (2), which summarizes the experimental data obtained by Suginuma and Satozake:[10]

$$\log P = 7.690 - 1519/T \qquad (1)$$

$$\log P = 7.878 - 1574.49/T \qquad (2)$$

in which P and T represent the vapor pressure and absolute temperature, respectively.

From the slope of Equation (1) the molecular heat of vaporization of liquid nickel carbonyl is calculated to be 6.92 kcal, as compared with the average heat of vaporization of 7.202 kcal per mole obtained from Equation (2). Extrapolation of Equation (1) to 760 mm pressure gives a boiling point of 43.0°C. The boiling point calculated from Equation (2) is 42.1°C.

Mittasch[1] observed a temperature of -25°C for the melting point of nickel carbonyl. From the intersection of the vapor pressure curves for liquid and solid nickel carbonyl Anderson[2] obtained a triple point at -22°C.

3. Experimental

The direct action of carbon monoxide on nickel powder was utilized for the synthesis of nickel carbonyl in accordance with the procedure of Gilliland and Blanchard.[7] Nickel formate was prepared by the action of formic acid on nickelous hydroxide, precipitated from

nickel chloride solution with aqueous sodium hydroxide. The solution of nickel formate was evaporated to fractionally crystallize the product, which was washed with alcohol. Three crystallizations of nickel formate were made to give additional purity in the starting material.

The preparation and purification of nickel carbonyl were made in the glass system shown in Fig. 1. Following the chamber in which nickel carbonyl was formed, all connections were made with ground glass joints to avoid the decomposition of nickel carbonyl resulting from contact with rubber. The reduction of nickel formate to nickel powder was made with commercial hydrogen gas purified by passage over uranium powder heated to 500°C in a combustion tube. Hydrogen, serving as the reducing agent, swept the gaseous reaction products from the system, which was heated to a maximum temperature of 190°C.

Carbon monoxide was generated by the action of sulfuric acid on formic acid. The evolved gas was freed from oxygen, carbon dioxide, and other acidic impurities by passage through a six-normal potassium hydroxide solution containing sodium pyrogallate. The gas was then dried by passage through a tower filled with Drierite before storage in the reservoir or passage over the nickel powder.

The product from the direct combination of carbon monoxide and nickel powder was solidified in a bulb immersed in a cooling mixture of dry ice and trichlorethylene. Unreacted carbon monoxide and other noncondensable gases were removed by evacuation. Further purification was obtained by distillations at 0°C during which the first and last fractions were rejected.

The yield of nickel carbonyl in these preparations was quite low.

Commercial nickel carbonyl supplied by The Matheson Company proved to be a convenient source of material for the determinations to be made. The commercial material was solidified to permit removal of carbon monoxide by evacuation. Purification was completed by distilling off half of the liquid at room temperature. Thermal decomposition of samples from the residual liquid made possible an analysis for carbon monoxide and nickel content. These analyses showed that the residual liquid was nickel tetracarbonyl.

Studies of the properties of nickel carbonyl were made in the system illustrated in Fig. 2, which could be evacuated to a pressure less than 0.01 micron. To protect the vacuum pumping system from nickel carbonyl vapors, a combustion furnace, maintained at 180°C, was inserted in the line to decompose the nickel carbonyl.

Temperature measurements were made with the use of a calibrated thermometer or a copper-constantan thermocouple calibrated at the temperatures of boiling water, ice and water, and solid carbon dioxide. The emf values were obtained with a Rubicon portable potentiometer, which could be read with an accuracy of 0.005 mv, corresponding to about 0.15°C. For temperatures in the vicinity of room temperature, a Sargent viscosimeter bath was used.

