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The Disposition of Work Energy Applied to Crystals*

C. G. MAIER** AND C. T. ANDERSON***

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The experiments described in this paper were initiated for the purely practical purpose of securing data to be used for an energy balance of the process of comminution of solids. The technologic problem is not considered here but rather the antecedent fundamental and scientific one of attempting to describe the thermodynamic properties of crystals as a function of particle size. It has been customary to ascribe observable variations in the properties of crystalline materials of large or fine particle size to a change of free energy, entropy or heat content resultant from the subdivision. Consideration of the first law of thermodynamics with reference to the application of work energy to crystals allows for only two obvious possibilities: (1) The heat produced in the crystals by the applied work is equal to it, whence no change of intrinsic energy of the material can occur; or (2) part only of the work appears as heat and the intrinsic energy of the crystals must increase. In this latter case, it is supposed that the energy corresponding to the increase of intrinsic energy is "stored" in the surficial layers of the crystal particles. We shall offer no apology for approaching the problem of testing these alternatives in a strictly empirical manner and for presenting data which may seem to contradict much of

previous theory and experiment concerning the "surface energy" of solids. However tempting a review and criticism of previous attempts to measure or theoretically define this quantity might be, the elementary approach represented by our work now seems essential for understanding of the anomalous results, both of ourselves and others. Experimental test based on the first law, as expressed above, obviously could be either by (1) attempting to determine the change of intrinsic energy of fine compared to coarse particles of suitable materials or (2) by comparing the work and heat during the comminution process. Both of these experimental alternatives are described below. Thus we shall first describe experiments upon the heat of solution of fine and coarse calcite, designed to reveal measurable differences of intrinsic energy due to comminution. Further, we have investigated the specific heat at low temperatures of similar samples of calcite, and later of finely drawn wires of copper and aluminum in the annealed compared to the cold-worked state, referring to that part of the intrinsic energy represented by heat content. Finally, in the case of copper and aluminum, we have adopted the second experimental alternative of comparing the work and heat during a drawing process.

PART I. HEATS OF SOLUTION OF FINE AND COARSE CALCITE

THE mineral calcite was chosen for a test of the change of intrinsic energy due to comminution for a number of excellent experimental reasons. Its heat of solution in hydrochloric acid is near 4000 calories per formula weight and Bäckström¹ had reported a difference of 60 calories per f.w. between large crystals and a sample ground to 10-micron size. Such a

quantity should be easily detectable, even with only fair calorimetric precision, in comparison with the total of 4000. The rapid and easy solution in acid, the high purity obtainable in natural crystals and the ease of precise analysis commend this choice further.

Experimental work

The calorimetric method used to determine the heat of solution of calcite samples of varying fineness has been described previously by one of us² in connection with the heat of solution of zinc oxide and no essential change of method or accuracy was made in the present experiments. The limiting sensitivity of the calorimeter is approximately 1 calorie.

The rate of dissolution of calcite, in very fine sizes, was so great that excessive foaming ordinarily took place. This difficulty was easily

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¹ Bäckström, J. Am. Chem. Soc. **47**, 2438 (1925).

² Maier, J. Am. Chem. Soc. **52**, 2159 (1930).

remedied by tying several thicknesses of surgical gauze about the thin walled flask used for the calcite container. This flask was broken inside the gauze bag so formed at the appropriate instant. The first evolution of gas after breakage of the flask distends the bag and prevents further ingress of acid until the carbon dioxide has escaped. The dissolution of calcite proceeds smoothly by successive distentions, and is complete for the finest sizes in about 4 minutes from the instant of breaking. By using a smaller or greater number of layers of gauze, it was possible to bring the total time of dissolving to within practically identical limits for sizes from $\frac{1}{4}$ inch to 0.5 micron, thus insuring the greatest degree of comparableness in the necessary calorimetric corrections.

Materials. The hydrochloric acid used for dissolution of the calcite was of C. P. grade, without further purification. It was diluted to a concentration of $1\text{HCl} : 20\text{H}_2\text{O}$. Analysis by gravimetric means showed the actual HCl content to be 9.192 percent and the theoretical HCl content 9.191 percent. Before use, this acid was saturated with CO_2 at $23\text{--}24^\circ\text{C}$, by using gas which had been saturated with water vapor above an identical HCl solution.

Well-developed calcite crystals were selected and prepared in three sizes. Two coarser sizes, prepared by simple crushing were $-4+6$, and $-200+270$ mesh, separated by standard screens. A third sample was prepared by grinding in a mechanical agate mortar, with frequent classification by means of an air elutriator, arranged as described by Roller.³ The particle size of the final product was fairly uniform and determined by microscopic means to average near 0.5 micron. The minimum visible size was greater than 0.1 micron and the maximum near 1 micron but there were relatively few particles of limiting sizes.

The finest size calcite had a very low apparent density, and to secure sufficient compactness so that an adequate amount could be put into our calorimetric containers and to improve the thermal conductivity of the material, it was compressed into pellets. A pressure of about 2 tons per sq. in. was used in the press, resulting in

fairly dense pellets, which were again pulverized to a size approximating 14–35 mesh.

Experimental procedure. Samples of 50.0375 grams (vacuum basis), or $\frac{1}{2}$ formula weight, were sealed, after careful drying at 105°C , into thin-bottomed flasks, as described in the previous reference. The weight of hydrochloric acid used was 595.19 grams, corresponding to $1.5\text{HCl} : 30\text{H}_2\text{O}$, without, however, any attempt to correct for dissolved CO_2 , which is small in this strength acid. Calorimetric determinations were: (1) Determination of the initial heat capacity of the calorimeter by direct electrical methods, under such conditions that the final temperature was near 24.6°C . About 7000 calories of heat were generated by the accurately calibrated manganin heater. (2) When thermal equilibrium had been attained the flask was broken and a conventional determination carried out. The attempt was made to finish near 25°C . (3) After this latter test the heat capacity was determined again over the range from $25\text{--}26\frac{1}{3}^\circ\text{C}$ by repetition of (1).

Calculation of results. The method of calculation of results has been described in the previous paper but it may be repeated here that the temperature coefficient of the reaction, ΔC_p , is directly determined by the difference between the heat contents measured under (3) and (1) and that the constancy of this quantity is an excellent check upon satisfactory operation of the calorimeter. Systematic errors are referable to the energy determinations. Recalibration of the standard cells and resistances used imply no error here greater than 1 part per 100,000.

In converting international joules to 15° calories, the factor 1/4.184 was used. The final figure of the resistance thermometer reading has been dropped in each case, except as mentioned hereinafter.

The chief source of uncertainty is in correction of the temperature rise. The calorimeter comes to thermal equilibrium in 5 to 8 minutes so that calculation by a graphic Regnault-Pfaundler method is eminently satisfactory but the heat exchange with the surroundings is erratic to about 1 percent near the adiabatic point, probably due to the well-known adsorbed film effect on the gold-plated calorimeter shell. The known uncertainty due to this cause is approximately 5 calories; for this reason, no greater

³ Roller, U. S. Bur. Mines Tech. Paper 490 (1931).

TABLE I. Heat of solution of 0.5CaCO_3 in $1.5\text{HCl} : 30\text{H}_2\text{O}$.

