102° with perhaps a slight tendency toward 104°. No significant uncertainty in the values of $\overline{q/q_{\text{obs}}}$ is introduced by the question of the best weights to be used in taking the average.

From the qualitative comparisons and these consistency measures we believe it is very unlikely that the correct bond angle value lies outside limits given by our final result $\angle\text{FNF} = 102.5 \pm 1.5°$. Our final values for the nitrogen-fluorine distance $r_{\text{N-F}} = 1.37 \pm 0.02$ Å. and the fluorine–fluorine distance $r_{\text{F...F}} = 2.14 \pm 0.02$ Å. are taken from plots of the values of $r_{\text{N-F}}$ and $r_{\text{F...F}}$ (from Table I) as functions of the assumed bond angle. The quoted uncertainties for these quantities we also regard as limits of error within which the correct values almost certainly lie. They include the variation corresponding to the quoted uncertainty of the bond angle and the estimated uncertainty of $\overline{q/q_{\text{obs}}}$ ($\pm$ 0.007, corresponding to $\pm$0.01 Å. in $r_{\text{N-F}}$) for the given bond angle.

Acknowledgment.—We are indebted to Professor Burg for the sample of nitrogen trifluoride and to Professor Pauling, especially for discussion of the dipole moment problem. The late Dr. Horace Russell, Jr., helped us in making the photographs.

Summary

An electron-diffraction investigation of nitrogen trifluoride has been made. The molecule may be represented by a symmetrical, pyramidal model with bond distance $r_{\text{N-F}} = 1.37$ Å. and bond angle $\angle\text{FNF} = 102.5°$ ($r_{\text{F...F}} = 2.14$ Å.), values which are almost certainly in error by less than $\pm$0.02 Å. for the distances and +1.5° for the bond angle.

A simple interpretation, which should be applicable to other, analogous situations, is given for the very small dipole moment and relatively small bond angle of the nitrogen trifluoride molecule, in contrast to the relatively large dipole moment and bond angle of the ammonia molecule.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

Some Heats of Wetting of Unit Surfaces[1]

BY FRANK L. HOWARD[2] AND J. L. CULBERTSON

Introduction

Previous studies in this Laboratory and elsewhere have shown interesting correlations between heats of wetting of various solid–liquid systems and such other properties as the apparent density of the pulverized solid,[3] polarity,[4] adsorptive capacity,[5] coking quality of coal,[6] and hygroscopicity of soils.[7] Most of the available data have been reported in terms of the weight of solid wetted. However, in the study of surface phenomena it is desirable that the pertinent thermodynamic data be based on the surface area involved.[8]

Harkins and co-workers[8,9,10] have reported heats of emersion (the reverse of heats of wetting, as used here) on this basis for a number of systems, and have discussed in detail the theory and the experimental difficulties of such measurements.

This investigation was designed to measure the heats (enthalpies) of wetting of solid surfaces in terms of the wetted surface area.

Experimental

The solids chosen were the sulfides galena and sphalerite, the halides sylvite and fluorite, and quartz. With one exception, the solids employed were selected mineral crystals; these were reduced by dry milling to powders with specific surface area ranging, approximately, from 0.1 to 2 square meters per gram. (The sylvite was C. P. KCl.) Water, *n*-heptane and carbon tetrachloride as wetting liquids represented polar, non-polar and polarizable types, respectively.

The pulverized solid sample, of from 5 to 20 g., was weighed into the powder chamber of the wetting apparatus (Fig. 1), evacuated at 300° for an hour, then sealed under vacuum. The liquid reservoir chamber was filled with the wetting liquid, plus enough powder to ensure saturation with the solid phase. This precaution was deemed desirable to avoid any possible error from heat of solution of the solid phase in the liquid. Carbon tetrachloride and *n*-heptane, when used, had activated alumina or sodium amalgam added to maintain their anhydrous condition. A loop of fine constantan wire was engaged with the hook-shaped septum between the reaction and reservoir chambers. The wetting apparatus was then inserted in the calorimeter and permitted to come to thermal equilibrium at 25°.

The adiabatic calorimeter comprised two concentric metal vessels, the inner one containing the wetting apparatus, while the outer one carried a compensating heating coil which served to maintain the temperature equality

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[1] From a thesis submitted by Frank L. Howard to the Graduate School of The State College of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948. This paper was presented at the San Francisco Meeting of the American Chemical Society, April, 1949.

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[3] Culbertson and Winter, THIS JOURNAL, **59**, 308 (1937).

[4] Boyd and Harkins, *ibid.*, **64**, 1190 (1942).

[5] Harman and Parmelee, *J. Am. Ceram. Soc.*, **28**, 110 (1945).

[6] Cannon, Griffith and Hirst, Proc. Conf. Ultra-fine Structure of Coals and Cokes, Brit. Coal Utilization Research Assoc., **1944**, 131; *Chem. Abstracts*, **39**, 1274.[2]

[7] Behrens, *Z. Pflanzenernärh., Düngung u. Bodenk.*, **40**, 257 (1935).