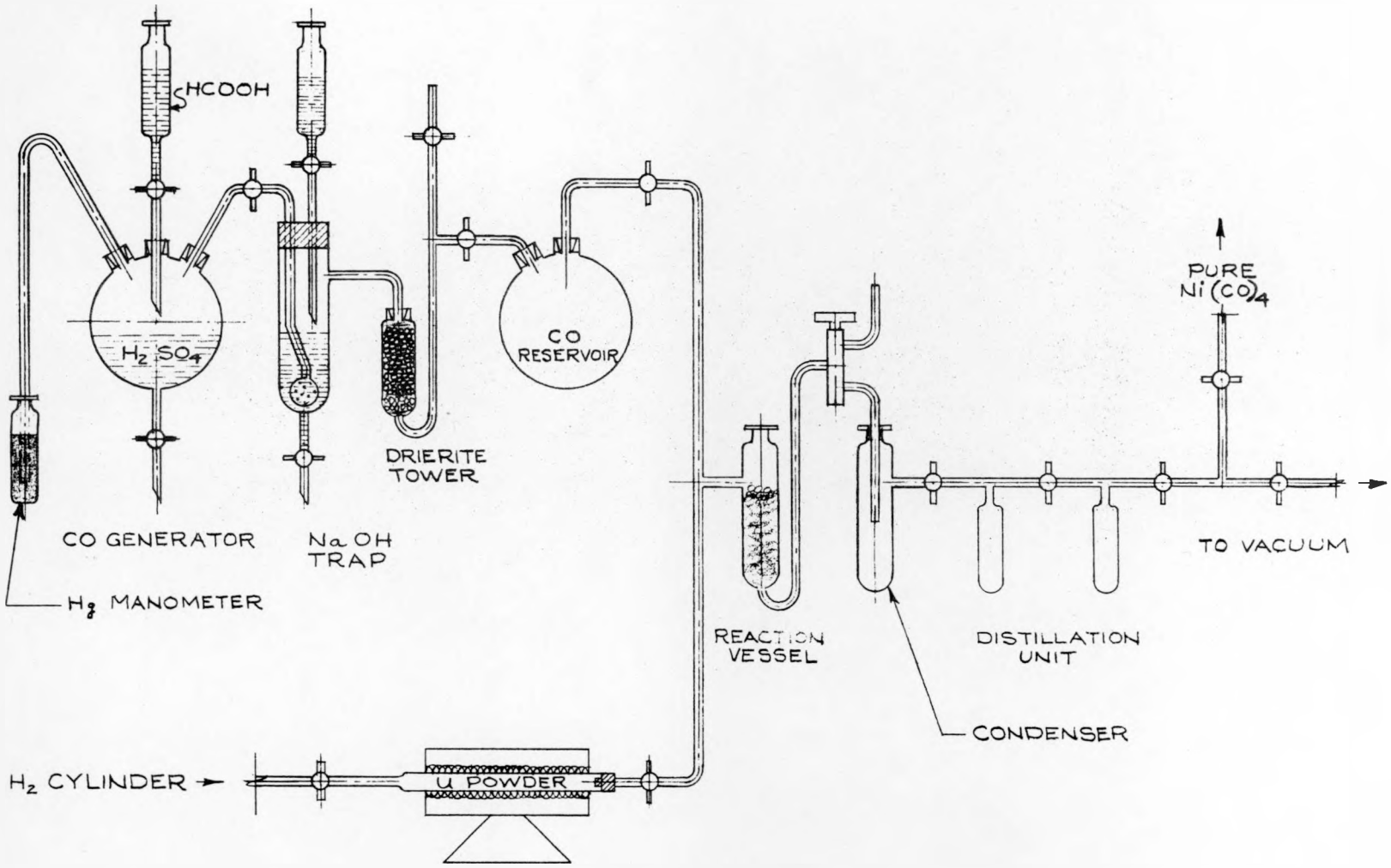

Fig. 1 System for $Ni(CO)_4$ preparation and purification

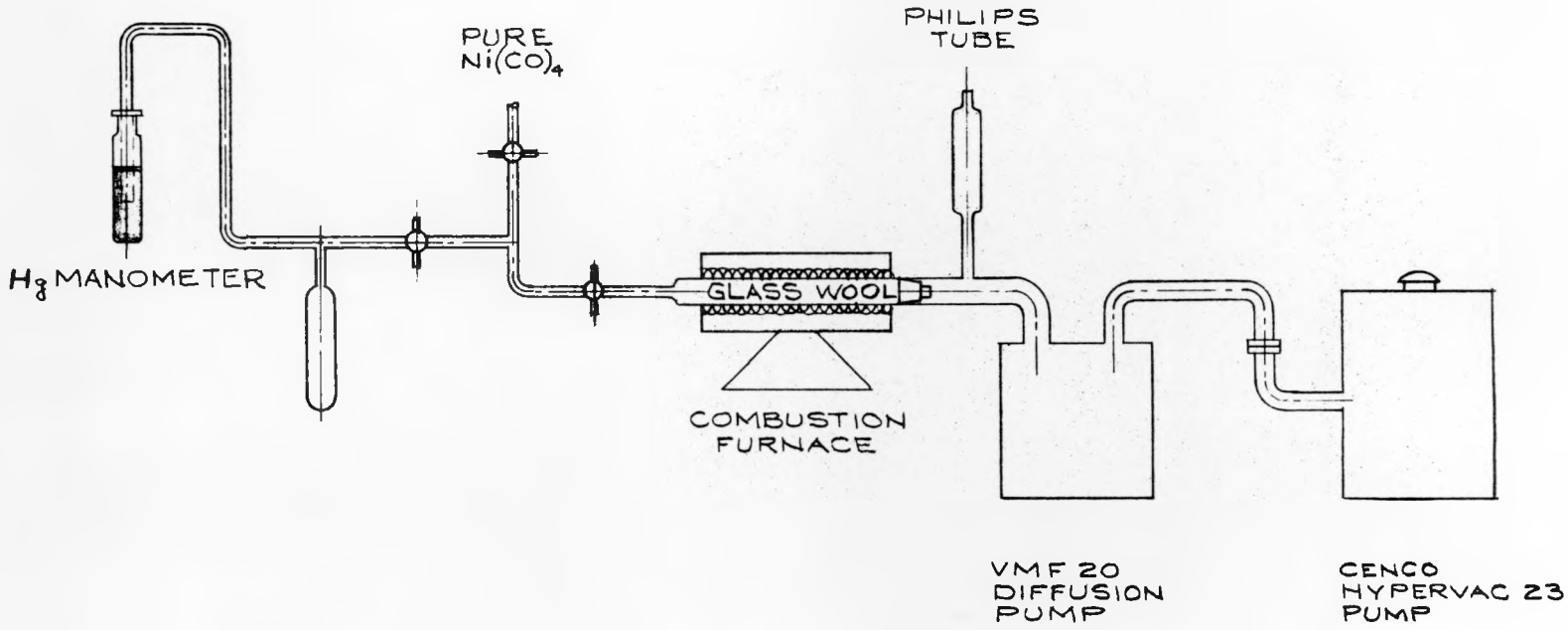

Fig. 2 Vapor pressure and vacuum units

Temperatures were held constant within ± 0.05°C, as close as could be read on the mercury thermometer used.

The vapor pressure of nickel carbonyl was determined by an equilibrium method with a mercury manometer, using a cathetometer to read the mercury level. These readings could be made within ± 0.05 mm. The completion of each series of measurements required about one week, so it was necessary to make corrections in the observed values for fluctuations in barometric pressure.

Pressure measurements at each temperature were made at 10-minute intervals until two successive readings agreed within 0.1 mm. Generally, thermal equilibrium had been reached after twenty minutes. Some difficulty was experienced in obtaining reproducible results approaching the equilibrium temperature by heating and by cooling in the region just below the melting point of nickel carbonyl because of a supercooling effect with the liquid.

Although thermal decomposition of the nickel carbonyl at the lower temperatures was not a problem, the reaction between nickel carbonyl and adsorbed oxygen on the vessel walls is known to form carbon monoxide and nickel oxide. The solubility of this carbon monoxide in the liquid nickel carbonyl could cause a lowering of the vapor pressure, or the partial pressure of this liberated gas might cause the readings to be too high. If nickel carbonyl which had been been solidified and subjected to vacuum was warmed to 0°C for several hours, the resulting vapor included noncondensable gases exerting a partial pressure of 4-6 mm. This effect was