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Thermodynamics of the metallic state is a comparative newcomer in an old and respected discipline. Novel problems are involved because of the tendency of metals to form phases stable over widely variable composition ranges. Phases may be segregated, the degree of order may vary, and equilibrium may be attained only slowly. These difficulties are unusual in chemical practice and most chemical thermodynamicists, realizing this, have avoided measurements on metals. Others, who are well able to measure a calorie with accuracy, have fallen into the trap and have produced measurements of materials whose initial or final states have not been defined with accuracy. On the other hand, thermodynamics has not been prominent among the tools of the physical metallurgist who well know how to prepare samples. As the subject became important, many publications have appeared in which calorie measurement has been done with lamentable accuracy.

Happily, these days are departing and a veritable flood (comparatively) of thermodynamic measurements on metallic systems is appearing most of which describe measurements of respectable accuracy.

The principal purpose of nonmetallic thermodynamics measurements is the quantitative determination of the stability of compounds. From this the course of many chemical reactions may be found without the necessity of other measurements. In metallic systems, besides this aim, the data provided as a basis of theories of metal physics are particularly important. Thus, heats of formation provide a measure of the relative energies of metallic bonding, while phase changes, changes, in degree of order, changes in magnetic state, or other changes involving energy can be detected from thermodynamic measurements. There are also anomalies in heat capacity that are still not explained and must be due to as yet unsuspected types of transformation.

In this paper we shall mention some of these problems and, particularly, the attempt to develop techniques which will permit thermodynamic measurements previously impossible. It is convenient to begin the discussion at the lowest temperatures and proceed to higher temperatures.

Measurements below room temperature with very few exceptions (such as the heat of fusion of mercury) are confined to Cp measurements. At these temperatures insulation of the calorimeter is relatively easy because of the low radiation heat transfer coefficient. Adequate techniques have been developed to measure Cp within a fraction of a percent from a few tenths of a degree Kelvin to room temperature.

At the lowest temperatures there may be a large Cp anomaly due to magnetic interaction between the nucleus and external electrons; this interaction is the source of the hyperfine structure found in spectra. For most elements the anomaly has not been measured because it occurs at temperatures below the measured region or, in some cases, it does not exist. An increasing number of measurements of this anomaly are appearing in the literature, particularly of those elements where the effect is large, as in the rare earths. This field is most inadequately surveyed and we may expect the effort to increase.

The electronic contribution to Cp can be identified and determined for most elements at temperatures well within the range of an ordinary liquid helium calorimeter. In nonmetals electrons contribute appreciably to Cp only at very high temperatures, because the energy states are widely spaced. In metals, on the other hand, the electronic levels of the "free" electrons are very closely spaced, more closely spaced than the energy levels of lattice vibration. Hence there is a low-temperature region where most of the Cp is due to electronic excitation and this term, which increases linearly with T, can be measured. At higher temperatures, the lattice vibrational contribution, which increases with T^3, becomes so large it masks the electronic contribution. The magnitude of the electronic contribution is usually expressed as the constant, γ, so that $C_{electronic} = \gamma T$.

The value of γ depends on the spacing of the levels, that is, the density of states near the Fermi surface. This is surely of considerable importance in any theory of metallic bonding. Values of γ have been determined for most elements (Fig. 1). It is striking that the transition metals, which have d as well as s and p electrons near the Fermi surface, have much higher values of γ than the others.

Very little has been done to study the electronic term in alloys although clearly this should give important clues as to the nature of bonding in the alloy. That complex relations would be uncovered by these studies is shown in Fig. 2, a study of the Cr-Fe system.[1]

Many anomalies are found in low-temperature Cp measurements. These are caused by transformations occurring at ferromagnetic Curie temperatures, antiferromagnetic Neel temperatures, or other second order transformations. For some of these anomalies such as, for example, a prominent one in the Cp of europium at 16°K, no explanation has yet been found. Study of these anomalies is important in the physics of metals. Although the low-temperature Cp values have been determined for most of the elements, practically nothing has been done for alloys.

A fourth field for which low-temperature Cp measurements are pertinent is the determination of absolute entropies. According to the Third Law of thermodynamics, the entropy of elements and ordered alloys at 0°K is zero. At any temperature, T,

$$S_T = \int_0^T Cp\, dT/T$$

Absolute entropies at 298.15°K have been determined for most metallic elements (Fig. 3). Hardly any work has been done on alloys. Even if the measurements were made, disordered alloys do not have zero entropy at 0°K.