Exp. No.	Aver. part. size, mm	Initial heat capacity	Final heat capacity	ΔC_p	Temp. rise, $^{\circ}\text{C}$ ΔT	Cooling rate correction	Corrected temp. rise, $^{\circ}\text{C}$	Final temp., $^{\circ}\text{C}$	ΔH_T $\frac{1}{2}\text{CaCO}_3$	ΔH_{298} $\frac{1}{2}\text{CaCO}_3$	Mean ΔH_{298} per CaCO_3	A. D. of M.
1	4.0	5671.0	5697.9	26.9	0.3603	-0.0135	0.3468	24.62	-1966.7	-1953.6	- 3913.8	± 4.6
2	4.0	5681.2	5709.6	28.4	0.3465	-0.0017	0.3448	25.04	-1958.9	-1960.3		
7	4.0	5670.5	5702.1	32.4	0.3498	-0.0038	0.3460	24.85	-1962.0	-1956.8		
3	0.065	5695.5	5723.6	28.1	0.3406	+0.0021	0.3427	25.22	-1951.8	-1959.4	- 3912.8	± 4.0
4	0.065	5671.5	5701.9	30.4	0.3471	-0.0015	0.3456	25.01	-1954.4	-1954.7		
8	0.065	5723.7	5748.8	25.1	0.3425	-0.0008	0.3417	24.98	-1955.8	-1955.1		
5	0.0005	5700.7	5726.5	25.8	0.3673	-0.0030	0.3643	24.80	-2075.6	-2068.7	-(4132.4)	
6	0.0005	5656.9	5685.0	28.1	0.3715	-0.0042	0.3673	24.60	-2077.8	-2064.0		

relative precision than 10 calories per formula weight is claimed for these experiments. The absolute accuracy may be no better than several times this amount, due rather to such factors as imperfect saturation of evolved gases by water vapor, ununiformity due to the very rapid completion of the reaction and other secondary effects, rather than to the calorimeter characteristics.

Experimental results. The results of eight determinations of heat of solution of three sizes of calcite are presented in Table I, the order of measurement being the sequence of experiment numbers.

In correcting the results of these experiments to a final temperature of 25°C the observed value of ΔC_p , averaging 28 calories, has been increased by 4.5 calories to represent the heat content of $\frac{1}{2}\text{CO}_2$ lost by the system. No corrections for heat of vaporization of water with the CO_2 or for external work done by the CO_2 in its escape have been made. The chief interest is in comparison of results for varying degrees of fineness.

At first glance, the results of Table I would indicate that Bächström's result of an increased heat of solution of 60 calories per f.w. for 10-micron size material was approximately confirmed by the figures for 0.065- and 0.0005-mm sizes, showing an apparent increase of $4132.4 - 3912.8 = 219.6$ cal/f.w. for this range.

Had our experimental work ceased at this point, publication of our results would have burdened chemical literature with still one more erroneous figure for "surface energy," although the result would no doubt have been con-

ventionally acceptable, if unremarkable, as falling in with previous determinations. In this case, however, we were fortunately constrained to make precise analyses of the materials used. Reference to previous attempts at determination of the energy differences of fine and coarse materials shows them to be singularly free from this elementary precaution.

Analyses of materials

The thermal decomposition of calcite at 1000°C in a slow stream of pure, dry nitrogen was found to be a precise method of analysis for these relatively pure samples, with the use of a conventional combustion train. Water and carbon dioxide evolved were weighed after collection by fresh calcium chloride and ascarite and their sum was compared with the loss in weight of sample. By using a clear silica-glass tube and careful preliminary drying, the combined H_2O and CO_2 checked the loss in weight of a 4-gram sample to within 0.2 milligram in all cases.

Analysis of the sample crushed to 0.065 mm showed a CO_2 content of 43.973 percent, without correcting weights to a vacuum basis. An approximate correction to vacuum would indicate 43.959 percent CO_2 . Based on the atomic weights 40.07 for calcium and 12.005 for carbon, the theoretical CO_2 content of calcite is 43.972 percent and the purity of this sample was at least 99.970 percent.

In the case of the 0.5-micron size, calculation from the CO_2 content showed only 98.656 percent CaCO_3 . Since the weight of CO_2 and water found by analysis checked the loss in weight of the

calcite during decomposition to within 0.2 milligram, the composition of the impurity may be calculated on the assumption that it consisted only of $\text{Ca}(\text{OH})_2$ and H_2O , the actual figures being 0.726 percent $\text{Ca}(\text{OH})_2$ and 0.618 percent H_2O . No silica (from the mortar used in grinding) could be detected in this sample.

It is apparent that this percentage of $\text{Ca}(\text{OH})_2$ would produce serious error in the heat-of-solution tests 5 and 6, of Table I. The most recent measurements of the heats of solution of $\text{Ca}(\text{OH})_2$ in hydrochloric acid have been made by Thorvaldson and Brown⁴ who used acid of concentration 1:200 and obtained as best value 30,850 cal._{20°}, at 20°C, per formula weight. In the present work it was thought necessary to repeat the determination of the heat of solution of $\text{Ca}(\text{OH})_2$, by using the concentrations of HCl and CaCl_2 as obtained after dissolution of $\frac{1}{2}\text{CaCO}_3$ in 1.5HCl : 30H₂O, thus representing approximately identical final conditions and eliminating heat-of-dilution effects as much as possible. For this purpose, the solutions obtained in experiments 7 and 8 of Table I were again placed in the calorimeter and the heat of solution of two samples of slightly less than 1 gram each of CaO, which had been hydrated with the same proportion of water as corresponded to the 0.5-micron sample analysis, was determined.

The samples of CaO used were from the previous analysis of calcite and undoubtedly were of high purity. In these determinations of heat of solution, the last figure of the resistance thermometer reading was retained (because of the low temperature rise involved). The data themselves are shown in Table II.

The final result for $\text{Ca}(\text{OH})_2$ shown in Table II indicates that the heats of dilution involved in comparison with the result of Thorvaldson and Brown are substantially negligible in this case. By using the figure 413.9 calories per gram, corresponding to $\Delta H = -30,670$, the results of experiments on the 0.5-micron calcite of Table I may be corrected as follows: 100.075 grams evolve 4132.4 calories but contain 98.730 grams CaCO_3 and 0.7264 gram $\text{Ca}(\text{OH})_2$; but $0.7264 \times 413.9 = 300.7$ calories evolved due to the

TABLE II. Heat of solution of $\text{Ca}(\text{OH})_2$ in $\frac{1}{2}\text{HCl} : 1\text{CaCl}_2 : 30\text{H}_2\text{O}$.

	Experi- ment 1	Experi- ment 2
Weight CaO used, grams	0.9270	0.9418
Heat capacity of calorimeter, calories	5689.0	5658.0
Temperature rise, °C, uncorrected	0.08116	0.09249
Cooling-rate correction	+0.00812	-0.00159
Corrected ΔT , °C	0.08928	0.09090
Final temperature, °C	25.16	25.03
Heat of solution, per gram $\text{Ca}(\text{OH})_2$, calories	414.6	413.2
ΔH per $\text{Ca}(\text{OH})_2$, average, calories	-30670	15°

hydroxide; the net, $4132.4 - 300.7 = 3831.7$ corresponds to $3831.7 \times 100.075 / 98.730 = 3883.4$ calories per CaCO_3 , corrected. This figure is 29.4 calories less than for the 0.065 mm material.⁵ The correction for impurities known to be present in the 0.5-micron size more than accounts for the difference observed.

