2. Measurements of the partial molal heat capacities of the constituents and the specific heats of aqueous sodium chloride at several temperatures, and of hydrochloric acid at 25°, are given.

3. The partial molal heat capacity of the solute is found to vary approximately as the square root of the molality in dilute solutions, and that of the solvent as the 1.5 power of the molality.

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THE SUBLIMATION PRESSURES OF SUBSTITUTED QUINONES AND HYDROQUINONES

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At the request of Professor J. B. Conant, we undertook to find approximate values of the sublimation pressures of a series of substituted quinones and corresponding hydroquinones at 25°. The materials were those described by Conant and Fieser.[1] The measurements were made by the quartz fiber manometer previously described by one of us.[2] In some cases it was necessary to work at a higher temperature in order to obtain measurable pressures. This required that the gage and connecting tubing should be heated in order to prevent condensation. The gage was mounted in an oven and calibrated at different temperatures against a McLeod gage, using pure dry air. In accordance with theory, the reading of the quartz gage, for a given pressure and temperature in the McLeod gage, was found independent of the temperature of the quartz gage, except that the intrinsic damping constant, called Z in the previous articles referred to, increased slightly with rise in temperature. This increase was allowed for in the subsequent measurements.

The substances were placed in an appendix close to the quartz fiber gage and maintained at the desired temperature, while the gage and connections were kept somewhat hotter. Except while a reading was in progress, the system was continuously pumped with a diffusion pump, access of mercury vapor being prevented by the interposition of a carbon dioxide cold trap. During a reading, the gage was cut off from the pump and cold trap by a ground-glass valve operated by a solenoid. The valve was not lubricated, and undoubtedly leaked slightly, but this leakage was presumably negligible in comparison with the rate of evaporation from the surface of the substance. Two hours of pumping was generally sufficient to remove all traces of solvent from which the substances had been crystallized, and produce pressures that did not decrease on further pumping, and were therefore accepted as true sublimation pressures. In a few cases, however, it was necessary to volatilize the substance completely

[1] Conant and Fieser, THIS JOURNAL, **45**, 2194 (1923).

[2] Coolidge, *ibid.*, **45**, 1637 (1923); **46**, 680 (1924).

by heating to 100°, and allow it to condense in a different part of the system, before constant results could be obtained.

The pressures involved all lie within the "lower range" of the gage, that is, the range within which the molecular mean free path exceeds the dimensions of the fibers, so that no knowledge of the viscosity of the vapor being measured is required. In interpreting the gage readings, the air pressure corresponding to each observed damping time was first read from the calibration curve, and divided by the square root of the ratio of the molecular weight of the substance to that of air, in order to give the pressure of vapor which would give the observed reading *if the place where this pressure existed were at the same temperature as the McLeod gage by which the instrument was calibrated* (20°). The result was then corrected to the actual temperature by multiplying by the square root of the ratio of this temperature to 293°K. (The theory of this correction is given in the last cited paper.)

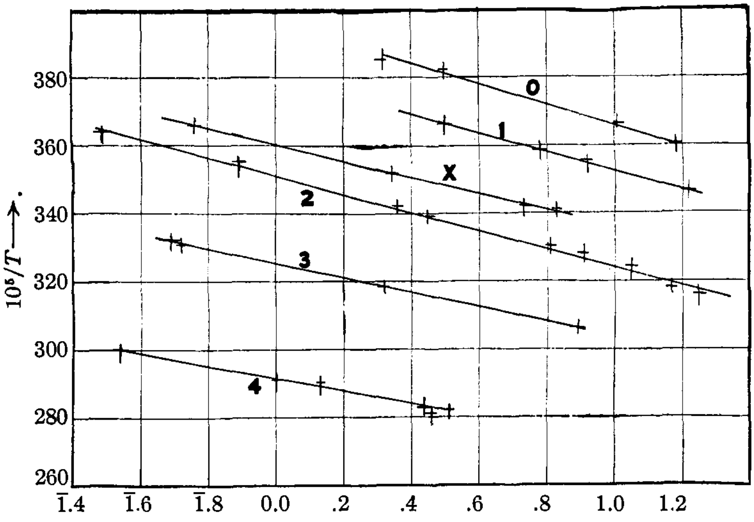

Fig. 1.—Vapor pressure of quinones.

