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THE ROLE OF CALORIMETRY IN THE THERMODYNAMICS OF METALS AND ALLOYS

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Ralph Hultgren

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## THE ROLE OF CALORIMETRY IN THE THERMODYNAMICS OF METALS AND ALLOYS

Ralph Hultgren

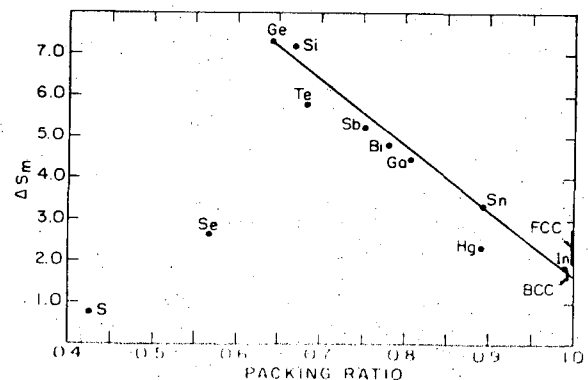
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 Department of Materials Science and Engineering, College of Engineering  
 University of California, Berkeley, California

There is an energy associated with practically every physical or chemical change of a material. Because enthalpy (or heat) differs only a little from energy, and because it usually is much more easily measured, let us hereafter discuss enthalpy.

In some cases the enthalpy is the quantity of determining importance, as for example, the heat of combustion of a fuel. We will consider, however, the enthalpy as a measure of stability of alloy phases, and as an important quantity in understanding the nature of physical and chemical changes. For example, the enthalpy of formation of an alloy from its elements is a direct measure of the energy of bonding between atoms of an alloy minus the energy of bonding between the same atoms in the elementary states. These values should be important in developing a theory of the nature of the metallic bond.

For another example, the enthalpy of melting divided by the melting temperature is the entropy of melting, a measure of the disorganization introduced when a solid melts to form a liquid. Slide 1 shows that for many metals there is a correlation between the closeness of packing of atoms in the solid state and the entropy of melting. The closest packed elements most resemble the liquids and have  $\Delta S_m \sim 2.0$ ; the less closely packed the crystals are, the less they resemble the liquids; entropies trend upward to 7. Such large entropies of melting cast doubt

on theories of the liquid state where liquids are regarded as consisting of fragments of the solid crystal lattice. The exceptional elements, S and Se deviate obviously because the liquid does resemble the solid.



Usually, enthalpies are most accurately measured by calorimetry.

We can divide the enthalpies desired into three classes:

SLIDE 2

- (1) Low-Temperature Heat Capacities (below 298°K)
- (2) High-Temperature Heat Capacities and Heat Contents
- (3) Enthalpies of Chemical Reaction (Enthalpies of Formation).

Thermodynamics of alloys has, until recently, been a neglected subject.

Chemists doing thermodynamic measurements did not understand and dis-trusted alloys; metallurgists understood alloys, but did not do thermodynamics.

Slide 3 shows the trends through the years to its present popularity.

SLIDE 3

Number of Binary Systems Reported per Year

Year	Cp<298°K	Cp>298°K	ΔH	Total
before 1929	0	7	30	37
1930-1939	0.5/year	5.3/year	11.3/year	17.1/year
1940-1949	1.5/year	3.2/year	2.0/year	6.7/year
1950-1959	6.2/year	8.8/year	18.2/year	33.2/year
1960	21	20	67	108
1961	29	24	58	111
1962	36	23	59	118
1963	58	25	37	120
1964				

Low-Temperature Heat Capacities. This is the area in which measurements are increasing the fastest. Moreover, recent measurements are mostly at temperatures below 4°K, even below 1°K, for reasons which will become apparent. Measurements at low temperatures are designed to determine one or more of the following:

SLIDE 4

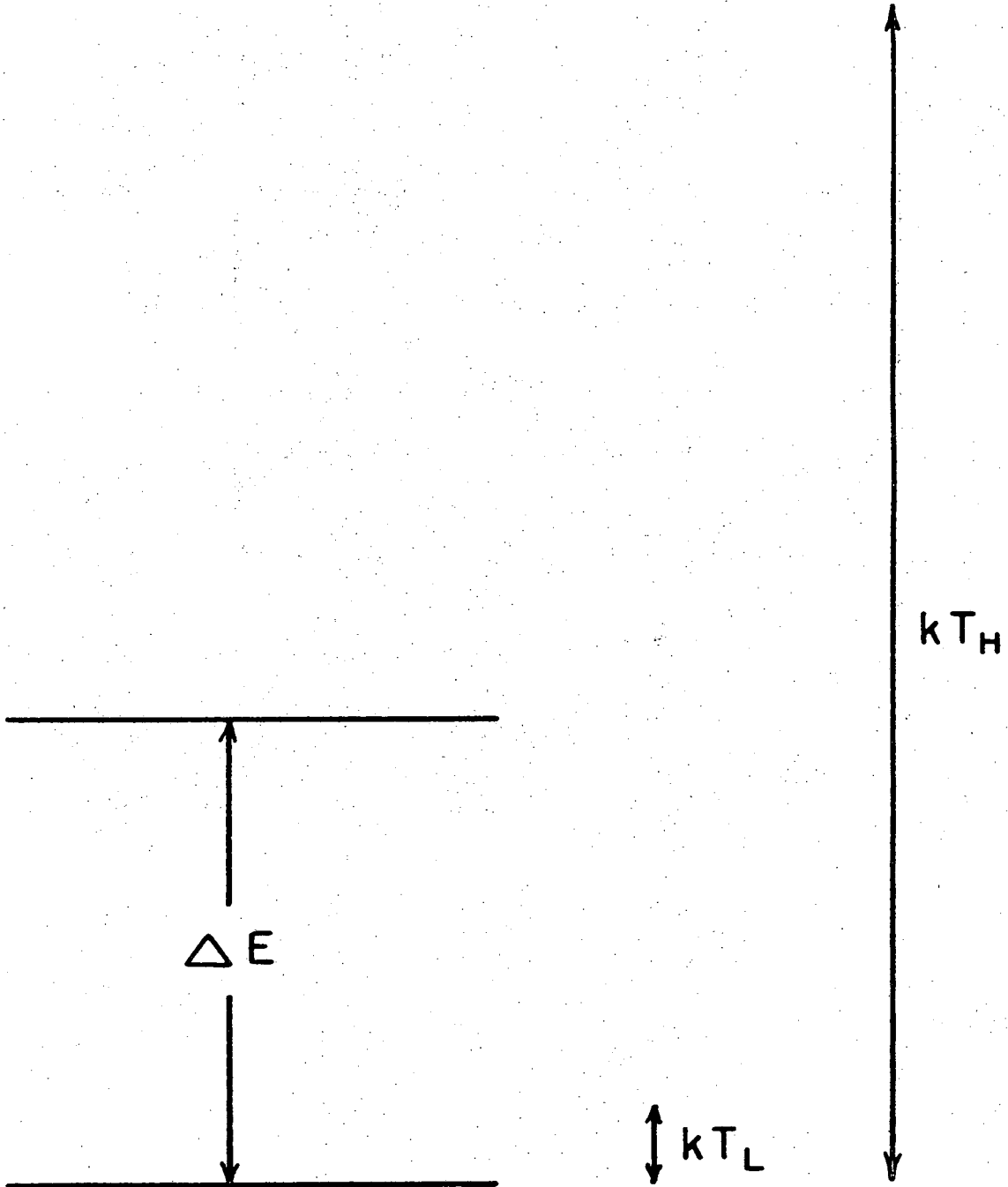
- (1) Nuclear-electronic interaction contributions to Cp
- (2) Electronic excitation contributions to Cp

- (3) Atomic vibrational contributions to  $C_p$
- (4) Absolute entropies.

Before going into this in detail, let us consider some elementary facts about quantum theory. As you know, Dulong and Petit observed in 1819 that heat capacities of all solids near room temperatures was approximately 6.2 cal/g-atom. This was eventually explained by classical statistical mechanics as due to the energy of vibration of atoms in the space lattice. Each atom had 6 degrees of freedom; 3 in potential energy and 3 in kinetic energy. Since with each degree of freedom there was associated an energy of  $\frac{1}{2}kT$ , each atom had a vibrational energy,  $E = 3kT$ , and the energy of a g-atom was  $3RT$ . Hence  $C_v = 3R = 5.96$  cal/g-atom. Adding the small dilational term,  $C_p - C_v$ , brought the  $C_p$  up to Dulong and Petit's value. However, at low temperatures,  $C_p$  falls off, becoming 0 at  $0^\circ K$ . The reason for this remains a mystery until Einstein explained it on the basis of the quantum theory in 1907.

SLIDE 5

Let us consider for simplicity a substance with only two energy levels with an energy  $\Delta E$  between them. At  $0^\circ K$ , a material will be at the lowest possible energy level. It can absorb energy from its surroundings only in quanta of the size,  $E$ . Thermal energy of the surroundings are in quanta of average size approximating  $kT$ . However, there will be a Boltzmann distribution and some of the quanta will be considerably larger. Even when  $kT$  is much smaller than  $E$ , there will be a small  $C_p$ , but obviously, it will approach 0 at  $0^\circ K$ . A quantum at an excited level, will soon be given off to the surroundings. However, using Boltzmann statistics, the number of quanta at the excited level can be calculated for any temperature.