PART II. ENTROPY CHANGE DUE TO COMMUNITION

Fine and coarse calcite

Specific-heat determinations were made by Anderson on the original sample of calcite crushed to 0.75 mm average size and compared with similar determinations on the 0.5-micron size as used above. These results have been published.⁶

After correction for the impurities in the fine calcite it was found that the two sets of data were experimentally identical in the lower temperature ranges (50 to 150°K) but that the fine material showed a slight progressive increase of specific heat compared to coarse above this range. Near ordinary temperatures this difference became slightly less than 1 percent as a maximum. Had the difference persisted to low temperatures the conclusion that a real difference

⁴ Thorvaldson and Brown, J. Am. Chem. Soc. **52**, 80 (1930).

⁵ If appropriate corrections for external work and heat of vaporization of water above the solutions used are made and the differences in quantity of CO_2 evolved taken into account, this discrepancy becomes 28.9 calories in the same direction. The reason for the overcorrection is discussed in more detail in connection with density determinations below.

⁶ Anderson, J. Am. Chem. Soc. **56**, 340 (1934).

of heat content existed might have been warranted but it is known that the maximum errors in calorimetric work of this sort appear near ordinary temperatures and have been shown by other work to lie near 2 percent as a maximum, with an average uncertainty of about 1 percent. The differences observed in this case were, then, only as great as the supposed experimental error and the results are inconclusive as far as calcite is concerned. The differences observed in the higher temperature ranges certainly were no greater than those naturally ascribable to the effect of the poor heat conductivity of the fine material, even after its compression to granules.

Work upon metallic wires

The factors causing rather high calorimetric errors of specific-heat determinations in the method used for measuring this quantity at low temperatures are minimized considerably when metallic samples are in question. Not only is the mass of sample carried by a given calorimeter much greater, but more important is the fact that high thermal conductivity greatly reduces the necessary calorimetric corrections constituting the chief source of error of this method. We therefore decided again to attempt to observe possible entropy differences in samples of cold-worked as compared to annealed metals.

The fundamental difference in the nature of the comminution process when carried out upon calcite, or by drawing wires, is obviously that the first produces new external crystal surfaces, whereas the second process may produce new internal crystal surfaces. It will be more suitable to postpone more searching inquiry into the differences and analogies in the two cases until all the experimental evidence has been adduced.

Experimental

The calorimeter used to determine the specific heats at low temperatures has been previously described by one of us.⁷ The sample of copper wire was specially prepared for us of deoxidized metal through the courtesy of the Bell Telephone Laboratories, who furnished it to us in the form of hard-drawn wire. It had been drawn from 0.180 to 0.010 inch without annealing and in such a way as to insure every precaution against self-

annealing. It was further drawn by us to 0.0075 inch, and the final wire was cut into small pieces approximately 0.010 inch long. Enough quantity was prepared for two calorimeter samples, one of which was annealed at 400°C for 16 hours in a high vacuum.

The aluminum was of high purity (99.985 percent) and was drawn from No. 16 B & S to about No. 32 B & S gauge in a manner similar to the copper. The annealed sample was heated in a high vacuum at 460°C for 18 hours.

The samples used for specific-heat measurements were of the following masses: Hard-drawn copper, 595.1 grams; annealed copper, 603.9 grams; hard-drawn aluminum, 180.5 grams; annealed aluminum, 175.2 grams. The experimental results are shown in Tables III to VI, where the specific-heat values are given in 15° calories, with 4.184 as the conversion factor, joules to calories.

To compare the results of the measurements on the hard-drawn with the annealed samples, each of the authors has independently plotted the original experimental points, drawn suitable smooth curves through them and compared interpolated common temperature results as read

TABLE III. *Specific heat of hard-drawn copper at low temperatures.*

T°K	C _p per g-atom	T°K	C _p per g-atom
54.14	1.734	153.5	5.031
56.72	1.853	190.3	5.314
60.18	2.102	213.4	5.508
69.63	2.619	240.4	5.636
83.23	3.198	261.0	5.718
101.5	3.886	279.3	5.772
126.3	4.509	294.3	5.829

TABLE IV. *Specific heat of annealed copper at low temperatures.*

T°K	C _p per g-atom	T°K	C _p per g-atom
53.29	1.728	152.8	4.952
57.72	1.952	188.2	5.281
60.56	2.127	209.6	5.481
72.29	2.732	241.7	5.644
84.19	3.210	267.5	5.749
99.20	3.809	288.1	5.792
123.1	4.444	291.9	5.805
		293.0	5.802

⁷ Anderson, J. Am. Chem. Soc. 52, 2296, 2712 (1930).

TABLE V. *Specific heat of hard-drawn aluminum at low temperatures.*

$T^{\circ}\text{K}$	C_p per g-atom	$T^{\circ}\text{K}$	C_p per g-atom
56.18	1.177	126.5	3.886
59.60	1.368	141.7	4.247
63.86	1.562	163.4	4.637
75.44	2.092	185.0	4.913
79.99	2.296	200.4	5.105
84.45	2.483	219.6	5.298
90.24	2.722	241.1	5.452
92.85	2.810	257.4	5.537
100.6	3.104	272.8	5.633
112.5	3.494	290.6	5.729

TABLE VI. *Specific heat of annealed aluminum at low temperatures.*

$T^{\circ}\text{K}$	C_p per g-atom	$T^{\circ}\text{K}$	C_p per g-atom
54.80	1.129	164.2	4.647
58.42	1.289	186.2	4.932
61.84	1.472	199.4	5.100
69.99	1.856	218.9	5.307
83.96	2.457	243.8	5.486
97.68	2.994	257.5	5.558
112.4	3.533	278.9	5.698
124.6	3.849	296.3	5.741
141.0	4.239		

from these curves. Thus it was found that the mean algebraic difference between hard-drawn and annealed copper was -0.001 calorie/degree/gram-atom, with an average deviation of the mean ignoring the algebraic sign of the difference of 0.011. In the case of aluminum the mean algebraic difference was -0.006 , with an average deviation of 0.009 from the mean.

Further, low temperature specific-heat measurements recently have been made in the University of California laboratories, under the direction of Professor Giauque, of single crystals of copper and aluminum; we have compared our results with these at the same temperatures as in comparing differences, with the use of Meads' interpolation of his own data.⁸ To complete the picture, we have further calculated the average deviation of the points experimentally determined from the smoothed curves drawn for our

⁸ Meads, P. F., Ph.D. Thesis, University of California, 1932.

TABLE VII. *Average deviations of specific heats 50–290°K calorie/degree/gram-atom.*

Material	Form	Average deviation of orig. determinations from smoothed curve	Average differences of C_p between points at 13 interpolated temperatures, 50° to 290°K
Copper	Single crystal		+0.020
	Hard-drawn	0.009	— .011
Aluminum	Annealed	.016	+ .034
	Single crystal		— .009
	Hard-drawn	.006	
	Annealed	.010	

own results. All these figures are summarized in Table VII.