avoided by allowing the system to remain at room temperature for four hours, after which the nickel carbonyl was solidified and the residual gases were removed by evacuation. This treatment apparently allowed any decomposition reactions to proceed to completion, since an entire series of vapor pressure measurements could then be made below room temperature without liberating noncondensable gases.

Above room temperature, condensation of nickel carbonyl in the manometer capillary became a source of difficulty and error. A manometric system was employed in which the mercury was contained in the bulb with the nickel carbonyl. Corrections for the expansion of the mercury and other thermal effects were made from measurements with air and an external manometer. In this system nickel carbonyl samples had to be carried through a freezing, evacuation, and melting cycle between measurements to avoid an accumulation of carbon monoxide. This cycling was continued until reproducible values were obtained at each temperature.

The melting point determinations were made after condensing the nickel carbonyl in a vertical tube, so constructed that an inner thermocouple well was surrounded by the material. The usual time-temperature cooling and heating curves were obtained for the determination of the melting point at the equilibrium pressure of nickel carbonyl.

4. Results and Discussion

Nickel carbonyl formed by the action of carbon monoxide on a purified nickel powder is a colorless liquid, as compared with the yellow liquid described by Mittasch.[1] Solidification by slow cooling gives a transparent solid. Carbon monoxide is very soluble in liquid nickel carbonyl, but this impurity is eliminated by solidification and subsequent evacuation.