For alloys whose entropies of formation have been determined by high-temperature thermodynamic measurements, it should be useful to determine low-temperature Cp values to find the entropy of formation at 0°K. When sufficient values have been so determined, it might be possible to estimate the 0°K entropies of other alloys.

Low-temperature Cp values contribute to our understanding of atomic bonding forces since they depend on the crystal lattice vibration.

Measurements of Cp become increasingly difficult as the temperature is raised. Temperature measurement, maintenance of temperature, uniformity of spatial distribution of temperature, deterioration of sample or calorimeter, addition of measured energy to the calorimeter, and many other factors become increasingly important as the temperature is raised.

To assist in insulating the calorimeter, most high temperature measurements are adiabatic; an effort is made to keep the surroundings at the same temperature as the calorimeter. However, the radiation heat transfer coefficient increases with the cube of the temperature, so the errors multiply correspondingly. Considering these obstacles, it is not surprising that until recently few measurements of Cp at elevated temperatures had been made and that these rapidly lost validity as the temperature approached 700-1000°C.

Because of these obstacles, most high-temperature heat capacities have been derived from heat content measurements. In this method the sample is heated to a high temperature, T, then dropped into a calorimeter near room temperature, where the calories given off in cooling can be accurately measured. To allow for heat lost during the drop, usually the heat contents of empty and full containers are both determined. The heat capacity can be found from the slope of the heat content versus temperature curve; $Cp = d(H_T - H_{298.15})/dT$. Heat capacities obtained in this way are reliable if the heat capacity does not change rapidly with temperature. However, the accuracy of the heat content measurements is not sufficient, for example, to trace details of a Cp anomaly.

Heat capacities and heat contents of most of the metallic elements have been measured with reasonable accuracy to moderately high temperatures. There is a great need to carry these measurements up to much higher temperatures for many of the elements. Figure 4 indicates the temperatures to which experimental measurements extend. Much remains to be done in extending them higher with the present well established techniques. Many of the measurements do not extend as high as the melting point, and particularly, the entropies of melting are poorly known as can be seen from the vacant spaces in Fig. 5.

A key problem of metal thermodynamics is to increase the temperature to which accurate Cp or heat content measurements may be made. To increase the operating temperature of the usual adiabatic calorimeter is tedious and laborious, progress is slow, and difficulties continually multiply as the temperature goes up, because of the rapid increase of the heat transfer coefficient and the problems of containers, etc.

A promising approach is to enormously increase the speed of measurement, electronically recording energy added and temperature. As long ago as 1939[2] Langmuir and Malter analysed temperature fluctuations during alternations of ac current passing through a sample. These and later attempts at rapid measurement have in general not given acceptable values at high temperatures until recently. Some of the pulse heating methods are now giving promising results; I shall particularly mention the work of Cezairliyin[3] at the National Bureau of Standards.

In his calorimeter a tubular sample is heated at the approximate rate of 6600°K per second by a pulse of electrical energy. Radiation from the inside of the tube passes through a small hole to a photoelectric cell, which records the temperature in millisecond units simultaneously with the energy record in the same time units. This method has clear advantages in time spent! In less than a second results are obtained which would take weeks by drop calorimetry. Of course, the results might not be true equilibrium results. If phase or other changes with temperature occur in the sample with increasing temperature, the measurement time might not be sufficient to allow them to occur. There is also under construction at the NBS a microsecond calorimeter which might even take measurements in the liquid sample after it has melted but before it has time to collapse!

Alloys have received inadequate coverage on heat content or Cp measurements. In general, alloys obey Kopp's law of additivity of Cp pretty well except where anomalous changes occur. Most measurements have been for the purpose of tracing magnetic, degree of order, or phase changes in alloys. Care must be taken in these measurements to allow sufficient time for changes in equilibrium in the alloy during the measurement. Heat contents are not meaningful if phase changes occur during cooling unless the phase changes occur very rapidly (so they are complete) or very slowly (so they occur to a negligible extent).

For measurement of heats, entropies, and Gibbs energies of formation of alloys the techniques are difficult. None of them are universally applicable; most techniques can be applied only to a very limited number of systems. There is a significant amount of thermodynamic data on only a small fraction of binary systems and an extremely small number of ternary systems. Our last complete survey was in 1963; the statistics are shown in Table 1.