[8] Harkins and Boyd, THIS JOURNAL, **64**, 1195 (1942).

[9] Basford, Jura and Harkins, *ibid.*, **70**, 1444 (1948),

[10] Jura and Harkins, *ibid.*, **66**, 1356 (1944).

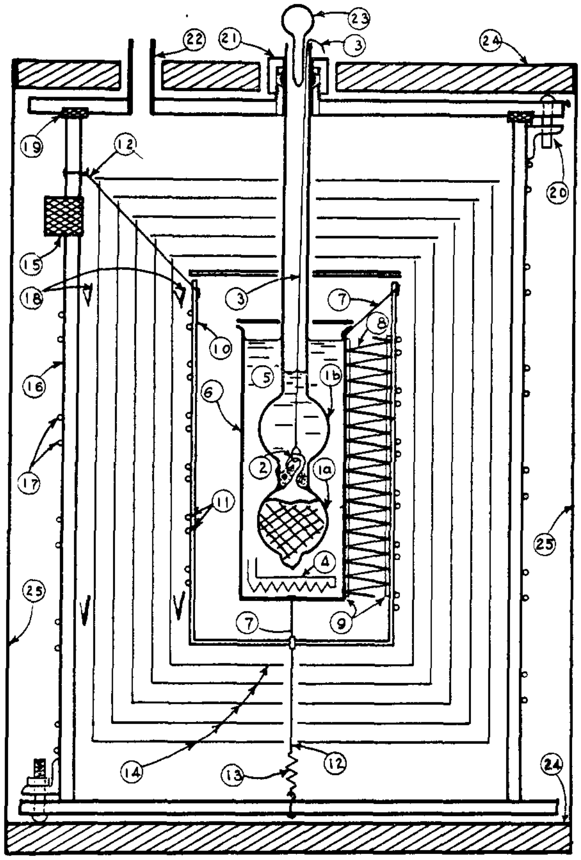

Fig. 1.—Calorimeter parts: 1a, powder chamber; 1b, liquid chamber; 2, hook-shaped frangible seal between chambers; 3, wire for breaking seal; 4, calibration heater coil, No. 40 Manganin DSC, 205.0 ohms; 5, heat-transfer fluid (vacuum-pump oil); 6, inner calorimeter vessel, $1^1/_2''$ × 4″, 24-gage brass, nickel plated; 7, four-wire suspension of inner calorimeter vessel; 8, row of thermocouples between inner and outer vessels; 9, thermocouple shields, 0.003″ brass shim stock; 10, outer calorimeter vessel, 3″ × $5^3/_8''$—16-gage copper; 11, outer vessel balancing heater, 30.9 ohms; 12, four-wire suspension of outer vessel and radiation shields; 13, tension spring; 14, radiation shields of aluminum foil, 0.0007″, on wire frames; 15, connector plug for leads to thermocouple groups and heaters; 16, evacuated jacket vessel, $6^1/_8''$ × 11″—$^1/_4''$ steel; 17, jacket heater, 300 ohms; 18, thermocouples between outer calorimeter vessel and jacket; 19, vacuum gasket under jacket lid; 20, angle clip and aligning pins; 21, vacuum-tight packing gland; 22, outlet nipple to vacuum pump; 23, loose glass plug to reduce diffusion through reaction vessel neck; 24, insulating board covers; 25, draft shield.

of the two vessels. This equality was judged by means of a thermel of 100 pairs of copper–constantan junctions arranged in rows between contiguous walls of the two vessels and connected with a sensitive null-point galvanometer. Heat transfer was reduced by 4-wire suspension of each vessel, by disposing five aluminum foil radiation shields concentrically about them, and by placing this entire assembly under vacuum. The vacuum-tight jacket was also maintained at the temperature of the calorimeter vessels, through the use of another heater and thermel. Various of the structural details were adapted from designs by Ward,[11] Gucker,[12] Whipp,[13] and others. Figure 1 shows a vertical section through the calorimeter and wetting apparatus assembly.

To measure the heat of wetting, the hook-shaped partition was broken by means of the wire loop, permitting atmospheric pressure to force the wetting liquid into the evacuated lower chamber and to wet the powdered solid. The heat of wetting released in the inner calorimeter vessel was balanced by a measured amount of electrical heating supplied to the outer vessel to maintain the temperature equality of the vessels. This "balancing heat" was then immediately compared with the balancing heat required for a known heat increment produced in the inner vessel by a carefully calibrated electrical heating coil. The heat of wetting was then computed from these three quantities, correcting, if necessary, for the rate of drift of temperature.

Discussion

The results, computed as calories per square meter of solid surface,[14] are presented in Table I. With the exception of the value for the sylvite–carbon tetrachloride system, each figure is based on two or more measurements. Sample weights ranged from about 5 g. for the sylvite to 15–25 g. for the samples of galena. Within the limits of reproducibility of the method, the heats of wetting were independent of sample size and solid–liquid ratio.