0—Benzoquinone
1—Monochloroquinone
2—2,6-Dichloroquinone
3—Trichloroquinone
4—Tetrachloroquinone
X—*p*-Xyloquinone

The results obtained are given in Table I. When the logarithms of pressure are plotted against reciprocal temperatures, the points lie as well as could be expected upon straight lines, as shown in Figs. 1 and 2. These lines were extrapolated, where necessary, to find the desired pressures at 25°. From the slopes of the lines, rough values for the heat of sublimation have been calculated. These quantities are given in Table II, together with the values of the constants in the equations of the form $\log P = A - B/T$ which best represent the observations.

Table I

Sublimation Pressures in Microns of Mercury

Benzoquinone		Hydroquinone	
Temp., °C.	Pressure	Temp., °C.	Pressure
−13.3	2.1	52.7	0.55
−10.8	3.2	56.4	1.1
+ 0.5	10.2	69.2	4.3
5.3	15.2	72.2	5.9
Monochloroquinone		Monochlorohydroquinone	
− 9.0	0.8	32.6	0.7
0.0	3.2	40.8	1.8
6.4	6.0	48.3	4.6
9.6	8.3	60.7	16.8
16.3	16.7	..	..
2,6-Dichloroquinone		2,6-Dichlorohydroquinone	
1.3	0.3	50.9	0.45
9.3	.8	51.4	.6
19.3	2.3	58.7	1.3
22.1	2.8	59.9	1.5
29.8	6.4	72.1	4.5
31.8	8.2	..	..
36.3	11.3	..	..
40.8	14.7	..	..
41.8	17.6	..	..
Trichloroquinone		Trichlorohydroquinone	
27.8	0.5	41.3	0.55
29.4	.55	51.2	1.6
41.3	2.1	62.2	6.0
54.4	7.7	..	..
Tetrachloroquinone		Tetrachlorohydroquinone	
60.2	0.35	76.8	0.6
70.7	1.0	85.7	1.35
71.7	1.3	..	..
80.7	2.7	..	..
81.2	3.2	..	..
82.7	2.9	..	..
P-Xyloquinone		*P*-Xylohydroquinone	
0.0	0.6	58.7	0.27
..	..	59.2	.32
11.3	2.2	75.0	1.4
19.3	5.9	80.2	2.5
20.3	6.8	88.0	5.5

It appears from internal evidence that the probable error in the pressures is of the order of 10%, corresponding to about 1° temperature change.

The means at hand for controlling the temperature of the substance during measurement were rather crude, and no better accuracy could have been expected. The slopes, and therefore the sublimation heats, are probably correct within 5%.

In the case of tetrachlorohydroquinone, the volatility was so low that only two readings were made at temperatures rather close together, so that the slope of the curve through them, and therefore the pressure at 25°, and the sublimation heat cannot be determined with the same certainty as in the other cases. The values given in Table II were found by drawing a straight line through the experimental points. The slope of this line, and therefore the sublimation heat, is considerably less that in the

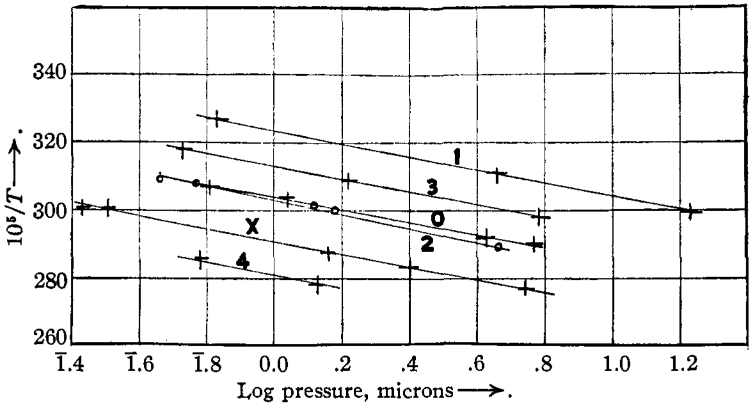

Fig. 2.—Vapor pressure of hydroquinones.