Table 1. Thermodynamic Data in 1963

Total Number of Binary Systems (76 metals)	2556
Total Number with Significant Data	166
Studied by:	
electrochemical potential	77
vapor pressure	41
direct calorimetry	73
liquid tin calorimetry	43
aqueous calorimetry	24
distribution coefficients	5

Not only have very few systems been studied; most of the work has been done on the easier systems, so that whole areas of the periodic table have had little or no work. Very little has been done with the high-melting transition metals in the middle of the periodic table.

Determination of the Gibbs energies of formation of alloys involves the measurement of equilibria since thus far Third Law determinations of entropies are nonexistent. Equilibrium with a solid involves equilibrium of a surface. The surface must be in equilibrium with the interior; else the measurement is meaningless. For alloy phases, which commonly exist over a range of compositions, this means the rate of diffusion must be sufficient to restore any changes in surface composition which occur while equilibrium is being established. For most alloys the equilibrium must be measured at an elevated temperature, with all the attendant difficulties.

Except for low-melting alloys like the amalgams, electromotive force measurements with aqueous electrolytes are therefore not applicable. Most emf measurements have been made at modest temperatures (500°-800°K) with fused salt electrolytes. Care must be taken that the main reaction is correctly identified, that all other reactions are excluded, and that the electrolyte conducts ionically and not electronically. In general the electropositivity of the reacting component must be considerably greater than the electropositivity of all other components for the electrolyte used. Even then it is a laborious and difficult task to find a suitable electrolyte for a given problem. Results cannot be credited except when reversibility is established by lengthy tests. Each system measured may require individual research.

From a successful cell, the partial molal Gibbs energy of formation, $\Delta\bar{G}_B$, of only one component is measured. However, if this is measured over a range of compositions which includes one at which $\Delta\bar{G}_A$ is known, the values for the other component and for the integral Gibbs energy may be calculated from Gibbs-Duhem integration.

The application of electrochemical measurements on a wide scale will probably take place only slowly. Many alloy pairs are not suited, for example, their electropositivities may not differ enough. Existing electrolytes are not applicable to many others. One of the most promising steps at present is the use of solid electrolytes.

Solid electrolytes must have high ionic conductivity, usually from lattice vacancies. Thus a solid solution of CaO in the ZrO_2 lattice has an anion vacancy for every Ca ion. $O^=$ is therefore mobile. The oxygen pressure must be kept high enough to prevent reduction of Zr^{++++}; otherwise electrons can freely move between Zr ions of differing charges. A number of such cells have been made to work successfully, from which the activity of O in compounds may be measured.

Vapor pressure measurement has perhaps more promise than electrochemistry but has been exploited even less. Usually a system in which only one component has an appreciable pressure is preferred, since with these chemical analysis of the vapor is unnecessary. However, the usual measurement is of a rate of evaporation (Knudsen, Langmuir, transport method) which may be subject to serious errors from surface depletion.

As the more volatile component evaporates, its concentration on the surface of the alloy drastically decreases unless it is replaced by diffusion from the interior. Thus measured vapor pressures are too low unless the rate of diffusion is rapid compared with the rate of evaporation. Fortunately, standard techniques of varying hole size in the Knudsen method, or varying gas flow rates in the transport method, make depletion detectable, while it can be instantly seen in the Knudsen torsion effusion method. Even so, in many alloy systems studied by vapor pressure methods, the activities found are much too low.

A static method of measuring vapor pressures would be particularly desirable for alloys since it would solve the problem of surface depletion. One of the most promising ideas is the absorption spectrum study of vapors in equilibrium with the alloy. This has already proved practical and accurate.[4] Two or more components might be studied in the same vapor. The Gibbs-Duhem relation would provide an internal check of accuracy. Probably a method could be developed to convert absorption coefficients into absolute vapor pressures. Even without this, it should be noted that the activity is the ratio of two pressures: that of the component in the alloy to the pure component, so that absolute measurements would be unnecessary.