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For  $T$  very small there will be very few quanta at the higher level; for  $T$  large, the levels will be equally populated.

For each population, the entropy can be calculated;  $S = k \ln W$  where  $W$  is the number of complexions. For  $N$  quanta equally populated (high  $T$ ),  $S = R \ln 2$ . From entropy as a function of  $T$ ,  $C_p$  can be calculated;

SLIDE 6  $C_p = \int T dS/dT$ . For two levels, the result of Slide 6 is found. Of course, with vibrational quanta, there are more than 2 levels, the entropy and  $C_p$  go on increasing; the  $C_p$  eventually reaches  $3R$ .

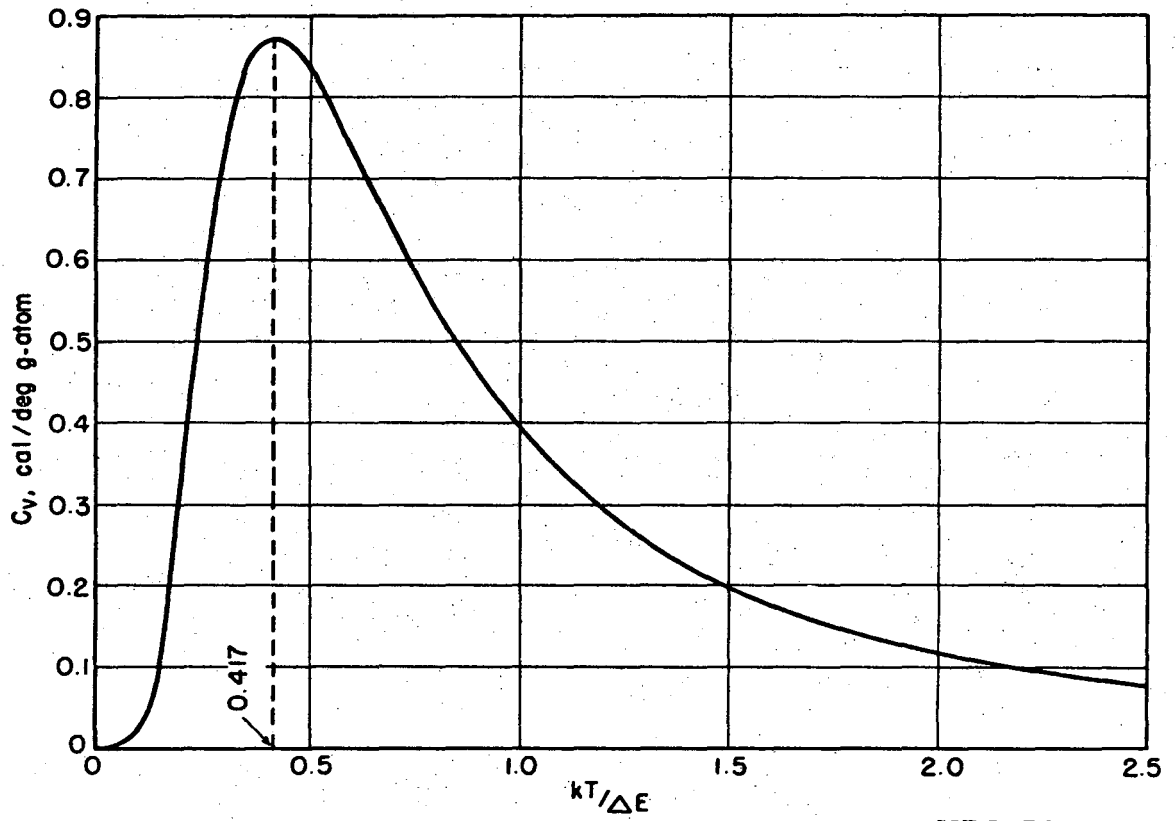
Let us now consider the information obtainable from low-temperature measurements:

(1) Nuclear-electronic interactions: The magnetic moment of the nucleus interacts with the magnetic moment of the electrons, splitting the energy levels. The split levels are so near to one another, that they are fully excited at very low temperatures. The effect of these splittings have been measured for only a few elements and for no alloys. The  $C_p$  anomaly is usually found only at a fraction of a degree Kelvin and may have disappeared at  $1^\circ\text{K}$ , hence it is not detected unless measurements have been carried out at these extremely low temperatures; this has become possible only recently. Holmium is the most striking of these as is seen on Slide 7. Most elements show no such effect; rare earths show the most important ones but even for these many show none, others only below  $1^\circ\text{K}$ .

