[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE HEAT OF SUBLIMATION OF CARBON DIOXIDE

BY JOHN W. ANDREWS[1,2]

RECEIVED MARCH 16, 1925 PUBLISHED JUNE 5, 1925

Thus far no experimental data on the heat of sublimation of carbon dioxide have been reported. It is possible to calculate the heat of sublimation from the vapor-pressure equation,[3] combined with the Clausius-Clapeyron equation, but this involves certain assumptions that might vitiate the results.

When the existing data are utilized in an attempt to check the third law of thermodynamics, a discrepancy of several entropy units is found. It was thought that this discrepancy might be due, in part at least, to this calculated value of the heat of sublimation and it was to locate, if possible, this error that the present work was undertaken.

Experimental Part

The method for the experimental determination of the heat of sublimation of carbon dioxide consisted in subliming a definite quantity by an electrical current, measuring the energy input and the volatilized carbon dioxide.

The carbon dioxide used for this work was from a cylinder of commercial material, the snow being obtained by allowing the liquid carbon dioxide to escape from the inverted cylinder into a canvas bag. The gas itself contained a small amount of air and water. A test was made on the solid to ascertain whether air was adsorbed on its surface, but the vapor from the solid was completely absorbed by soda lime. The water remained with the solid, but the vapor pressure of water at this temperature is far too low to be of any consequence.

Preliminary tests showed remarkable insulation properties for the snow. A resistance wire wound upon cardboard and imbedded in the snow charred the cardboard upon the passage of fairly heavy current, showing the need for good thermal contact.

A number of attempts to insure thermal contact were unsuccessful. A sludge of alcohol and carbon dioxide was tried but with no better results, and the use of such material involved additional uncertainties as to the partial molal heat of solution, should the liquid not resaturate.

One partially successful form of apparatus consisted of a Dewar flask in which two concentric glass tubes were imbedded, with the carbon dioxide snow. By this arrangement of tubes, the gas was forced to pass over solid carbon dioxide for a distance of approximately 30 cm. Even under these conditions one could not be sure that the gas was not superheated. It was only by keeping the snow in actual contact with the heating element that superheating could be avoided. With this in mind, the final form of apparatus shown in Fig. 1 was designed.

The heating element, a Therlo wire of approximately 20 ohms resistance, was tied to a sheet copper disk which rested on three copper wires soldered through a 4cm. brass

---

[1] This communication is an abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Du Pont Fellow in Chemistry, University of Illinois, 1923–24.

[3] Onnes and Weber, *Verslag Akad. Wetenschappen Amsterdam*, **22**, 226 (1913).

tube, 15 cm. long. The wires were soldered about 5 cm. from the end which was to be the lower. The upper end was fitted with a cap that sat flush with the sides, and was ground so as to be reasonably air-tight. The lower end was notched.

A lead cylinder 4 cm. long fitted into the tube just loosely enough to slide freely. Copper wires were soldered to the Therlo heating element and led from the lower end of the brass tube. About 20 cm. additional of copper wire was allowed at the top to enable the rubber stopper through which the carbon dioxide delivery tube passed to be removed while the apparatus was being charged. Potential taps were taken off 2 cm. below the rubber stopper, so that slight heating effects of the copper leads were accounted for. A copper-constantan thermoelement was suspended in the glass delivery tube, the tip being within the rubber stopper. All leads were brought out through a hole in the glass tube, and the hole was sealed with de Khotinsky cement.

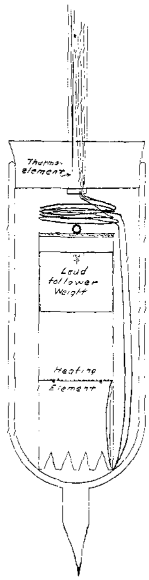

Fig. 1.

To charge the apparatus, carbon dioxide snow was packed into the lower end of the brass tube and the tube was set into the Dewar flask, which was 3 cm. deeper than the length of the brass tube. A few grams of snow was placed in the bottom of the Dewar tube. Pulverized snow was then packed around the tube, which had a 0.5cm. clearance on all sides. Snow was put into the upper part of the brass tube to such a height that the lead follower weight would just go in, the cover was put on, 1 cm. or more of snow added to cover the entire tube, and the stopper tightly inserted. A paper was then tied around the top of the flask, and the entire top flooded with a 50% mixture of vaseline and kerosene. This mixture remains waxy at low temperatures while vaseline alone becomes brittle and cracks.