Heats of formation are determined from temperature coefficients of Gibbs energies. However, in taking the slope with temperature, errors in measuring the Gibbs energies are multiplied so that it often occurs that satisfactory equilibrium measurements give temperature coefficients which are of poor accuracy. Direct heats of reaction, like heat capacities, become more difficult and more subject to error as the temperature at which the calories are measured is increased. Direct reactions at moderate temperatures (700°-800°K) are being measured with accuracy. Promising attempts are being made to develop calorimeters which measure heats of reaction between metal powders[5] and with liquid iron.[6]

Before metal thermodynamics reaches maturity, a great deal of experimental work needs to be done. Much of this consists of applying proved techniques, but it is especially necessary to develop new and better methods of measurement at high temperatures.

ACKNOWLEDGEMENT

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Electronic Cp

$\gamma \times 10^4$

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	n	H																H	He
2	He	Li 4.18	Be 0.55											B 0.0	C 0.03	N	O	F	Ne
3	Ne	Na 3.3	Mg 3.04	Al 3.48									Mg 3.04	Al 3.48	Si 0.0	P	S	Cl	Ar
4	Ar	K 5.	Ca 7.17	Sc 24.6	Ti 8.25	V 23.	Cr 3.80	Mn 28.	Fe 12.0	Co 11.3	Ni 16.8	Cu 1.64	Zn 1.58	Ga 14.4	Ge 0.0	As X	Se	Br	Kr
5	Kr	Rb X	Sr 8.70	Y 24.4	Zr 7.10	Nb 18.8	Mo 4.95	X	Ru 8.0	Rh 13.	Pd 22.6	Ag 1.47	Cd 1.64	In 3.6	Sn 4.20	Sb X	Te 0.0	I	X
6	X	Cs X	Ba 6.5	La 24.1	Hf 5.8	Ta 13.5	W 2.7	Re 5.6	Os X	Ir X	Pt 16.0	Au 1.80	Hg 4.5	Tl 6.1	Pb 7.5	Bi 0.15	Po	At	Rn
7	Rn	Fr X	Ra X	Ac X	Th 11.2	Pa X	U 26.	Np X	Pu X	Am X	Cm								
6a					Ce 2.5	Pr 40.	Nd Anom	X	Sm 31.	Eu 13.8	Gd Anom	Tb 21.7	Dy 22.7	Ho 23.9	Er 31.	Tm 42.9	Yb 6.93	Lu 27.	

Figure 1. Values of γ for the Electronic Heat Capacity, $C_{(electronic)} = \gamma T$.

