# CCXV.—*The Vapour Pressure of Nickel Carbonyl.*

By John Stuart Anderson.

The vapour pressure of nickel carbonyl was determined by Mittasch (*Z. physikal. Chem.*, 1902, **40**, 1) by the dynamical method, and by Dewar and Jones (*Proc. Roy. Soc.*, 1903, **71**, 427) by introducing the liquid over the mercury in a barometer tube, but the results so obtained are discordant. In the present research, the vapour pressure has been measured by an equilibrium method, precautions being taken to eliminate the probable cause of discrepancy in the earlier results.

It is known that in the presence of small quantities of air or oxygen nickel carbonyl is decomposed with formation of carbon monoxide. Preliminary experiments showed that such decomposition always tended to occur, giving rise to an increase in pressure, and that concordant results could be obtained only after every trace of adsorbed air had been removed from the walls of the vessel by strong heating in a vacuum. To render this possible, an all-glass apparatus with a glass spring indicator was used, the pressure within being balanced on the outer side of the spring.

## EXPERIMENTAL.

Nickel carbonyl was introduced into the storage bulb *A* of the simplified vacuum apparatus (Fig. 1) and purified by fractional distillation. To guard against any trace of leakage over long periods, the apparatus was constructed with mercury valves of the type described by Stock (*Ber.*, 1917, **50**, 993). The purification was followed by measurements of vapour pressure. The bulb *A* was immersed in a bath at — 40°, tap 1 opened, and the U-tube *B* cooled in liquid air. With tap 4 open, the volatile portion was distilled into *B* in the stream of the vacuum pump, the small volatile head fraction thus obtained being rejected. Taps 1 and 4 were closed, and the liquid was distilled into one of the small bulbs $E_1$, $E_2$, etc., which were sealed off at the constriction. The bath was allowed to warm to — 35° while a second fraction, consisting of nearly half the residue, distilled into *B*. With taps 1 and 4 closed, this was allowed to melt and then re-frozen to remove from the solid any imprisoned gas, which was pumped off with the mercury-vapour pump. The U-tube was immersed in a beaker of well-stirred ice, and the vapour pressure at 0° of the fraction read on the manometer *M*. This fraction was then transferred to *C*, a second large fraction taken from *A*, and its vapour pressure at 0° determined. The tail fraction was rejected. The middle fractions were combined and the process was repeated. Two such series of operations usually sufficed to give middle fractions of identical vapour pressure at 0°, indicating homogeneity.

The tube used for the vapour-pressure measurements (Fig. 2) was sealed on to the apparatus at *D*, an electric furnace placed around it, and heated to 350—400° for an hour under the vacuum of the mercury pump. On cooling, some nickel carbonyl was distilled into *C*, and from this a convenient quantity was transferred to the tube by cooling *F* with liquid air. With the carbonyl in *C* and *F* frozen, the tube was then pumped out and sealed at *S*.

FIG. 1.

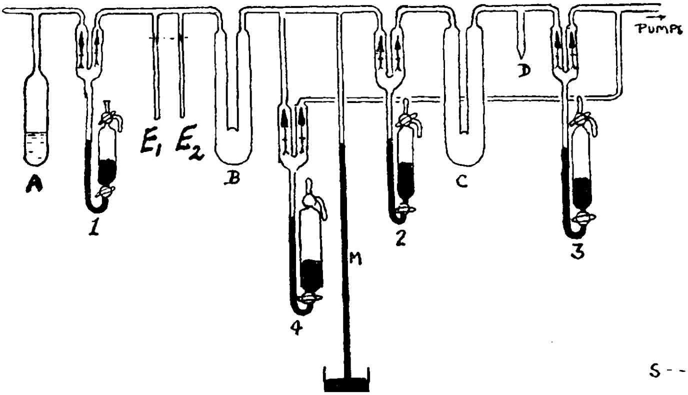
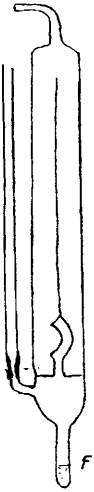


FIG. 2.



*Measurement of Vapour Pressure.*—The vapour pressure at temperatures below that of the room was determined by immersing the tube in an alcohol–ether bath in a wide, deep Dewar flask, and lowering the temperature by blowing in successive small quantities of liquid air. The pressure on the upper side of the spring was varied and measured in the usual manner.