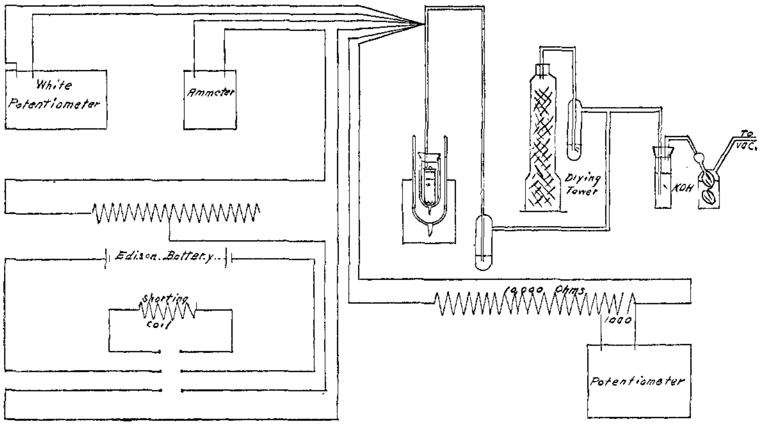

Fig. 2.

This Dewar apparatus was then immersed in a larger Dewar vessel, in which was a sludge of alcohol and carbon dioxide sufficient to surround the smaller flask to a zone about two-thirds of the way up the side, and care was taken that no sludge should touch the stopper or glass delivery tube, as the small temperature difference between the snow and the sludge was sufficient to condense a small amount of the out-going gas. Through the walls of the Dewar vessel, however, there was no such effect. The set-up is shown in Fig. 2.

The current was supplied by a battery of 15 Edison cells, and was varied by a resistance in series. It was measured by a Siemanns and Halske shunt ammeter, calibrated before the run. The potential drop across the heating element was measured by means of a Leeds and Northrup Student type potentiometer, using a volt box. All resistances and standard cells were checked before using.

The carbon dioxide was absorbed in a strong potassium hydroxide solution and weighed. Two bulbs were used: the first was a glass tube with large inlet tube for the removal of most of the gas; if this were not used the normal absorption apparatus would be clogged with potassium carbonate within a very few seconds.

In order to eliminate the back pressure of the solutions, suction was applied and air allowed to flow in freely with the carbon dioxide, water vapor and carbon dioxide first being removed from the air by passing the air through a drying tower loosely packed with soda lime and sodium hydroxide sticks. A Y-tube carried both gas streams into the absorption apparatus. The traps contained sulfuric acid and were merely to allow the rate of flow to be watched, and to indicate condensation of gas within the apparatus by backing up of the sulfuric acid in the tube. A head of about 3 mm. of sulfuric acid was kept on the air side, while a 1cm. head was kept on the carbon dioxide side.

When the apparatus was satisfactorily packed, a zero rate was established within a few minutes. The controlling switch was then thrown, the time noted, and the potentiometer and the ammeter were read. While runs were not in progress, the battery was shorted through a resistance coil of the same resistance as that of the heating element.

Most of the runs were made for five-minute periods, with currents varying from 0.1 to 0.5 amp. It was expected at first that the resistance would vary owing to the heating of the element, but the value of E/I for numerous runs showed an average of 18.94 ohms with closely concordant individual readings, and this value was used, the energy being calculated as E^2/R instead of as $E \times I$ as at first planned. There were several advantages in this; the elimination of the reading of one instrument was an experimental advantage, but theoretically the results were more sound, as the ammeter could be read only to three places while the potentiometer could be read to four, and a composite value of E/I was probably more accurate than any individual reading of the ammeter.

The standard cell used in connection with the potentiometer was checked against a freshly prepared cell which had reached a constant value, and was assumed to be 1.0184 v. It varied from this cell by less than 0.1 millivolt. It was also checked against a number of older standard cells and differed from none of them by more than 0.2 or 0.3 mv.

A thermo-element showed that the outgoing gas was never more than a few hundredths of a degree warmer than the solid carbon dioxide, and only by raising the current to a value considerably higher than that used in any of the runs could the gas be superheated as much as 0.1°.

The total error from instrument readings was not over 0.4%, but in spite of this the values were somewhat discordant, and the first few were so erratic as to be discarded entirely. Whenever the apparatus was freshly packed, the first few runs were almost invariably high, and only after several runs had been made did the value become stable and reproducible. Owing to the difficulty of getting good thermal contact and the high insulating properties of the carbon dioxide snow itself, it is doubtful whether more could be expected.

The results are given in Table I.

TABLE I

EXPERIMENTAL RESULTS

Potentiometer	Weight G.	Time Min.	ΔH
0.5384	0.7587	5	6368
.5394	.7648	5	6341
.53405	.7042	5	6750[a]
.5337	.7819	5-2″	6112
.3688	.3586	5	6322
.3688	.3701	5	6121
.5505	.8195	5	6164
.4141		5	
.2924	.9473	10	6026
.3707	.3510	5	6525[a]
.6931	1.2857	5	6228
.6838	1.2827	5	6076
.80015	1.7380	5	6140
.5088	0.6929	5	6227
.5095	.7047	5	6140
.4128	.4207	5	6752[a]
.4127	.4427	5	6412
.5539	.8250	5	6199
			Av. 6205

[a] Owing to the close agreement, in general, of the values in this table it seemed advisable to omit the three exceptionally high values from the average.