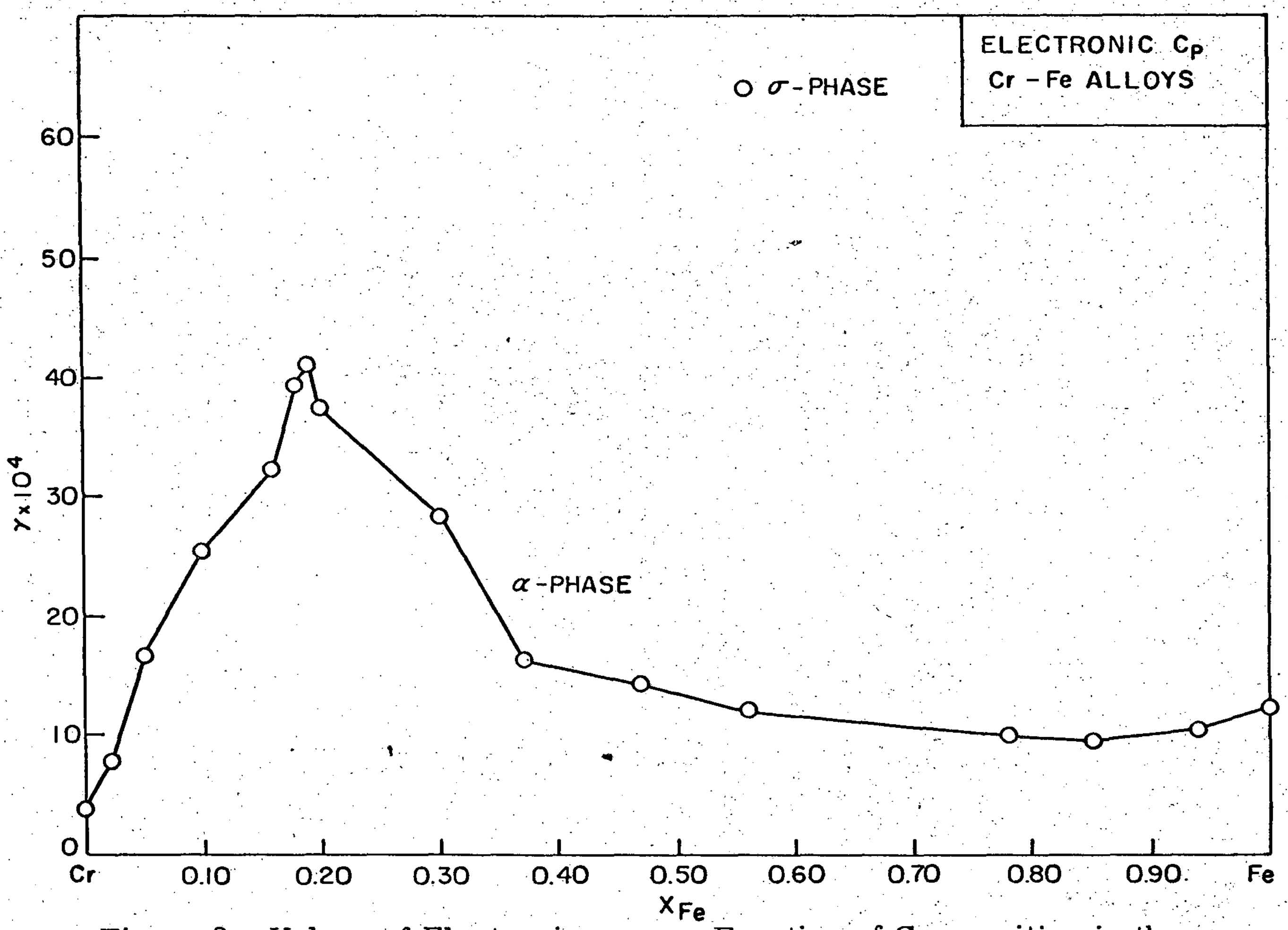
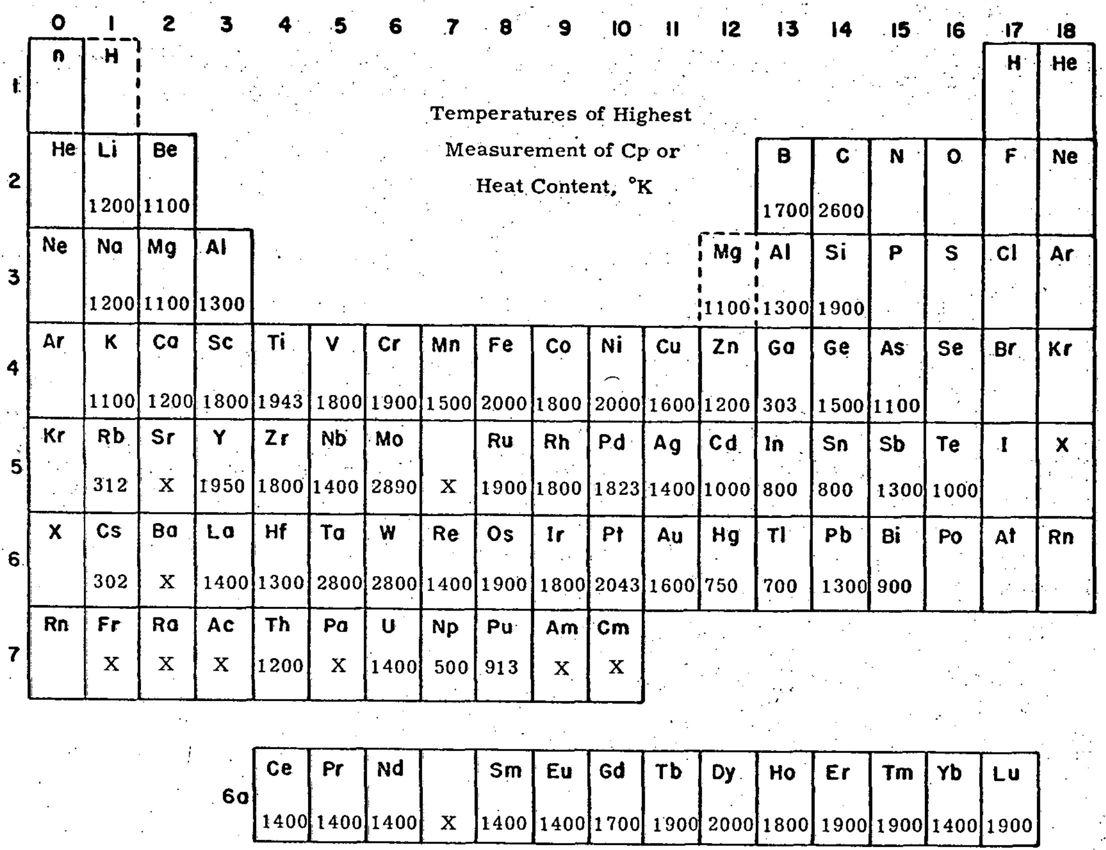