These comparisons leave no question as to the absence of detectable effect on heat content as *directly measurable* entropy due to the cold working of copper and aluminum, since the differences observed between cold-worked and annealed samples are of the same magnitude as the uncertainty of the original measurements. Furthermore, it is noted that the differences between our results and Meads' for single crystals are of the opposite sign from those expected if cold working increased the "randomness" of the metal atoms, in that the single crystal had slightly higher heat contents at the same temperature.

We shall not discuss here the considerable number of references in the literature purporting to show the effect of mechanical working upon the specific heat of metals but shall only refer to the fact that our results confirm those of Eucken and Werth⁹ on copper and shall point out further that the relative accuracy of the measurements reported above is on the average better than 0.2 percent. In comparing our results with those of Meads' on single crystals, the specific-heat values near liquid-air temperatures are practically identical and only in the higher temperature ranges does an average difference of about $\frac{1}{2}$ percent occur. This laboratory is on the same temperature scale as that of Professor Giauque but a slight difference in method of applying

⁹ A. Eucken, and H. Werth, Zeits. anorg. Chemie **188**, 152 (1930).

temperature gradient and cooling-rate corrections in the two laboratories is probably sufficient to account for the differences observed in the upper ranges of the experimental measurements.

PART III. COMPARISON OF WORK AND HEAT IN A WIRE-DRAWING PROCESS

It seems obvious from the above that if any difference of entropy exists in pure metals resulting from crystal size or mechanical work it is not detectable with the precision of measurements now obtainable and if it exists at all must come in as "zero-point" difference. Aside from this, it was apparent that even if the entropy change were strictly zero in going from single crystals to annealed or cold-worked wires, a change of heat content still might be entirely ascribable to a change of free energy. Further, it is experimentally impracticable to determine the possible difference of heat content of such a metal as aluminum in various conditions by heat-of-solution experiments. If a gram-atom is dissolved in HCl, some 127,000 calories are evolved, in which the experimental problem of finding the looked-for quantities of perhaps less than 100 calories difference would be nearly insuperable. In a wire-drawing process, however, a drawing tension just below the ultimate strength of a No. 18 gauge wire requires work to be done at a rate of approximately 200–300 calories per gram-atom. Comparison of heat and work in such a process then offers the best possible chance of determining possible changes of heat content of a few calories magnitude, which may be associated with the severest possible cold working.

Experimental arrangements

To carry out the necessary measurements for comparing work and heat in a wire-drawing process the calorimeter used for the calcite-dissolution experiments was so modified that a bobbin of wire and die could be submerged in it and a special device was arranged for measuring the tension of the wire continuously as it was being withdrawn from the calorimeter; the resulting product of length of wire and tension furnished the required work quantity for comparison with the heat shown by the calorimeter.

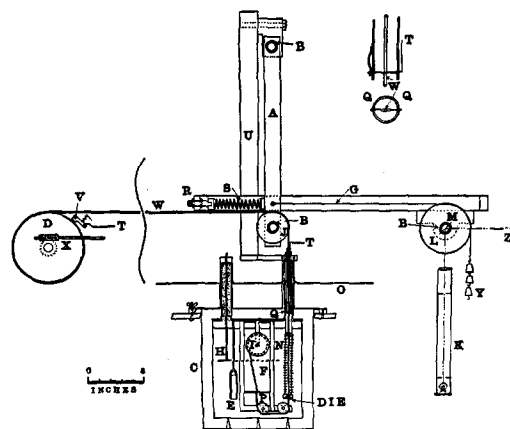


FIG. 1. Diagram of apparatus for comparing work and heat in wire drawing.

The arrangement is shown more or less schematically in Fig. 1. In calorimeter *C* the reciprocating stirrer *H* and the resistance thermometer *E* are unchanged, compared with the previously described reference. Frame *F*, of light-weight but fairly rigid brass angles, carries the bobbin *I*, containing the sample of wire to be drawn, and pulleys *P*, which serve to carry wire to the die, which is externally supported through one of the calorimeter chimneys by the structure *N*. The upper half of *N* is a thin-walled Bakelite tube, whose upper end is clamped firmly to external upright *U*, which also serves to support the tension meter. The lower half of *N* consists of a series of thin copper washers mounted on $\frac{1}{8}$ inch drill-steel rods with a driving fit. This construction serves the twofold purpose of stiffening the supporting members for the die socket while still permitting free access of calorimeter fluid to the wire and further increasing the thermal conductivity of that part of the calorimeter near the wire which is just through the die.

Even with the precautionary measures taken to assure transmittal of residual heat from the drawn wire to the calorimeter by means of *N*, it was found, after a few experiments had been performed, that the wire during drawing emerged from the bath several tenths of a degree above the calorimeter temperature. A loop thermocouple was then installed at *Q*, an enlarged section being shown at *Q-Q*. The wire drawn passes through a crossed loop of No. 36 constantan

wire held in slight tension by a small spring and the sliding contact, which is nearly frictionless, constitutes the hot junction of a thermel. Constantan lead T of $Q-Q$ goes to a cold junction in ice and the other lead is carried through the wire, being drawn as described later.

The tension-measuring device consists of pendulum-like arm A suspended near its upper end from the rigid member U and carrying a nearly frictionless sheave J at its lower end. There are ball bearings B at each end and wire W makes a right-angle turn over sheave J . Upright member U also carries a cross-member R serving to support an adjustable spring S , opposed to which is a fine-tension piano-steel wire G . G makes several turns over the nearly frictionless and well-balanced wheel L , which carries mirror M mounted on its shaft, the whole being held taut by weights Y . A beam of light from slit projector K is reflected by the mirror to a scale several meters farther along Z .

Arm A is free to swing through a small arc about its upper ball bearing. Weights Y are adjusted to correspond to about 90 percent of the tension in wire W , the remainder of the tension being taken up by the spring S . With this device a sensitivity of about 3 grams was obtained when an ordinary automobile valve spring at S and an optical beam of about 3 meters were used. Since the total tension was usually near 5000 grams the sensitivity was near 0.05 percent but the accuracy naturally was somewhat worse than this because of fluctuations of tension when the drawing was in progress.

After leaving the tension meter the wire was wound upon the accurately turned steel drum D which was rotated at a constant predetermined speed by worm drive X . A revolution counter and indicator, not shown in the drawing, recorded the revolutions of D from which the length of wire was calculated from the accurately measured diameters of drum and wire. The accuracy of determinations of wire length by this method was checked several times by actual measurement of wire on the drum and found to be within 0.1 percent.

A contactor, V , carried off the thermel lead corresponding to the couple whose hot junction was at Q . This contactor and its electrical connection T were of the identical metal as the

wire, that is, aluminum when aluminum wire was drawn and copper for the copper-wire experiments. Lead T was carried to the ice bath for the cold junction connection.

Oil thermostat O , in which the calorimeter jacket was submerged, was maintained at a constant temperature near 25°C, with a variation of not more than 0.002° throughout the experiment.