Some of the experimental data obtained in the measurements of the vapor pressure of nickel carbonyl are presented in Table I. The plot (Fig. 3) of log P against 1/T from these data gives a straight line, with only the 16.10°C measurement showing a slight departure from the line. From the slope of -1578 ± 3, the molecular heat of vaporization of nickel carbonyl is 7.22 ± 0.01 kcal. The complete equation relating the vapor pressure of liquid nickel carbonyl and the absolute temperature is

$$\log P = 7.8843 - 1578/T \qquad (3)$$

Extrapolation of this equation to 760 mm Hg gives a boiling point of 42.2°C. These measurements of the vapor pressure gave an equation which is nearly identical with that reported by Suginuma and Satozaki.[10]

Figure 4 is a plot of P versus t, °C.

TABLE I

Vapor Pressure of Nickel Carbonyl

t, °C	0.00	16.10	21.10	28.50	35.10
P, mm Hg	128.05	271.40	332.32	450.00	582.65

During the course of these vapor pressure measurements, decomposition of nickel carbonyl was negligible. At 35.10°C this was still true for clean equipment, but during repeated measurements the accumulation of a nickel film on the vessel walls and a film of nickel amalgam on the mercury surface was accompanied by an increased rate of decomposition of nickel carbonyl. It became necessary to clean the equipment to avoid the error caused by the partial pressure of the liberated carbon monoxide.

In the measurement of the vapor pressure of solid nickel carbonyl, temperature control was not as precise as for the liquid. However, the rate of change in sublimation pressure with temperature was not as great. The data for the vapor pressure of nickel carbonyl below the melting point are listed in Table II. The plot of log P_s against 1/T in Fig. 3 shows greater deviation from linear behavior. The weighted average for the slope between these