SLIDE 7

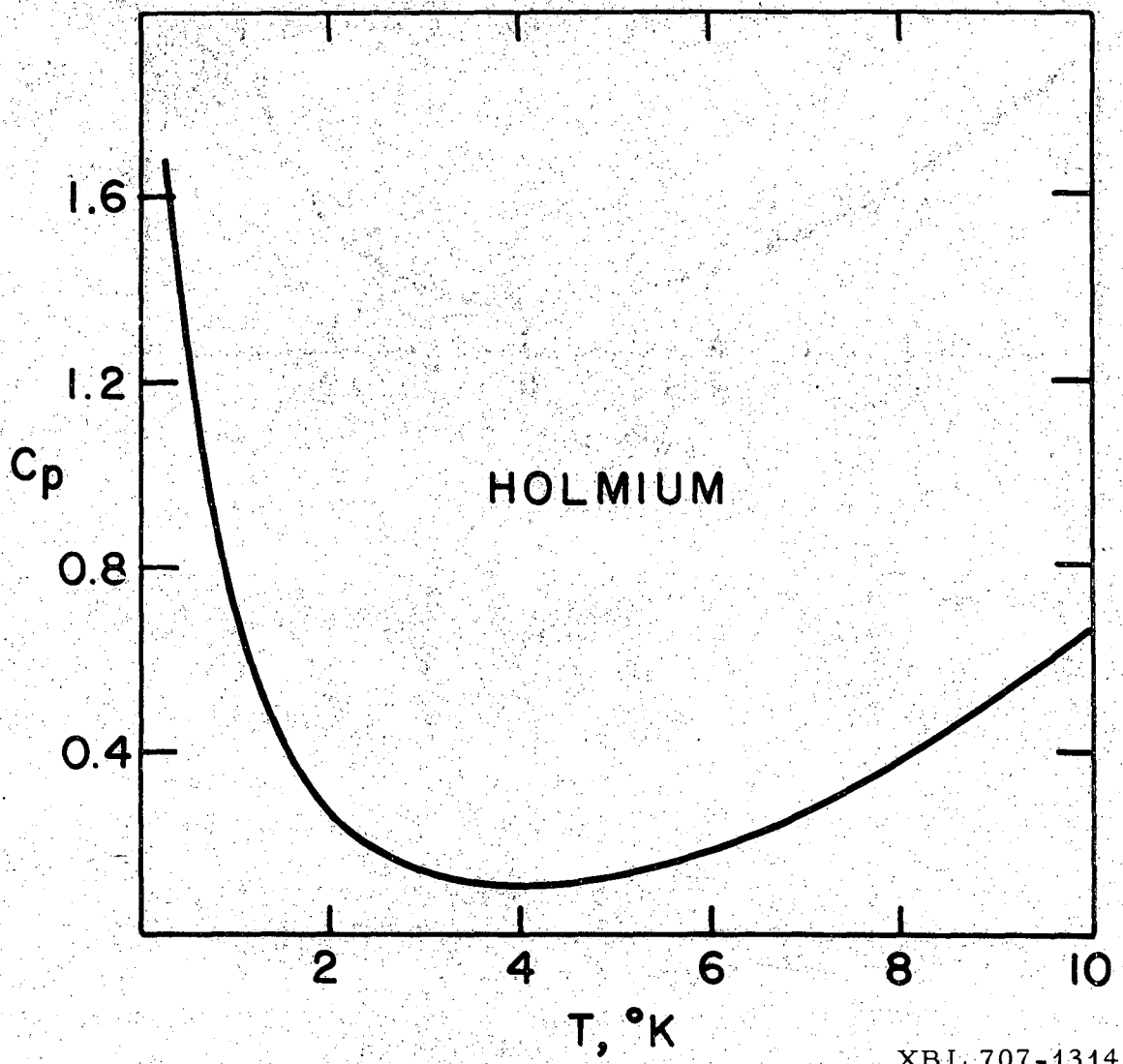
(2) Electronic Excitation. For nonmetals the first excited electronic level is high above the lowest level so electrons contribute to  $C_p$  only at high temperatures. For example, the monatomic gases of metals may serve as examples of nonmetals. The temperature where electrons contribute





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Slide 6



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SLIDE 8 appreciably to  $C_p$  are shown in Slide 8:

Lowest T for Electronic Contribution to  $C_p$  for Monatomic Gases

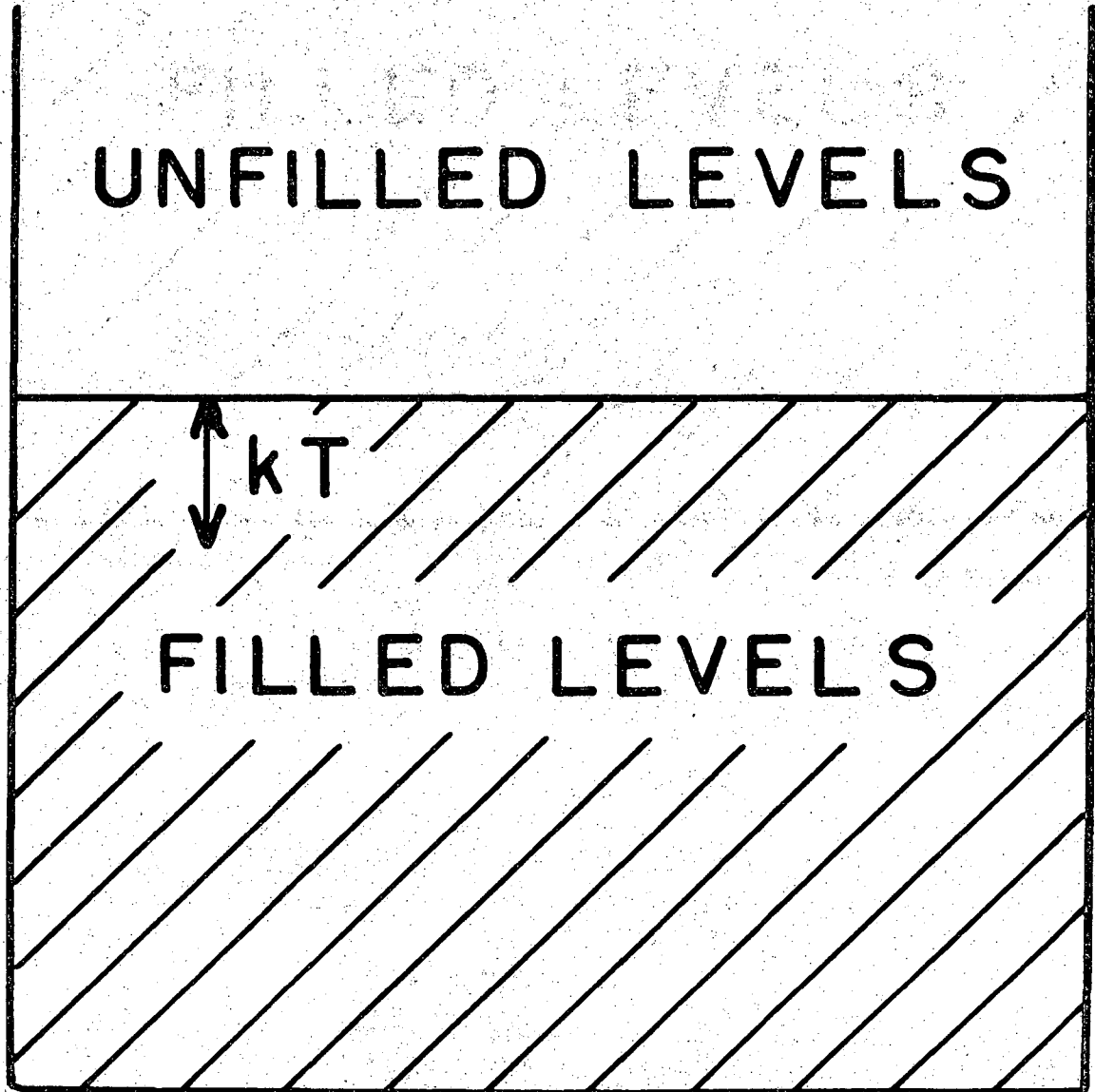
Silver	>2500°K
Aluminum	<298
Beryllium	2000
Chromium	800
Iron	298
Molybdenum	1100

For the metallic state, the situation is quite different. The bonding electrons in a metal are in closely spaced levels of a "free" electron gas. Since it is a Fermi gas, only the electrons in levels near the top contribute (Slide 9).