The question of calorimetric fluid, which had also to serve as a lubricant for the die, was very troublesome at the beginning of the experiments. A light lubricating oil was found to have such low thermal conductivity and low fluidity that a lag of 20 minutes was observed in reaching thermal equilibrium. Kerosene was next tried and found to have a thermal lag of only 3 minutes but the die was not lubricated and the wire badly cut in drawing. Without efficient lubrication the tension meter fluctuated violently. Several experiments were performed with the wire on bobbin I coated with beeswax and with the use of a saturated solution of beeswax in kerosene as the calorimetric fluid. This adequately lubricated the die and had a low initial thermal lag but gave rise to secondary thermal effects, after a drawing experiment was concluded which were finally shown to be due to slow saturation of the kerosene with beeswax. Because the temperature coefficient of solubility of beeswax in kerosene is enormous a temperature rise of only a few tenths of a degree caused anomalies of 50 calories or more. We finally used kerosene containing as lubricant 10 percent of a soluble sulphurized lubricant, such as is used commercially for lubricating screw-cutting dies in automatic machinery. This liquid had adequate lubricating qualities and a thermal lag of only about 4 minutes and was free from detectable thermal after-effects. It had, however, a rather high coefficient of change of specific heat with temperature (2 percent per degree), which necessitated a correction in calculating results.

Experimental procedure—calorimetric

The heat capacity of calorimeter and contents was determined before and after each wire-drawing experiment. An accurately calibrated manganin heater (not shown in the drawing) was used for this purpose and current was

measured with a White double potentiometer and timed with a calibrated stop watch. Resistance, e.m.f., and time standards were checked at appropriate intervals to insure no systematic error. The heating current was adjusted to simulate the normal temperature rise during the drawing process, with a total temperature rise of about 0.3° which was measurable by the resistance thermometer used to a relative accuracy of about 0.0002° . The mean temperature of the initial heat-capacity determination was near 24.5°C and of the final near 25.5°C .

The actual measurement of heat developed usually occupied about 2 hours, the temperature rising from near 24.7 to approximately 25.0° . In calculation of the heat evolved the heat capacity of the calorimeter was corrected for one-half of the heat content of the wire withdrawn and to the mean temperature during the drawing process.

Tension measurements. Weights Y were so adjusted during each experiment that a deflection of 20 cm of the light spot opposite Z was secured. This usually allowed for any slight variation in the tension without going off scale. The position of the spot was read every minute during the drawing time. Since calibration of the tension meter showed almost exactly a linear relationship between tension and deflection, the simple average of these readings was taken as representing the work-tension.

Calibration of the tension meter was repeated after every experiment. It consisted of replacing wire W with a fine piano-steel wire similar to G but fastened at the normal die position. A ball-bearing pulley was substituted for drum D , care being taken that its top tangent was aligned accurately with the normal position of W and a system of weights of known mass, similar to Y , suspended from it to give the same position of the light spot as the average during the draw.

Length of wire. Drum D and the wire were measured with good micrometer calipers and the length of wire was calculated upon the assumption that the length was the number of turns times the circumference of a circle, with diameter equal to the sum of the drum plus 1 wire thickness. This was found to check closely with a number of actual measurements of wire removed from the drum.

Corrections. As has been stated, it was found that the wire leaving the calorimeter, even with the slow rate of withdrawal of 25 meters per hour, was several tenths of a degree above the bath temperature. The constantan-aluminum or constantan-copper thermel at Q reached a steady state intermediate between calorimeter bath and outside temperature before drawing, under static conditions. When the drawing started, the temperature at Q rose for some 8 to 10 minutes, then showed only a slight change corresponding to the drift of the calorimeter or surrounding temperatures. It was substantially at a steady state. It was assumed that this temperature increase represented the true excess of heat of the wire with respect to the bath. The motion of the wire obviously was so slow as not to affect appreciably the heat flow in the vertical section of wire which controlled the actual temperature at Q . The product of this temperature rise by the specific heat of the wire actually withdrawn, as determined by the average of readings taken every 10 minutes during an experiment, was added to the calorimetric heat.

Tension-meter corrections. As the wire passes over sheave J of the tension meter it is stretched by the curvature and at the same time a certain amount of work is done external to the calorimeter which must be accounted for. The observed length of wire on the drum was then correctable by the stretch and the observed tension under static conditions by the equivalent friction at J . The actual friction of J was negligible, the apparent friction being due to bending the wire about the curvature.

These two corrections were evaluated for aluminum and copper wires by removing arm A and using sheave J as the pulley of an Atwoods machine in the usual way. The elongation and equivalent friction were found to be a function of the tension but nearly independent of the speed at which the wire passed over J . The results of such a calibration for each metal are given in Table VIII. The accuracy of the elongation determinations was about 2 percent and of the equivalent friction about 5 percent, the chief source of inaccuracy being the change of dimensions and properties of the metal during each pass over the sheave. Since the elongation correction is itself about 1 percent of the total

TABLE VIII. *Corrections for tension meter, for wire 0.0370 inch diam., 2-inch sheave.*

Measured tension, kg	Aluminum		Copper	
	Elongation, percent per pass	Apparent friction, kg	Elongation, percent per pass	Apparent friction, kg
3.0	0.615	0.114	0.300	0.169
4.0	0.982	0.120	0.392	0.176
5.0	1.465	0.132	0.488	0.186
6.0	2.295	0.212	0.590	0.201
7.0	3.45	0.320	0.715	0.218
8.0	(beyond ultimate strength)		0.855	0.243
9.0			1.060	0.282
10.0			1.395	0.354
11.0			1.980	0.489

length and the friction correction about 2 to 3 percent of the total tension the errors involved in the determinations of the corrections clearly are negligible compared with the totals involved.

Experimental results

In Tables IX and X the final results of the comparisons of work and heat in the drawing of aluminum and copper, respectively, are recorded. Details of calorimetric data and of the various items of correction mentioned above are not shown since details of procedure and accuracy involved by them have been discussed above.

The first four experiments of Table IX were made with beeswax as lubricant and, as previously explained, the thermal after-effects caused by this render these results somewhat erratic. The correction for sensible heat removed by the wire was not applied until after experiment 3, at which time the slip-thermel was introduced into the apparatus. The magnitude of the corrections introducible in the first three experiments, judged by the succeeding experiments, would be from 10 to 20 calories additional to the heat item.

In experiments 5 to 8 the wire used, stated by the manufacturer to be soft drawn, was not re-annealed after winding upon bobbin *I*. Probably the result of experiment 5 should be rejected in the average of these tests, but application of Chauvenet's criterion hardly seemed justifiable. At any rate, the average discrepancy between work and heat is less than the average deviation of the mean of the results and it must be concluded that no evidence of energy "storage" is disclosed by these tests, the accuracy probably being in the neighborhood of 1.0 percent; in other words, on the average at least 99 percent of the work energy appeared as heat.