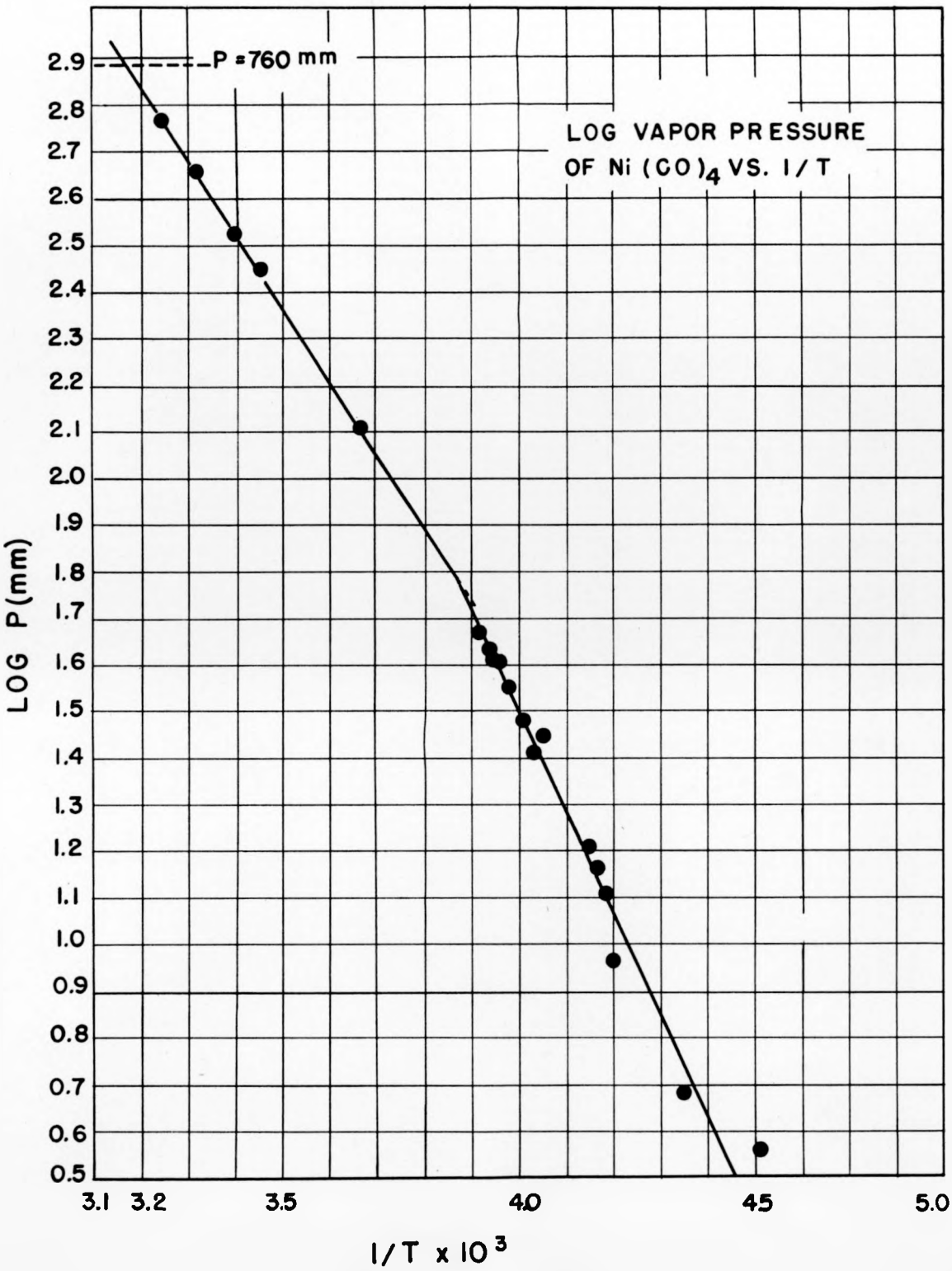

Fig. 3 Log vapor pressure of $Ni(CO)_4$ vs 1/T

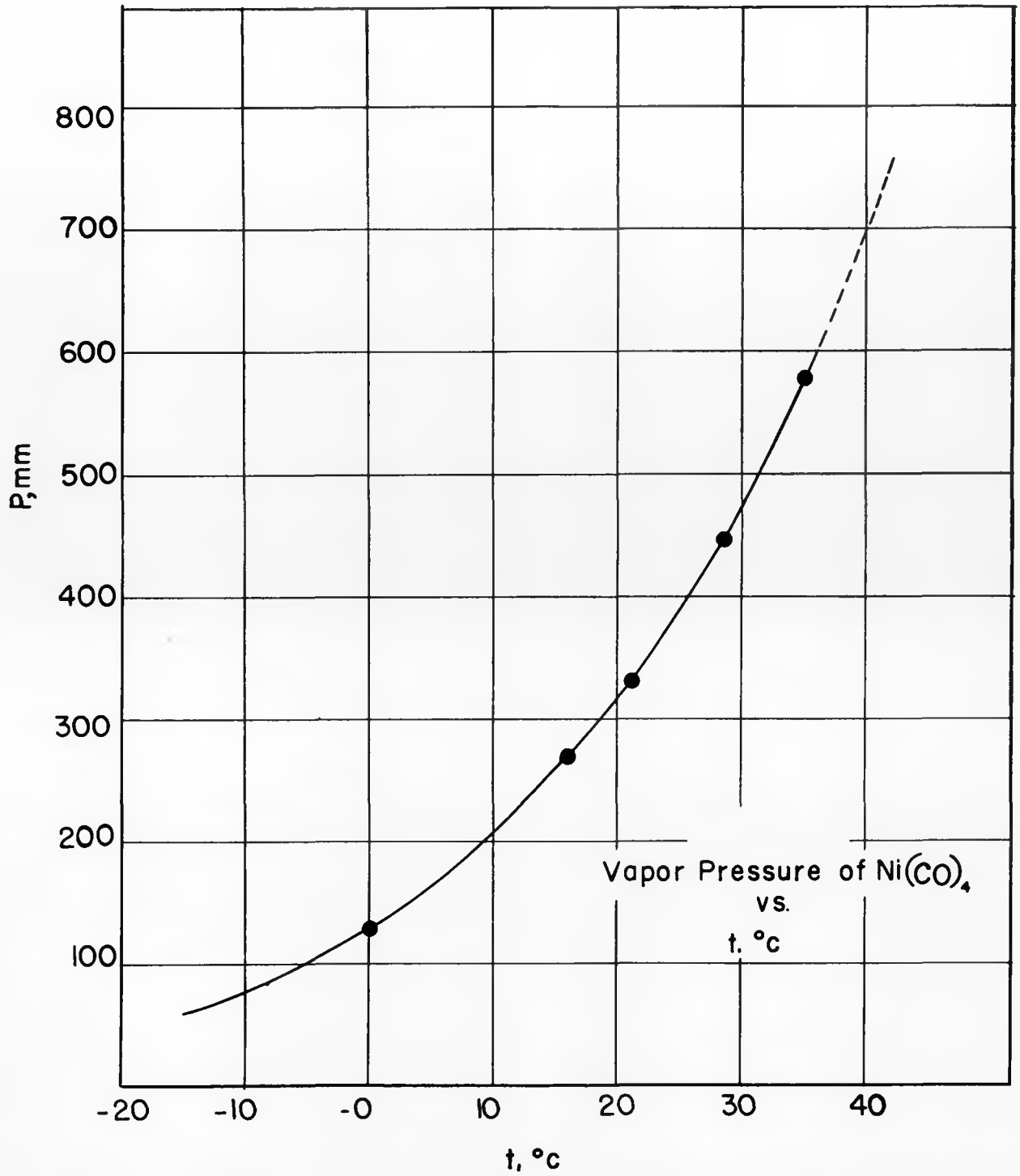

Fig. 4 Vapor pressure of $Ni(CO)_4$ vs t °C

points is -2173 ± 25, which gives a value of 9.94 ± 0.11 kcal for the molecular heat of sublimation. The sublimation pressure equation for nickel carbonyl is

$$\log P_s = 10.1897 - 2173/T \qquad (4)$$

Simultaneous solution of Equations (3) and (4) leads to the triple point at -15.0°C and 59.3 mm pressure. The melting point of nickel carbonyl observed at the equilibrium pressure was -17.2 ± 0.15°C. Comparison of this value of the melting point with those reported elsewhere suggests that impurities had caused a depression of the melting point in the earlier determinations.

TABLE II

Sublimation Pressure of Nickel Carbonyl

t, °C	P, mm Hg	t, °C	P, mm Hg	t, °C	P, mm Hg
-51.3	3.6	-31.6	16.2	-19.7	41.1
-43.0	4.8	-26.0	27.9	-19.4	41.0
-34.7	9.2	-24.7	25.7	-18.8	42.7
-33.7	12.8	-23.5	30.2	-17.7	46.7
-32.7	14.4	-21.6	35.7		

The melting point of nickel carbonyl seems to be the property which is most sensitive to the presence of impurities. Commercial nickel carbonyl, following the removal of free carbon monoxide, melted at -19.4°C; the vapor pressure of this material at 0°C was 127.8 mm Hg. Purification by two stages of distillation at 0°C caused the melting point to rise to -18.3°C and the vapor pressure at 0°C was increased to 128.3 mm. Subsequent distillations at the same temperature did not change the melting point. A further purification, consisting of sublimation at -25°C, brought the melting point to the reported value of -17.2°C. The vapor pressure of this sublimed product was 128.8 mm at 0°C. The vapor pressure measurement, which is more convenient experimentally, is apparently not a good criterion for the purity of the nickel carbonyl.

5. Summary