To utilize these data as a check on the third law, we must know the specific heats and the heats of transition of oxygen, carbon and carbon dioxide, together with the free energy and heat content of the reaction,

$C + O_2 = CO_2$. The entropy of graphite is well known to be 1.3. The data of Eucken[4] on the specific heat and heats of transition of oxygen give, for the entropy of oxygen, 24.1. From Eucken's data on the specific heat of the solid carbon dioxide the entropy of the solid can be calculated. This value is 16.66. The value of the heat of sublimation of carbon dioxide as here determined, 6205 calories, divided by the absolute sublimation temperature, 194.6°, gives 31.87. The specific heat of the gas is given fairly well by the equation, $C_p = 7.0 + 0.0071\ T - 0.00000186\ T^2$. Integration of $C_p\mathrm{d}\ ln\ T$ from 194.6° to 298° gives 3.66 for the entropy of the gas.

The data of Roth and Wallasch[5] on the heat of combustion of graphite are the only reliable data on this point. Their value is $\Delta H = -94{,}250$ calories. From the equilibrium data of Hahn,[6] of Haber and Richardt[7] and from specific-heat data, the free-energy equation of carbon dioxide has been determined,

$$\Delta F = -94{,}110 + 0.60\ T\ ln\ T - 0.00065\ T^2 + 0.0611\ T^3 - 3.74\ T$$

giving $\Delta F_{298} = -94{,}260$, whence $\Delta S = +0.05$. Combining these data we get, for the entropy of carbon dioxide, by direct thermal measurements, $S_{298°} = 52.19$, and by thermal and equilibrium measurements, $S_{298°} = 49.55$. The discrepancy is 2.64 entropy units or about eight hundred calories at room temperature—certainly a not very satisfactory check on the third law.

It is possible that this discrepancy may be connected with the crystalline form of the snow. Owing to its finely divided state an error due to the surface tension of the small crystals might be introduced. The magnitude of this error, however, at present cannot be ascertained.

Another possible source of error is in the determination of the specific heat of the solid carbon dioxide, due to the excessively high insulating properties of the snow, coupled with the rapidly changing heat content of the calorimeter and of the heating elements.

The values of the heat of combustion of carbon given by Roth and Wallasch cannot be questioned, it seems, but we may expect new values for the free energy of the carbon dioxide combustion reaction. The new value of the integration constant of the free-energy equation, determined by Eastman and Evans[8] from the equilibrium pressures of the oxides of iron, would change the entropy 1.44 units, but unfortunately in the wrong direction. Nevertheless, this work shows that the free-energy results are questionable.

---

[4] Eucken, *Ber.*, **18**, 4 (1916).

[5] Roth and Wallasch, *Ber.*, **46**, 896 (1913).

[6] Hahn, *Z. physik. Chem.*, **44**, 513 (1903); **48**, 735 (1904).

[7] Haber and Richardt, *Z. anorg. Chem.*, **38**, 5 (1904).

[8] Eastman and Evans, THIS JOURNAL, **46**, 888 (1924).

The author wishes to thank Professor Worth H. Rodebush for his help on this problem, and also to thank E. I. du Pont de Nemours and Company of Wilmington, Delaware, under whose Fellowship this work was done.

Summary

1. An attempt has been made to calculate the entropy of carbon dioxide from thermal data and from equilibrium data in an effort to furnish another check on the third law of thermodynamics.

2. The best values of the specific heats, heat contents and free energies of the components and reactions have been selected from the literature.

3. Experimental data on the heat of sublimation of carbon dioxide have been obtained with an accuracy of ±35 calories.

4. The results show a discrepancy of 2.64 entropy units between the value as calculated from thermal and equilibrium data on carbon, oxygen and carbon dioxide, and the value as calculated directly from the thermal data for carbon dioxide itself.

Urbana, Illinois

[Contribution from the Laboratory of Physical Chemistry, University of Wisconsin]

THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE AT LOW CONCENTRATIONS

By James K. Hunt and Farrington Daniels

Received March 19, 1925 Published June 5, 1925

The study of unimolecular reactions comprises an important branch of chemical kinetics. The specific decomposition rates of these reactions have been supposed to be independent of concentration, and on the basis of this assumption Perrin[1] has maintained that they must be independent of molecular collision. Lindemann[2] has pointed out, however, that we do not possess sufficient evidence to conclude that the specific reaction rate of a unimolecular reaction is independent of the concentration at low concentrations. The purpose of this investigation was to determine, if possible, whether or not there is ground for believing that a reaction of the first order may behave differently at low concentrations than at ordinary concentrations.

Recently a new importance has become attached to the study of unimolecular reactions. In a keen analysis, Rice[3] has denied the very existence of slow reactions of this type, maintaining that reactions which satisfy the equation for a unimolecular reaction and have been classed as unimolecular are in reality bimolecular, catalytic reactions. While admitting

---

[1] Perrin, *Trans. Faraday Soc.*, **17**, 546 (1922).

[2] Lindemann, *ibid.*, **17**, 598 (1922).

[3] Rice, This Journal, **46**, 2405 (1924).