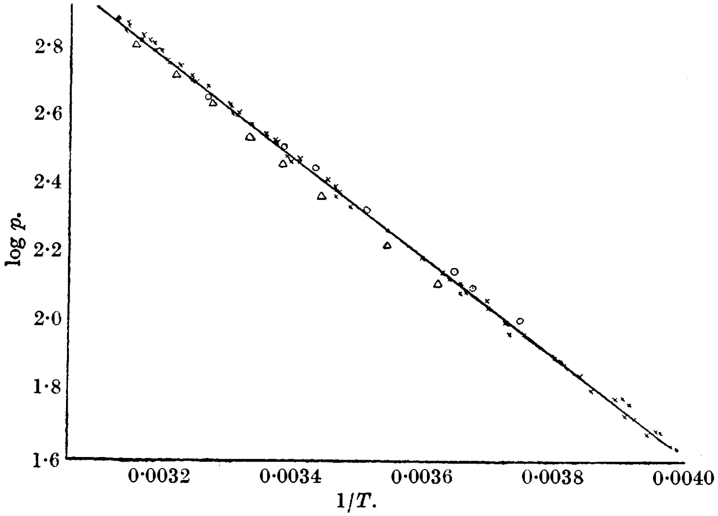
For temperatures above 15°, the tube was immersed in a beaker of water to a point well above the top of the spring. The bath was mechanically stirred, and due time allowed for the attainment of equilibrium in the dissociation $Ni(CO)_4 \rightleftharpoons Ni + 4CO$ before readings were taken.

The low temperatures were measured by means of a three-junction copper–constantan thermocouple, previously calibrated, and a pentane thermometer, and the upper temperatures by means of a standardised mercury thermometer. These were compared amongst themselves.

Measurements were made on five tubes containing nickel carbonyl from three different preparations. The dissociation $Ni(CO)_4 \rightleftharpoons Ni + 4CO$ first becomes apparent at 36° (Mond and Nasini, *Z. physikal. Chem.*, 1891, **8**, 150) so that the figures obtained above this temperature represent, not the vapour pressure, but the equilibrium pressure of the system. It was found that recombination after heating above 40° was frequently very slow, and for concordant results each sample could be used for one ascending run only.

The results obtained are shown on the log $p$–$1/T$ curve (Fig. 3), on which are also indicated the values found by Mittasch and by Dewar and Jones. The results of the present work lie fairly well between the other two sets of measurements, as would be expected if the discrepancy were due to decomposition of the carbonyl, which would lead to low results with the dynamical method and high values with the statical method.

Fig. 3.



× *This work.* ○ *Results of Dewar and Jones.* △ *Results of Mittasch.*

Taking into account all measurements, the line $\log p = 7{\cdot}690 - 1519/T$ may be taken as representing the variation of vapour pressure with temperature. From this may be calculated the following values :

| Temp., $T$—273 | 43·0° | 40° | 30° | 20° | 15° | 10° | 0° | −10° | −20° |
|---|---|---|---|---|---|---|---|---|---|
| *p*, mm. ......... | 760 | 685·5 | 474·2 | 320·6 | 260·6 | 209·9 | 133·7 | 82·4 | 48·3 |

The agreement of the best sets of experimental measurements with the calculated curve is close. From the slope of the log $p$–$1/T$ curve, the molecular heat of vaporisation = $6{\cdot}92 \times 10^3$ cals.

For the vapour pressure of the solid, the following values are obtained from the smoothed curve :

| | | | |
|---|---|---|---|
| Temp., $T$—273 .................. | −25° | −30° | −35° |
| $p$, mm. .......................... | 36 | 23 | 16 |

The intersection of the sublimation curve with the vaporisation curve of the liquid gives for the triple point, approximately, $T$—273 = −22° ; $p$ = 43 mm.

## *Summary.*

The vapour pressure of nickel carbonyl has been measured between − 35° and + 43°.

The vapour pressure of the liquid is given by the Rankine formula $\log p = 7{\cdot}690 - 1519/T$.

The molecular heat of vaporisation is found to be $6{\cdot}92 \times 10^3$ cals.

An approximate value for the triple point of −22° and 43 mm. is obtained from the curve.

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