In an effort to establish some criterion for the determination of the relative purity of nickel carbonyl to be employed in equilibrium and kinetic studies of the thermal decomposition reaction, measurements have been made to establish the vapor pressure-temperature relationships, boiling point, and melting point of nickel carbonyl.

Nickel carbonyl of high purity was obtained by the reaction of purified carbon monoxide with an active nickel powder prepared by hydrogen reduction of purified nickel formate. The nickel carbonyl was further purified by fractional distillation. Commercial nickel carbonyl was also employed in the investigations after purification by distillation and sublimation. The observed vapor pressure data were used in the derivation of Equations (3) and (4) which express the vapor pressure of liquid nickel carbonyl and the sublimation pressure of the solid, respectively, as a function of the temperature:

$$\log P = 7.8843 - 1578/T \quad (3)$$

$$\log P_s = 10.1897 - 2173/T \quad (4)$$

Equation (3) is nearly identical with that reported by Suginuma and Satozaki.

The average heat of vaporization is calculated to be 7.22 ± 0.01 kcal per mole and the molecular heat of sublimation of solid nickel carbonyl is 9.94 ± 0.11 kcal. Extrapolation to 760 mm Hg gives a boiling point of 42.2°C.

The melting point of purified nickel carbonyl occurred at -17.2°C, as compared with the value of -15.0°C obtained by simultaneous solution of Equations (3) and (4). The sensitivity of the melting point to the effect of impurities was demonstrated with commercial nickel carbonyl which melted at -19.4°C before purification, at -18.3°C after distillations at 0°C, and at -17.2°C after sublimation at -25°C. The vapor pressure of liquid nickel carbonyl at 0°C is of little value in evaluation of the purity of the material, since the impurities in nickel carbonyl are apparently volatile and exert a partial pressure contributing to the observed values.

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