0—Hydroquinone
1—Monochlorohydroquinone
2—2,6-Dichlorohydroquinone
3—Trichlorohydroquinone
4—Tetrachlorohydroquinone
X—*p*-Xyloquinone

TABLE II

CONSTANTS IN THE EQUATION LOG $P = A - B/T$, HEATS OF SUBLIMATION AND SUBLIMATION PRESSURES AT 25°

Substance	*A*	*B*	Heat of sublimation, calories per mole	Pressure at 25°, microns of mercury
Benzoquinone	13.00	3280	15,000	98
Monochloroquinone	13.74	3620	16,500	40
2,6-Dichloroquinone	12.85	3670	16,700	3.5
Trichloroquinone	15.03	4630	21,200	0.32
Tetrachloroquinone	15.06	5170	23,600	.0051
P-Xyloquinone	14.53	4030	18,400	10
Hydroquinone	16.46	5420	24,800	0.018
Monochlorohydroquinone	17.33	5370	24,600	.21
2,6-Dichlorohydroquinone	14.54	4800	22,000	.027
Trichlorohydroquinone	16.57	5300	24,200	.063
Tetrachlorohydroquinone	13.08	4650	21,200	.0030
P-Xylohydroquinone	15.36	5280	24,100	.0045

case of the other hydroquinones. If a line be drawn as well as possible through the experimental points, with the average slope of the other hydroquinone lines, the pressure at 25° comes out 0.0017 microns.

According to Stelzner[3] the sublimation pressure of hydroquinone at 169°, its melting point, is 14.1 mm. If the pressure curve for hydroquinone, as shown in Fig. 2, is extended to include this datum, the mean slope over the temperature interval involved corresponds to a sublimation heat of 24,000 calories per mole, or slightly less than the 24,800 indicated by the present measurements at ordinary temperatures. This is excellent agreement, for if the specific heat of crystalline hydroquinone exceeds that of its vapor, the heat of sublimation should decrease with rising temperature.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF CAMBRIDGE UNIVERSITY]

THE DECOMPOSITION OF ETHYL ALCOHOL AT THE SURFACE OF THORIA

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Sabatier[2] showed that ethyl alcohol could undergo two important types of decomposition, one to ethylene and water, a reaction promoted chiefly by oxide catalysts, and the other to hydrogen and acetaldehyde promoted by metals. Many catalysts promote both reactions. Contrary to the view of Sabatier, but in agreement with the work of Brown and Reid[3] we have found that thoria prepared by precipitation with ammonia yields approximately equal volumes of ethylene and hydrogen. The surface decomposition, both of alcohol and of formic acid, presents points of interest in that two types of decomposition proceed at the surface of the same catalyst. Two hypotheses have been suggested to explain this fact. On one view[4] the two reactions proceed on the same surface and the proportion of each reaction is determined by the kinetic condition or phase of the molecules that bombard the surface. On the other view, each reaction is promoted by a different type of active area or "patch" of the catalyst surface.[5] There seems to be a certain divergence of opinion as to the

[3] Stelzner, Landolt-Börnstein-Roth-Scheel, "Tabellen," Julius Springer, Berlin, 1923, 5th ed., p. 1375.

[1] Exhibition of 1851 (England) Scholar at Cambridge, 1924–1925–1926.

[2] Sabatier, *Ann. chim. phys.*, [8] **20**, 326 (1910).

[3] Brown and Reid, *J. Phys. Chem.*, **28**, 1077 (1921).

[4] Hinshelwood, *Proc. Roy. Soc.*, **100A**, 575 (1922); *J. Chem. Soc.*, **123**, 1014, 1333 (1923).

[5] Rideal, *Report Solvay Conference*, Brussels, 1925. Taylor, *J. Phys. Chem.*, **28**, 897 (1924); **30**, 145 (1926). Adkins, numerous papers; see especially THIS JOURNAL, **48**, 1671 (1926).