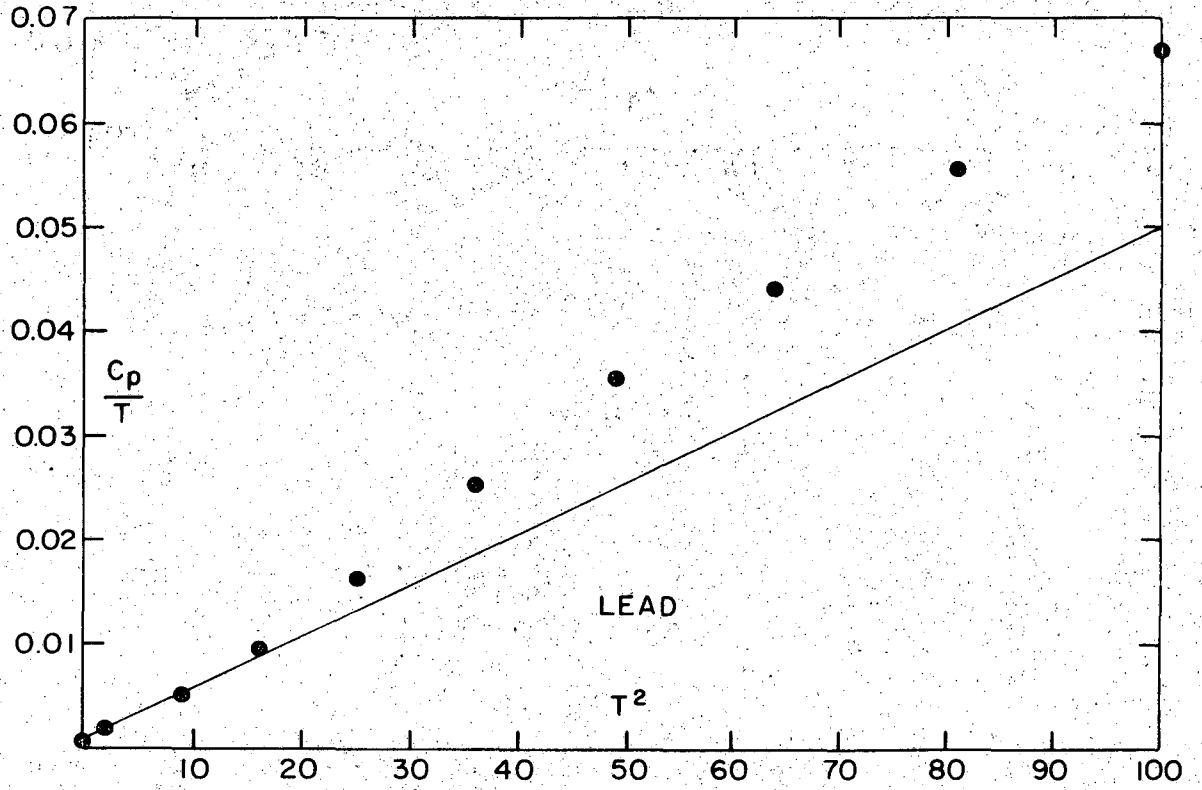
SLIDE 9 It can be shown their contribution is proportional to  $T$ , and begins very close to 0°K. In fact, near 0°K,  $C_p = \gamma T + \beta T^3$ ; the first term is the electronic term and the last is due to lattice vibration. By plotting  $C_p/T$  versus  $T^2$ , the electronic coefficient,  $\gamma$ , can be readily evaluated (Slide 10).

SLIDE 10 The magnitude of  $\gamma$  depends on the density of states; it is not proportional but increases more rapidly. However, it is objective evidence of the change of bonding during alloying and, as such, very interesting. SLIDE 11 shows in what a complex manner this may change during alloying.