It was suspected, however, that even if the original wire were truly soft drawn merely

TABLE IX. *Comparison of work and heat in drawing aluminum.*

Exp. No.	Lubricant	Condition of wire	Correction for heat of wire withdrawn	Corrected tension, kg	Corrected length, meters	Work, cal.	Heat, cal.	Discrepancy, $W-H$	Discrepancy per g-at. Al
1	BW	S.D.	U	4.494	53.00	557.6	512.6	+45.0	+12.4
2	BW	S.D.	U	6.434	43.93	661.9	665.8	- 3.9	- 1.3
3	BW(s)	S.D.	U	5.403	54.66	691.5	655.0	36.5	+ 9.6
4	BW(s)	S.D.	C	4.210	54.36	535.7	530.1	+ 5.6	+ 1.5
5	Sol	S.D.	C	5.496	51.50	663.0	644.5	+18.5	+ 5.2
6	Sol	S.D.	C	4.615	51.86	560.4	565.4	- 5.0	- 1.4
7	Sol	S.D.	C	5.161	52.37	632.9	638.9	- 6.0	- 1.7
8	Sol	S.D.	C	4.335	48.86	496.0	490.4	+ 5.6	+ 1.7
Average 5-8 = + 0.9 ± 2.5									
9	Sol	RA	C	4.580	51.87	556.3	537.1	+19.2	+ 5.4
10	Sol	RA	C	5.335	51.26	640.4	623.1	+17.3	+ 4.9
11	Sol	RA	C	5.305	51.27	636.9	628.9	+ 8.0	+ 2.3
12	Sol	RA	C	5.578	49.41	645.4	631.9	+13.5	+ 3.9
Average 9-12 = + 4.1 ± 1.0									

BW, wire coated with beeswax; BW(s), wire coated with beeswax used in sat. sol. beeswax in kerosene; Sol, kerosene +10 percent sulphurized oil; S.D., soft drawn; RA, re-annealed; U, uncorrected; C, corrected.

TABLE X. Comparison of work and heat in drawing copper.

Exp. No.	Corrected tension, kg	Corrected length, meters	Work, cal.	Heat, cal.	Discrepancy, $W-H$	Discrepancy, per/g-at. Cu	Remarks
1	10.724	46.69	1172.4	1096.7	75.7	16.1	Wire A
2	5.054	48.18	570.2	498.1	72.1	15.2	Wire A, die-polished
3	4.866	48.40	574.8	513.8	61.0	12.8	Wire A
4	3.392	48.61	386.2	362.6	23.6	(5.0)	Wire A, wire-polished
5	6.014	35.92	505.9	453.3	52.6	14.8	Wire A
6	7.722	49.76	899.7	825.6	74.1	15.0	Wire B
7	6.608	49.49	765.7	694.5	71.2	14.6	Wire B
Average omitting (4) 14.8 ± 0.7							Best results

winding it on bobbin *I* would entail sufficient cold working to cause an element of uncertainty in these results. In the four succeeding experiments, 9 to 12, the wire, after being wound upon the bobbin, was annealed carefully in a high vacuum at 350–400°C for 12 hours. In these tests, which are the best of those on aluminum, more concordant results were obtained and we believe that the discrepancy between work and heat of 4.1 calories per gram-atom is real. This figure corresponds to the statement that approximately 98 percent of the work energy appears as heat.

In the experiments on copper, the results of which are shown in Table X, tests 1 to 4 suffered somewhat from rather sharp fluctuations of the tension required for drawing. All the samples in Table X were wire which had been annealed on the bobbin at 350–400°C for 12 hours and it was shown that the fluctuations were due to unevenness of the wire and burring at the die. Various expedients of polishing the die or wire were tried and these resulted in the considerable variations of drawing tension shown. Tests 5 to 7 were made on wires carefully drawn by ourselves before winding upon the bobbin and constitute the best results obtained.

In this case there can be no doubt as to the reality of a discrepancy between work and heat which averages 14.8 calories per gram-atom, so that approximately 90 percent of the work appears as heat. The results show that the discrepancy is a function of the mass of wire and, by noting the effect of tension, it seems clear that it is also practically independent of the tension, provided it exceeds a certain rather indefinite minimum of about 5 kilograms for this

size wire. In this connection it should be noted that not all of the tension is due to the die as the wire was bent 5 times in the calorimeter about the pulleys and from the bobbin; further, it was found advisable for smooth operation to have a slight friction on bobbin *I* to insure straightening of the wire before entering the die. Most of this work energy appears as cold work in the wire but a small indeterminate amount was simple friction. All is accounted for, however, since it occurs within the calorimeter can.

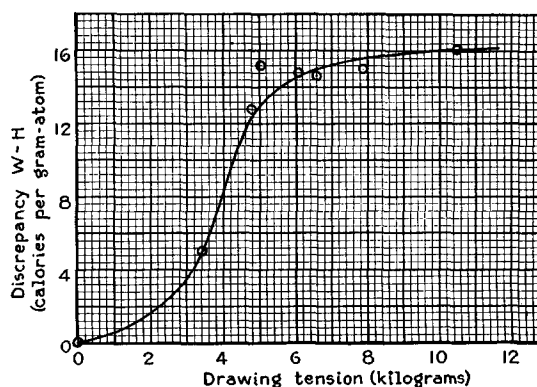


FIG. 2. Effect of tension on apparent energy storage in drawing No. 18 copper wire.

It must be true that at zero tension the discrepancy between work and heat would also be zero, whence a crude plot of discrepancy between work and heat *vs.* tension may be drawn, as in Fig. 2.

The experiments on copper probably are accurate on the average, to within 0.4 percent.

PART IV. CHANGES OF DENSITY DUE TO
COMMUNITION

It is strange that no serious attempt seems to have been made in the past to correlate density changes due to comminution with the supposed storage of energy in crystals. Compressibility β of a material is defined as $\beta = (1/v_0)dv/dp$, where v_0 is the original volume and dp the pressure increment. If it is assumed that the work energy stored in a system of crystalline particles due to comminution is the equivalent of that required to compress it to the same state, then

$$\beta v_0 \int_{p_0}^p p dp = - \int_{v_0}^v p dv = \int_0^w dw \quad (\text{work done on the system})$$

whence

$$p^2 - p_0^2 = 2w/v_0\beta$$

but $p^2 - p_0^2$ will differ but little from $(\Delta p)^2$ in the case of liquids and solids when p_0 is near 1 atmosphere and for appreciable volume changes. Then quite closely

$$-\Delta v/v_0 = (2w\beta/v_0)^{1/2} \quad \text{or} \quad w = (v_0/2\beta)(\Delta v/v_0)^2.$$

These equations should enable the density change to be calculated when the work "storage" is known, or conversely, fix the limits of possible "storage" whose measured density changes are determinable experimentally. We may, for example, calculate the expected density change based on the "surface-energy" measurements for sodium chloride of Lipsett, Johnson and Maass,¹⁰ who gave 395 ergs per sq. cm for particles of 1-micron average size, corresponding to 15.3 calories per mole. Thus for sodium chloride, with a compressibility of $43.2 \cdot 10^{-7}$ (pressure in atmospheres) and a density of 2.15, we find $\Delta v/v_0 = -0.014$, indicating that if the "surface-energy" figure is correct the density of the 1-micron crystals should be 1.4 percent greater than for large crystals, a change which certainly is easily detectable.