Figure 2. Values of Electronice γ as a Function of Composition in the Chromium-Iron System.

$S_{298.15}$

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	n	H																H	He
2	He	Li 6.69	Be 2.28											B 1.40	C 1.37	N	O	F	Ne
3	Ne	Na 12.1	Mg 7.81	Al 6.77									Mg 7.81	Al 6.77	Si 4.50	P	S	Cl	Ar
4	Ar	K 15.5	Ca 9.95	Sc 8.28	Ti 7.32	V 6.91	Cr 5.64	Mn 7.65	Fe 6.52	Co ? 7.18	Ni 7.14	Cu 7.97	Zn 9.95	Ga 9.77	Ge 7.43	As 8.4	Se	Br	Kr
5	Kr	Rb 18.1	Sr 12.5	Y 10.6	Zr 9.32	Nb 8.70	Mo 6.85	X	Ru 6.82	Rh 7.53	Pd 9.06	Ag 10.2	Cd 12.4	In 13.8	Sn 12.3	Sb 10.9	Te 11.8	I	X
6	X	Cs 20.2	Ba X	La 13.6	Hf 10.4	Ta 9.92	W 7.80	Re 8.89	Os 7.8	Ir 8.48	Pt 9.95	Au 11.3	Hg 18.2	Tl 15.3	Pb 15.6	Bi 13.5	Po X	At	Rn
7	Rn	Fr X	Ra X	Ac X	Th 12.8	Pa X	U 12.0	Np X	Pu 12.3	Am X	Cm X								
6a					Ce 15.3	Pr 17.7	Nd 17.0	X	Sm 16.6	Eu X	Gd 16.4	Tb 17.6	Dy 17.9	Ho 17.9	Er 17.5	Tm X	Yb X	Lu X	

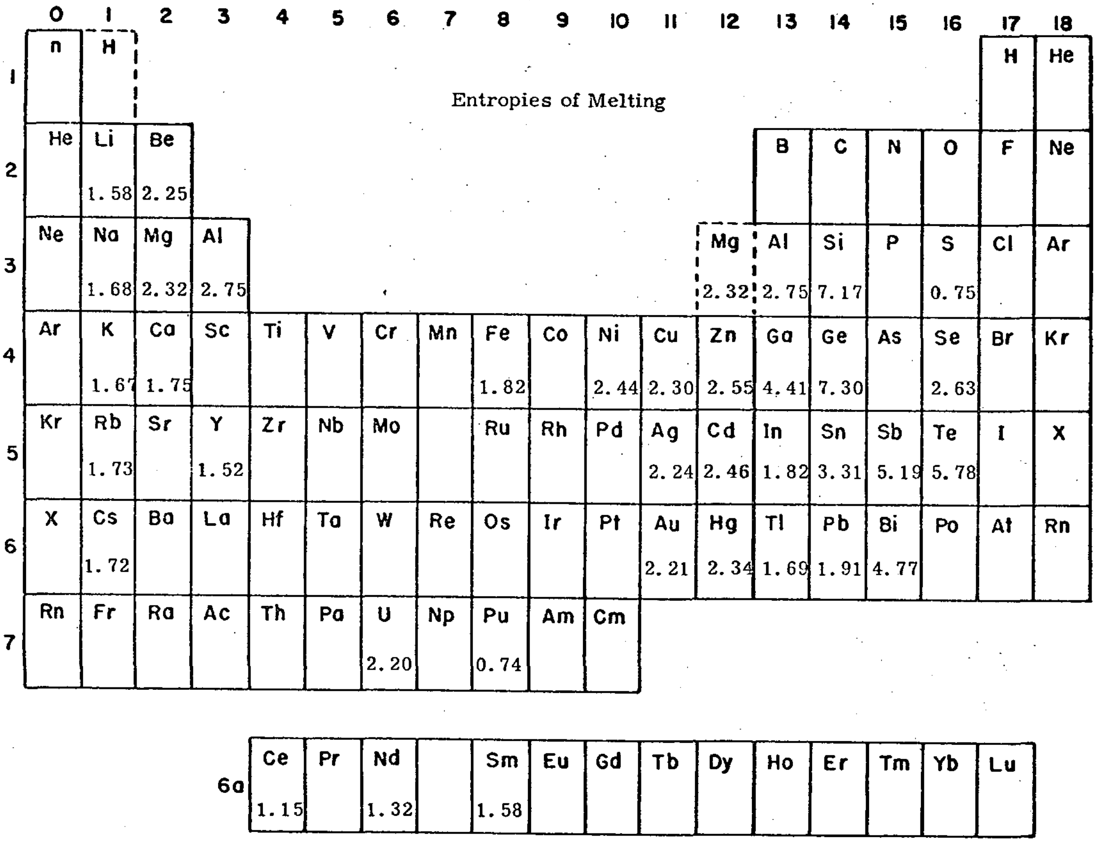
Figure 3. Absolute Entropies of Metallic Elements at 298.15°K.