TABLE I

Specific surface area, sq. m./g.	Solid	Liquid	Heat of wetting $-\Delta H$, cal./sq. m.	$-\Delta H$, kcal./g. atom
0.87	Sphalerite	H_2O	0.49	40
	(ZnS)	CCl_4	.31	25
		C_7H_{16}	.081	6.7
1.35	Fluorite	H_2O	.25	19.5
	(CaF_2)	CCl_4	.024	1.9
		C_7H_{16}	.042	3.3
0.206	Sylvite	CCl_4	.03	4
	(KCl)	C_7H_{16}	.082	10
0.120	Galena	H_2O	.63	68
	(PbS)	CCl_4	.11	12
		C_7H_{16}	.14	15
2.13	Quartz	H_2O	.21	
	(SiO_2)	CCl_4	.029	
		C_7H_{16}	.043	

Liquid surface enthalpies at 25° are: H_2O, 0.0284; CCl_4, 0.0132; and C_7H_{16}, 0.0082 cal./sq. m.

Boyd and Harkins,[8] Stockfleth,[15] and Wilke[16] have reported heat of wetting measurements on the system silica–water as follows: 0.14, 1.41 and 0.72 cal./sq. m., respectively. Heats of wetting per unit area of the other systems involved in this investigation have not, to the authors' knowledge, been reported previously.

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(11) Ward, *Proc. Roy. Soc.* (*London*), **A133**, 511 (1931).

(12) Gucker, Pickard and Planck, THIS JOURNAL, **61**, 459 (1939).

(13) Whipp, *Phil. Mag.*, [7] **18**, 745 (1934).

(14) Specific surface areas were determined by the Brunauer–Emmett–Teller adsorption isotherm method. We are indebted to Mr. P. M. Craven for these measurements.

(15) Stockfleth, Thesis, State Coll. of Wash., 1939.

(16) Wilke, Thesis, State Coll. of Wash., 1942.

Stockfleth's estimate of surface area by microscopic measurement of the quartz particles may be assumed to be low—that method neglects any surface roughness. Wilke employed stearic acid adsorption isotherms for his area measurement, an improvement over the microscopic method, but probably inferior in accuracy to the BET method. The present value is in fair agreement with that of Boyd and Harkins, who also used the BET method for surface area measurement.

The heats of wetting are compared with the surface enthalpies of the wetting liquids, as computed from their surface tensions and their rates of change of surface tension with temperature

$$H = \gamma + T(\partial\gamma/\partial T)_P$$

It will be noted that, although of comparable magnitude in some systems, the enthalpy decrease in the production of the solid–liquid interface is in these systems always greater than that increase accompanying formation of the liquid–vapor interface.

As a matter of interest, the results for some of the systems have also been examined from the chemical point of view. Before crushing, the fluorite crystals had been chiefly developed in the 111-type planes, the galena in 100-type, and the sphalerite about 50% in each of these types. Assuming the same distribution to hold in the powdered material, the surface area per gram atomic weight of the metallic atom in the surface planes was computed from the lattice constants of the unit cell. From this area and the heat of wetting per unit area, the heat of wetting per gram atom of the metallic component was derived.

In the systems investigated water consistently gave the highest heats of wetting. Except for sphalerite, the carbon tetrachloride systems had lower heats of wetting than did those involving *n*-heptane. Neither is polar, although carbon tetrachloride has a high polarizability. However, polarity, *per se*, may not be a controlling factor. For instance, Volman and Andrews,[17] in a recent investigation, have found no dipole moment effect in the adsorption of the *cis*- and *trans*-dichloroethylenes on activated carbon. Indeed, for many systems, dipole interaction could not explain the thickness of the adsorbed layer, since these forces decrease too rapidly with distance.

In the water–mineral systems examined here, the heat of the surface reaction is of a magnitude greater than that associated with dipolar interactions, and is comparable with heats of chemical reaction in bulk systems. The comparatively low heats of wetting of fluorite and sylvite, the most ionic of the crystals used, give further evidence against an adsorptive force scheme based solely on polarity effects.

It is unlikely that any one adsorptive force or type of bonding will adequately explain all the various effects observed in surface reactions. These reactions, which are responsible for heats of wetting and of adsorption, may well include all of those types found in bulk reactions, plus the additional factor of an orienting effect.

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Summary

1. A calorimeter suitable for measurement of small quantities of heat has been designed.

2. Heats of wetting at 25° have been measured for the systems involving water, carbon tetrachloride or *n*-heptane as the wetting liquid and sphalerite, galena, fluorite or quartz as the wetted solid, also for the systems sylvite–carbon tetrachloride and sylvite–*n*-heptane.

3. These heats of wetting have been reduced to a unit surface basis by means of Brunauer–Emmett–Teller adsorption isotherm measurements of the specific surface areas of the solids.

4. The relative and absolute magnitudes of these heats of wetting show evidence of chemical reaction rather than mere dipole interaction at some wetted surfaces.

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[17] Volman and Andrews, THIS JOURNAL, **70**, 457 (1948).