Considerations of this sort caused us to make precise density determinations of the various samples with which we worked. Carbon tetrachloride was used as the medium for these determinations, and the sample selected was

shown to have a density of 1.58244 at 26.00°C, which compares well with the figure 1.58248 obtained by interpolation from the data of Timmermans and Martin.¹¹ The specific-gravity bottle containing the density sample was filled in a vacuum desiccator, the tetrachloride being boiled at 25–20°C to insure elimination of occluded gas. Table XI shows the results of these determinations.

TABLE XI. *Densities of samples used, grams/cm³, vacuum basis.*

No.	Material	Form	Density A.D. of M.	Temp. of deter- mination
1	Calcite	0.8 mm particles	2.7133 ± 0.0001	25.0*
2	Calcite	0.065 mm particles	2.7131 ± 0.0001	25.0
3	Calcite	0.5 micron particles	2.6956 ± 0.0003	25.0
4	Hydrated lime	Paste	(2.078)	
3c	Calcite	0.5 micron, corrected	2.7236	
5	Copper	No. 32 wire, annealed	8.9209 ± 0.0005	21.2
6	Copper	No. 32 wire, hard-drawn	8.9140 ± 0.0002	22.0
7	Aluminum	No. 32 wire, annealed	2.7147 ± 0.0001	21.2
8	Copper	No. 32 wire, hard-drawn	2.7111 ± 0.0002	21.9

The question of the correction of the density of 0.5-micron calcite, shown in line 3 of Table XI, for the $\text{Ca}(\text{OH})_2$ and H_2O found by the analysis, was difficult. We finally hydrated some quicklime with an amount of water corresponding to the analysis of the impurity and made the rough density determination of line 4. The substance so prepared was a plastic mass that could not have uniform density and certainly was not in the same form as the film of impurity on the surface of the calcite particles, which had been dried at 105°C. However, by applying the result for the hydrated lime on the basis of additive *volumes* of impurity the maximum possible density of the fine calcite may be estimated in corrected form as given in line 3c.

These figures give for the possible change $\Delta v/v_0 = 0.0038$ in the formula derived from compressibility and if the compressibility is taken as $1.35 \cdot 10^{-6}$ we find the maximum possible energy storage to be 4.8 calories per CaCO_3 , a figure just slightly less than the experimental error of the heat-of-solution experiments. It is highly probable, however, that the density has been overcorrected by the above estimate, since the true density of the surface film of impurity must be greater than the figure obtained by

¹⁰ Lipsett, Johnson and Maass, J. Am. Chem. Soc. **49**, 1948 (1927).

¹¹ Timmermans and Martin, J. chim. Phys. **23**, 733 (1926).

measurement of the hydrated lime-water mixture; if the true figure were obtainable, a lower corrected density than 2.7236 for 0.5-micron material would result and the possible energy storage would then be less than 4.8 calories.¹²

In the case of the metallic wires, the hard-drawn material is less dense than the annealed and presumably recrystallized metal. This makes $\Delta v/v_0$ of the wrong sign for compression of the crystal lattice. However, it is obvious from the second form of the derived equation that energy can be stored by compression or expansion and we have therefore calculated the maximum storage of energy due to lattice distortion in a similar manner. Using $7.42 \cdot 10^{-7}$ and $13.85 \cdot 10^{-7}$ for the compressibilities of copper and aluminum when the pressure is in atmospheres, we find by application of the second form of the equation that the maximum storage of energy which can be accounted for on the basis of observed densities is 0.06 cal./g-atom for copper, and 0.15 cal./g-atom for aluminum, figures which are much less than the observed discrepancies 14.8 and 4.1 cal. in the wire-drawing experiments, and are indeed beyond the limit of conceivable accuracy of measurement by the methods obviously available. If the density of wires of this size is uniform throughout the cross section, the conclusion that the discrepancies found cannot represent energy stored by lattice distortion of pure crystalline metals seems valid. In cold-worked sections of larger size there seems to be unmistakable evidence in the literature for some

variation in density, but definite proof concerning the quantitative relationships involved must await further experimental work. It seems improbable that a sufficient variation in density can be present in wires of this size adequate to explain the observed energy discrepancies.

PART V. MEANING OF RESULTS

If the direct results of our experimental work are summarized, the conclusions would be as follows:

1. No evidence for increase of intrinsic energy of calcite due to comminution to 0.5-micron size could be found by heat-of-solution experiments; if such increase exists, it is less than 0.2 percent of the heat of solution and probably outside the limits of direct experimental disclosure.

2. Previous measurements purporting to show a considerable and readily detectable increase of intrinsic energy by this method are in error because of failure to correct for the change of composition produced in the sample by comminution.

3. We suspect, but have not proved, that previous measurements on other materials, by heat-of-solution methods, may be in error for the same reason and we would not accept such measurements unless adequate analytic evidence were adduced to prove that uncontaminated samples of very fine particles had been or can be produced.

4. It has been shown, to us, conclusively, that single crystals and hard-drawn and annealed specimens of copper and aluminum do not show differences of measurable entropy at 298°K greater than a few tenths percent, representing the accuracy of measurement, and that any actual difference must be accounted for by zero-point entropy.

5. Comparison of work and heat in the deformation of metallic crystals of copper and aluminum shows that only when carefully annealed samples are used can a discrepancy between work and heat be shown to exist. This discrepancy, for a given degree of cold working, is directly proportional to the mass of metal. It is not directly proportional to the degree of cold working but reaches a nearly constant value when a certain rather indefinite degree of cold work has been accomplished.

¹² The overcorrection of density and heat of solution results for fine material is explainable by the failure to use correct figures for the density and heat of solution of the adsorbed film. When lime was hydrated with the amount of water corresponding to the analysis of 0.5-micron calcite a plastic mass containing free water was formed but material of similar properties certainly did not exist at the surface of the fine calcite crystals, which had been dried at 105°C. The pseudohydrate corresponding to the analysis must exist only as an adsorbed film, as Thorvaldson and Brown showed that no hydrate of lime other than $1\text{H}_2\text{O} : 1\text{CaO}$ forms normally at 21°C. Both strontium and barium oxides, however, form octahydrated crystals with the evolution of heat when water is added to the lower hydrate forms. Hence the heat of solution of the pseudohydrate is less and its density greater than for the normal hydrate form; if correct figures could be obtained they would tend to cause greater concordance between the corrected figures for fine calcite compared to coarse.

An important conclusion of our experimental work is that any rigorous demonstration of measured differences in the properties of pure crystalline materials in different states of subdivision must prove that no change of homogeneity has accompanied the comminution. In the case of the calcite we have direct proof that the supposed increase of intrinsic energy was due to a change in composition rather than distortion of the crystal lattice. In the case of the deformation of the metallic crystals of copper and aluminum the evidence is less direct and not obtainable by chemical analysis but the hypothesis that the process of cold working produces a change of state of *part* of the metal is the only one fitting the experimental facts, including the density relations.