Temperatures of Highest Measurement of Cp or Heat Content, °K

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	n	H																H	He
2	He	Li 1200	Be 1100											B 1700	C 2600	N	O	F	Ne
3	Ne	Na 1200	Mg 1100	Al 1300									Mg 1100	Al 1300	Si 1900	P	S	Cl	Ar
4	Ar	K 1100	Ca 1200	Sc 1800	Ti 1943	V 1800	Cr 1900	Mn 1500	Fe 2000	Co 1800	Ni 2000	Cu 1600	Zn 1200	Ga 303	Ge 1500	As 1100	Se	Br	Kr
5	Kr	Rb 312	Sr X	Y 1950	Zr 1800	Nb 1400	Mo 2890	X	Ru 1900	Rh 1800	Pd 1823	Ag 1400	Cd 1000	In 800	Sn 800	Sb 1300	Te 1000	I	X
6	X	Cs 302	Ba X	La 1400	Hf 1300	Ta 2800	W 2800	Re 1400	Os 1900	Ir 1800	Pt 2043	Au 1600	Hg 750	Tl 700	Pb 1300	Bi 900	Po	At	Rn
7	Rn	Fr X	Ra X	Ac X	Th 1200	Pa X	U 1400	Np 500	Pu 913	Am X	Cm X								
6a					Ce 1400	Pr 1400	Nd 1400	X	Sm 1400	Eu 1400	Gd 1700	Tb 1900	Dy 2000	Ho 1800	Er 1900	Tm 1900	Yb 1400	Lu 1900	

Figure 4. Highest Temperatures of the Metallic Elements for Which Heat Contents or Heat Capacities are Experimentally Known (valid about 1965).



Entropies of Melting

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	n	H																H	He
2	He	Li 1.58	Be 2.25											B	C	N	O	F	Ne
3	Ne	Na 1.68	Mg 2.32	Al 2.75									Mg 2.32	Al 2.75	Si 7.17	P	S 0.75	Cl	Ar
4	Ar	K 1.67	Ca 1.75	Sc	Ti	V	Cr	Mn	Fe 1.82	Co	Ni 2.44	Cu 2.30	Zn 2.55	Ga 4.41	Ge 7.30	As	Se 2.63	Br	Kr
5	Kr	Rb 1.73	Sr	Y 1.52	Zr	Nb	Mo		Ru	Rh	Pd	Ag 2.24	Cd 2.46	In 1.82	Sn 3.31	Sb 5.19	Te 5.78	I	X
6	X	Cs 1.72	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au 2.21	Hg 2.34	Tl 1.69	Pb 1.91	Bi 4.77	Po	At	Rn
7	Rn	Fr	Ra	Ac	Th	Pa	U 2.20	Np	Pu 0.74	Am	Cm								
6a					Ce 1.15	Pr	Nd 1.32		Sm 1.58	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	

Figure 5. Entropies of Melting of the Metallic Elements as Experimentally Known in 1963.