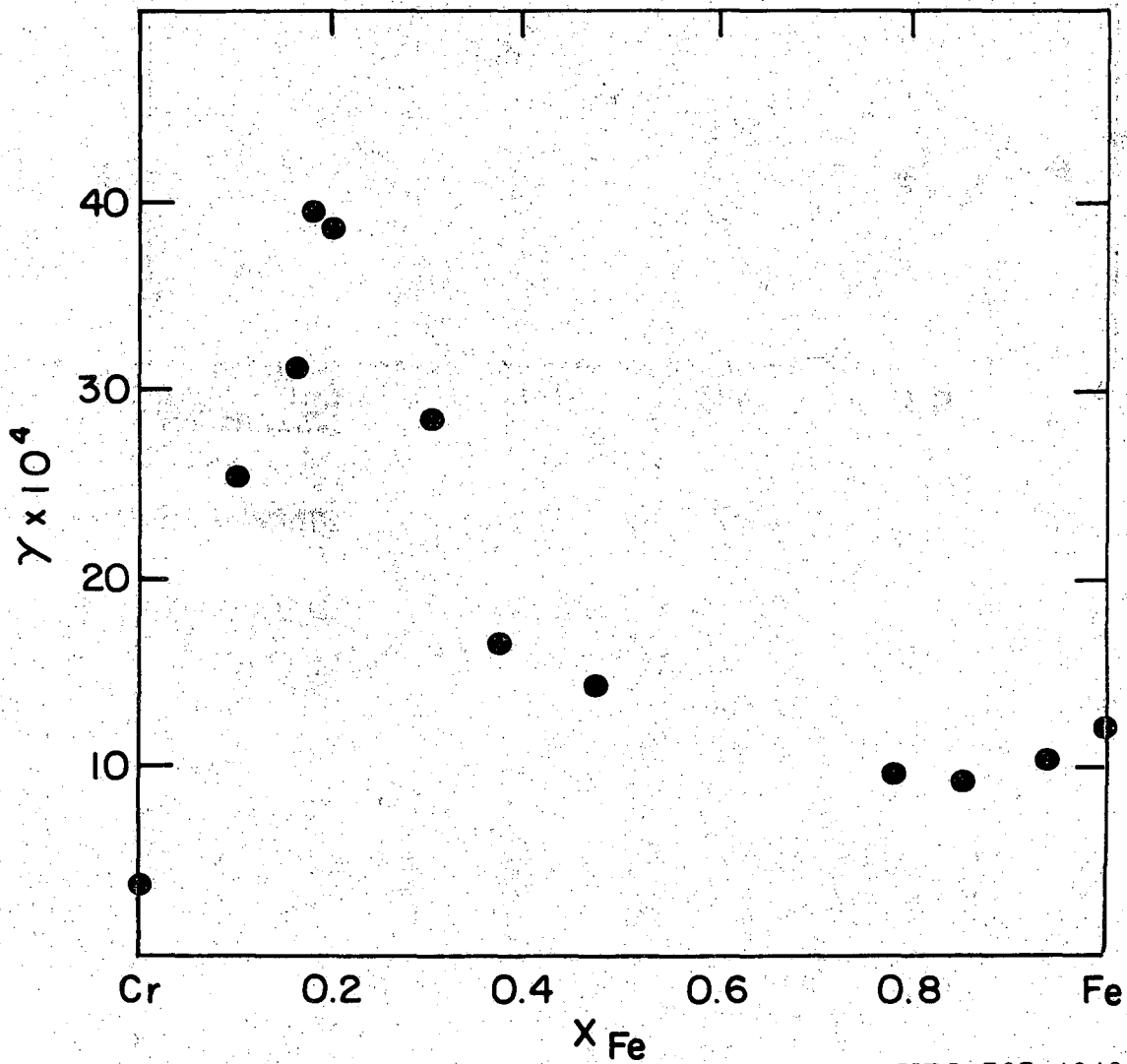
Atomic vibrational contributions to  $C_p$ . The Debye theory, an extension of Einstein's original work already mentioned, enables the entire curve of  $C_p$  versus  $T$  to be constructed from a measurement at a single temperature. The parameter determining the curve is the Debye temperature. Experimental points that follow the Debye theory would give a constant Debye temperature for measurements at all temperatures. Actually the Debye temperature



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varies somewhat with temperature of measurement, but not too badly except near 0°K where it changes considerably. The Debye temperature can be calculated also from elastic constants. Many of the measurements have the purpose of relating Debye temperature to elastic constants and to examining the causes of changing Debye temperatures.

Absolute entropies. The motive for many of the low-temperature Cp measurements is the determination of absolute entropies.

$$S_T = S_0 + \int_0^T C_p dT/T$$

For pure metals and ordered alloys  $S_0 = 0$ ; for disordered alloys  $S_0$  is the configurational entropy. If  $S_T$  is known for reactants and products of a chemical reaction,  $\Delta S$  is found, which may be combined with  $\Delta H$  to give  $\Delta G$ , or with  $\Delta G$  to give  $\Delta H$ .

High-Temperature Heat Capacities. Most measurements are made in the drop calorimeter and determine the enthalpy,  $H_T - H_{298}$ . These measurements are valuable only if the initial state and the final state are well established. Many measurements in the literature are valueless because this has not been done. From the enthalpy contents

$$C_p = dH/dT .$$

This is a good method of determining heat capacity only if the heat capacity is not changing rapidly with temperature. In that case the curve of  $H_T - H_0$  versus T is not accurate enough to yield a good slope. This method is not good enough to trace the Cp anomalies at the ferromagnetic Curie temperature or the details of changing Cp as the melting point is approached. Most good heat content measurements are limited to temperatures below 1500°K, though in recent years measurements higher than 2500°K have been made.

Drop calorimetry may sometimes be used to measure heats of reaction; clearly the latent heat of melting of a pure metal is readily determinable. In a eutectic alloy system where the liquid freezes to form the pure solid components, the heat of formation of the liquid alloy can, of course, be determined. Indeed, if the equilibrium heat effects are known at all temperatures, the entropy of formation, and consequently, also the free energy of formation, may be found. If the solid final state is not composed of the pure elements, it may be possible to make allowances for this and proceed as before.

A number of Oelsen calorimeters are being built in which the heat released and the sample temperature are measured continuously, so that the entire enthalpy content-temperature curve is determined in one experiment. Obviously, the experimental difficulties in making this precise are formidable. Furthermore, the results will be accurate only if equilibrium is attained at all temperatures, not only just the final state. It would seem this method could hardly ever be precise, but it might be useful for surveys and for approximate results.