A qualitative experiment which we performed seems illuminating. In connection with the use of the slip-thermel for measuring the loss of sensible heat in the wire withdrawn from the calorimeter, measurements were made to show that the tension in the wire constituting part of the thermel did not produce appreciable errors. Samples of the two wires (copper and aluminum) were placed upon a frame in such a manner as to constitute a thermel, strained copper *vs.* annealed copper, and strained aluminum *vs.* annealed aluminum. The frame work was partly immersed in liquid air and tension applied nearly to the rupture point of the wire, the thermal e.m.f. being noted. A typical test on aluminum was as follows: 0 tension, 3.50 microvolts e.m.f., all due to parasitic e.m.f.'s. When the tension was increased gradually to 5.5 kg the e.m.f. was $1.90\mu\text{v}$, that is, the e.m.f. due to tension was $1.60\mu\text{v}$. When the strain was removed the e.m.f. returned to $3.22\mu\text{v}$; brought back to 5.5 kg the thermel read $1.88\mu\text{v}$ and back to zero tension, $3.22\mu\text{v}$. In the case of copper, 0 tension, $-0.60\mu\text{v}$, 8.0 kg tension $+0.70\mu\text{v}$, back to zero tension $-0.70\mu\text{v}$.

The thermal e.m.f. due to strain was negligible as far as the slip-thermel readings were concerned, since practically constant tension was maintained during the use of the couple. Present interest centers in the fact that when the strain was removed the residual effect was only $0.28\mu\text{v}$ for aluminum and $0.10\mu\text{v}$ for copper in the first test and after the first straining later trials

showed no further effect if the original stress was not passed in succeeding tests.

From this experiment it seemed probable that if strictly pure metal were used no parasitic e.m.f.'s could be produced. We proceeded to draw a wire from spectroscopically pure zinc containing less than 0.0001 percent impurity, as the purest metal available. The wire was annealed carefully before test. The e.m.f. with zero strain was $+1.15\mu\text{v}$, with 1.0 kg tension $+0.50\mu\text{v}$, back to zero strain $+0.75\mu\text{v}$. The use of *chemically* pure metal did not eliminate the parasitic e.m.f.'s nor residual effects and since these could be due only to inhomogeneities we conclude that the inhomogeneity is *physical*. There are no allotropic forms of pure crystalline zinc, whence the inhomogeneity was either crystal orientation or due to the appearance of a form of zinc which was not crystalline and which we shall call the ω form, without specifying its nature at present. Since the original wire was carefully annealed, we ascribe the $+1.15\mu\text{v}$ parasitic e.m.f. to the effect of crystal orientation, the ω form presumably being absent because of recrystallization but we ascribe $1.15 - 0.75 = 0.40\mu\text{v}$ residual difference to the appearance of a new inhomogeneity produced by strain.

Unannealed wire of spectroscopically pure zinc is extremely brittle at liquid-air temperatures but when 0.05 percent lead was added to spectroscopically pure zinc and a new wire produced, the lead-containing wire had high ductility at liquid-air temperatures. Since it was still largely crystalline zinc, we conclude that the brittleness at this temperature is not due entirely to the properties of normal crystalline zinc but to the ω form produced. Thoroughly annealed wire (recrystallized) was brittle, because of grain growth; cast rods of spectroscopically pure zinc cannot be directly drawn, but a small amount of swaging produces ductility, so that a $\frac{1}{4}$ inch rod can be drawn after swaging to No. 32 wire without annealing and with an apparent increase of ductility. The hypothesis supposes the ductility to be due to the ω form in the spectroscopically pure metal and to lead in the inter-crystalline slip planes when the impure wire was made.

It is natural to associate the properties of the ω form produced by stresses beyond the elastic

limit on pure metallic crystals with those of an amorphous metal or supercooled liquid, a theory advanced by Beilby¹³ but severely criticized by physical metallurgists.¹⁴ Our tests on the discrepancy between work and heat in drawing enable us to make approximate estimates of the amount of ω -phase metal by two independent methods.

Consider first the densities of hard-drawn and annealed copper and aluminum. From the measurements of Bornemann and Sauerwald¹⁵ the density of liquid copper at the melting point is 7.982 and that of solid copper at the same temperature 8.350. According to Hidnert¹⁶ the thermal expansiveness of hard-drawn copper changes less rapidly with the temperature than the same copper annealed. Therefore the difference of density of pure crystalline copper *vs.* the ω form at room temperature is concluded to be greater than $8.350 - 7.982 = 0.368$ and less than $8.920 - 7.982 = 0.938$. Then the percentage of ω form in the hard-drawn wire used by us is less than $(8.9209 - 8.9140)/0.368 = 1.9$ percent, and greater than $(8.9209 - 8.9140)/0.938 = 0.74$ percent.

Similarly, in the case of aluminum, Bornemann and Sauerwald give data leading to the density 2.397 for liquid metal at the melting point and 2.558 for the solid, whence the observed density differences lead to the conclusion that the ω phase present is less than 2.2 percent and more than 1.1 percent.

As an alternative method of calculating the amount of the ω phase, comparison may be made between the heat of fusion for the metal in question and the differences of heat and work observed in the drawing experiments. The heats of fusion at the melting point of copper and aluminum are 3110 and 2550 calories; corrected to ordinary temperatures in a conventional

manner and assuming that the specific heat of the supercooled liquid is constant, the heats at 25°C would be approximately 2300 for copper and 2400 for aluminum, whence the calculated content of the ω phase is $14.8/2300 = 0.64$ percent for copper and $4.1/2400 = 0.17$ percent for aluminum.

Comparison of these results shows that while the calculated content of the ω phase is of the same general order of magnitude by the two methods, the figures can scarcely be said to confirm satisfactorily the hypothesis that the ω phase is essentially supercooled liquid. It should be noted, however, that the density results were obtained on finer wire (No. 32) than the energy discrepancy (No. 18 wire) and it may be supposed that the amount of the ω phase bears some nearly inverse functional relationship to the size of crystal particles formed by the drawing process.

In conclusion, we can only describe our work as having failed to disclose, by careful measurements of the energy changes in comminution, any change in energy content of certain crystal lattices due to decrease of particle or crystal size which is not ascribable to lack of homogeneity of small crystals. Such calculations of surface energy as those of Born and Stern¹⁷ or their later modifications by Lennard-Jones and Dent¹⁸ or by Dent¹⁹ on the surface energies of alkali halide crystals, seem to make the implicit assumptions that crystals may exist without other inhomogeneity than some rather minor distortion of the crystal boundary, or, its surface ions, but practically it remains to be proved that such a situation is either common or possible in nature. If chemical inhomogeneity (adsorbed films) or physical inhomogeneity (polymorphic change) is, as may be supposed, the inevitable concomitant of decrease of particle size, such calculations seem of little value in describing the properties of actual materials.

¹³ Beilby, *Aggregation and Flow of Solids*, Macmillan Company, London (1921).

¹⁴ Dean and Gregg, *General Theory of Metallic Hardening*, Pamphlet of Western Electric Co., Feb., 1927.

¹⁵ Bornemann and Sauerwald, *Zeits. f. Metallkunde* **14**, 155 (1922).

¹⁶ Hidnert, *Bur. Standards Sci. Papers* No. 410 (1921).

¹⁷ Born and Stern, *Sitz. Preus. Akad.* **48**, 901 (1919).

¹⁸ Lennard-Jones and Dent, *Proc. Roy. Soc. A* **121**, 247 (1928).

¹⁹ Dent, *Phil. Mag.* (7) **8**, 530 (1929).