Cp values may be directly measured "true Cp", in adiabatic calorimeters. Measurements become increasingly difficult as the temperature rises; few are accurate much above 1000°K. The reason for this is the radiation heat transfer coefficient, which increases with  $T^3$ .

Because of these difficulties, attempts are being made to develop other methods of determining Cp at high temperatures, often with scanty success. I shall mention only two promising attempts here.

At the U.S. National Bureau of Standards Cezairliyin has an apparatus

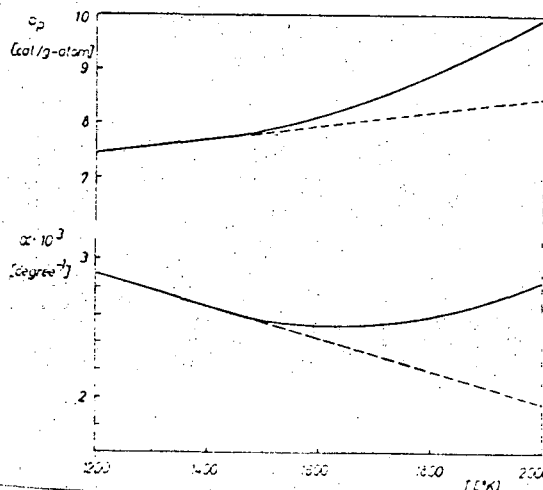


in which the sample is a long, hollow cylinder. A small hole bored near the middle allows a recording radiation pyrometer to "see" the opposite wall under conditions approximating a hohlraum, or black body. A large pulse of electrical energy heats the sample to a high temperature in a few milliseconds. Energy and temperature are recorded simultaneously as a function of time, giving the entire  $C_p$  versus  $T$  curve.

In the second promising method the sample is in the form of a wire perhaps 30 cm long. It is heated to the desired temperature by a direct current. Two very fine wires are attached to the sample about 5 cm apart near the middle of the wire. Through these wires the potential drop, and hence the resistance of the sample can be measured. Also, a small additional pulse of current can be applied periodically to the central part of the specimen. This leads to fluctuations of temperature from which  $C_p$  can be calculated.

Results on platinum obtained by Kraftmakher at Novosibirsk are shown in slide 12. Kraftmakher claims the rise in  $C_p$  below the melting point is entirely due to the formation of vacancies in the lattice. The number of vacancies he finds are several times as great as have been found in quenched samples; a reasonable result.

Slide 12



Enthalpies of Formation. This quantity is the only one considered for which calorimetry has a rival. If an equilibrium can be measured over a range of temperature, the entropy and enthalpy can be found from the temperature coefficient (Slide 13)

$$d\Delta G/dT = -\Delta S$$

Slide 13

However, measurable equilibria are hard to establish and it is easy for the

experimenter to make a mistake, in which case his result may be very far indeed from the truth. Even where measurable, well identified equilibria are established, usually, measurements are possible only over a limited range of temperature. Acceptable errors in  $\Delta G$  are multiplied when temperature coefficients are determined. Many results satisfactorily accurate in  $\Delta G$  are quite unacceptable in  $\Delta S$  and  $\Delta H$ . Calorimetric measurements are then very important even when  $\Delta H$  is known from equilibrium measurement. The calorimetric result is usually more accurate; even where it isn't, it is most reassuring to find a verification of a temperature coefficient, which reinforces the validity of the  $\Delta H$  and also of the  $\Delta G$ .

Heats of formation are most directly measured by inducing the metallic elements to react in the calorimeter. Pioneering work in direct reaction between liquid metals was done by the Japanese scientist, M. Kawakami, whose first work appeared in 1927. Many of these results have been found to be reasonably accurate. Others, however, especially between high-melting metals, are seriously in error. The primary difficulty is the measurement of calories at high temperatures, since the radiation heat transfer coefficient increases with the cube of the temperature. At present, attempts are being made with some success by Kubaschewski in Teddington, England, for reaction of metal powders.

A second method is to dissolve the alloy. The heat of solution of the alloy minus the heats of solution of the elements, is the heat of formation. Acid solution calorimetry has been extensively tried but has never proved satisfactory. The heat of formation sought is the small difference between large heats of solution; also, there is the problem of the heat content of the

escaping hydrogen, which may or may not be saturated with acid vapor.

Liquid tin solution calorimetry has been much more successful, even though the calories must be measured at temperatures above the melting point of tin.

It can be applied, however, only to the dozen or so metals which will dissolve in liquid tin at reasonable speeds and do not have vapor pressures too high.

Elliott at the Massachusetts Institute of Technology, has developed a very complex liquid iron solution calorimeter with some success at these most difficult temperatures. What is badly needed is a general method of determining heats of formation of the high-melting transition metals alloys.

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