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SOME ASPECTS OF HIGH-TEMPERATURE CHEMISTRY FROM THE VIEWPOINT OF CHEMICAL THERMODYNAMICS

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I. INTRODUCTION

In the last 10–15 years high-temperature chemistry has begun to develop rapidly into a new branch of chemistry. The concept of high temperature is relative and depends on the range of problems and phenomena considered. Some authors therefore prefer to relate high-temperature chemistry not to definite temperature limits but to various characteristics of the properties of substances and the observed relationships shown by the properties. Thus Brewer[1] defines high-temperature chemistry as the chemistry of systems at sufficiently high temperatures so that the oxidation states, compounds, and general chemical behaviour differ appreciably from those important at room temperature. Searcy[2] defines high temperatures as temperatures at which entropy differences play a major role in determining the position of equilibria of interest (under standard conditions). Using this definition, 3000°K is not a high temperature for the processes of nitrogen ionisation, but for many volatilisation processes, moderately high temperatures or even room temperature (or lower temperatures) could be regarded as high temperatures. There is some justification for this approach, but in the present paper the author prefers, in agreement with Margrave[3], to adopt, albeit arbitrarily, certain definite boundaries on the temperature scale.

In the wide range of temperatures which have now become accessible to a greater or lesser degree (10^{-6}–10^{8} °K), high-temperature chemistry concerns a relatively small interval (of 1–2 orders of magnitude) from about 1000°K to 10000°K (or possibly up to 50000°K), since at higher temperatures almost no molecules remain and atoms undergo increasing ionisation with the formation of plasma. The present paper deals chiefly with the thermodynamic properties of substances at these high temperatures. Other aspects will be touched upon, however, in the discussion of processes of vaporisation.

The marked increase in interest in the physics and chemistry of high temperatures was initially due to the demands made by certain branches of modern technology. This was further stimulated by better availability of high temperatures for experiments, development of methods of study at high temperatures, and the use of fast electronic computers for calculating the thermodynamic functions of various molecules, atoms, and ions at high temperatures using the methods of statistical thermodynamics. Statistical thermodynamics combined with new calculating techniques is widely used in high-temperature chemistry, and it is on this basis that most of the new information on the thermodynamic properties of substances at high temperatures is now obtained, partly because of the great difficulty of making calorimetric determinations even at moderately high temperatures. The methods of statistical thermodynamics are also based on experimental data, but these data are obtained from various types of spectra and by determination of the fundamental parameters of molecular structure (interatomic distances, etc.) by electron and X-ray diffraction studies, etc.

Experimental work in the field of high-temperature chemistry has been accompanied by theoretical work relating to the new experimental methods, methods for calculating thermodynamic properties, and the state of substances at high temperatures. Interest in high-temperature chemistry has also been stimulated by the fact that the previously widely-held views that all chemical relationships became progressively simpler at high temperatures and that there were no fundamentally new problems or phenomena, proved to be greatly oversimplified. The main trends observed on going to very high temperatures are an extremely marked increase in the reactivity of substances, an increase in reaction rates, and the development of processes involving the dissociation and decomposition of complex substances; these are obvious, but at the same time many elements form compounds at high temperatures corresponding to valence states (degrees of oxidation) which are not characteristic, or are unknown for these elements, at ordinary temperatures. Even the relationships between the properties of elements in the same Periodic Group are sometimes found to be more complex than those observed at ordinary temperatures. High temperatures lead to the appearance of species of new types, which may be simpler than the corresponding species at ordinary temperatures (for example CaCl, SiO, Al_2O, AlO, SO) or more complex (C_3, C_9, Na_2, Ge_8, Mg_2, Mo_5O_{15}, $Na_2(OH)Cl$, Ba_2O_3, etc.). At high temperatures, where the thermal motion of the species is capable of breaking chemical bonds, many radicals and free atoms exist in equilibrium with their parent molecules and become essentially molecules themselves. The processes by which they are formed may be quantitatively described by the thermodynamic parameters of the reaction (heat of reaction, entropy change, equilibrium constant, etc.). By determining their temperature dependence, it is often possible, by extrapolation, to obtain interesting conclusions for ordinary temperatures which cannot be arrived at by direct determination at lower temperatures. The tendency for molecules to be simpler at

increased temperatures and the simultaneous increase in the reactivity of atoms lead in particular to the appearance, in a relatively stable state at high temperatures, of diatomic species formed by the most varied combinations of atoms, such as OH, AlO, AlCl, MgCl, MgN, etc., whose existence does not tie up with the ideas on the valence states characteristic of the given elements to which we are accustomed at ordinary temperatures. Atoms of the halogens, oxygen, and hydrogen are able to form diatomic molecules with elements from a wide range of periodic groups (with the exception of the inert gases). At high temperatures, particularly when these are combined with high pressures, it is possible to obtain certain substances in crystalline modifications which cannot be produced at ordinary temperatures or which have been previously unknown (the synthesis of diamonds, cubic crystals of boron nitride, a new crystalline form of SiO_2, etc.).

Information on the change in the chemical and physical properties of elements and their compounds at high temperatures makes it possible to construct, as it were, a temperature axis perpendicular to the plane of the Periodic System and to examine not only the regular features of the properties of the elements and their compounds at ordinary temperatures but also the influence of temperature on these properties and on the relationships between them for different elements. At the present time, of course, high-temperature chemistry is only at the stage of the initial accumulation of material. Many facts revealed experimentally await theoretical explanation. Here the field is wide open for specialists in thermodynamics, statistics, and the theory of chemical bonding and structure. An interesting feature is that some of the fundamental concepts of the Debye–Hückel theory, developed for solutions of strong electrolytes, have been applied successfully to ionised gases.

In recent years there have been a number of international and local conferences [4-8] devoted to various problems in the field of high-temperature chemistry. Many reviews have been published [1-3,9-18]. Various aspects of high-temperature chemistry are now beginning to be more widely reflected in monographs and textbooks [19-25].

Considerable attention is now being paid to methods for attaining high temperatures, methods of measurement, thermal stability of materials and compounds, and their mechanical and other properties at high temperatures. There are a considerable number of papers, however, devoted to the influence of temperature on purely chemical and thermodynamic properties of substances.

The present paper will deal only with the chemical-thermodynamic properties of substances in the gaseous state at constant or varying pressures, and also with the corresponding chemical reactions and processes of vaporisation.

II. GASES AT CONSTANT PRESSURE

The basic equations

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

$$\Delta G^\circ = -RT \ln K_a \qquad (2)$$

are fully rigorous from the thermodynamic viewpoint and relate the changes in Gibbs free energy ΔG, enthalpy ΔH, and entropy ΔS for a given reaction to one another and to the value of the equilibrium constant K_a at a given temperature of T°K.

The reaction can proceed in the forward direction without the expenditure of work from an external source if $\Delta G < 0$, and the condition for equilibrium is that $\Delta G = 0$. Thus reaction in the direction indicated is favoured by high negative values of ΔH (*i.e.* considerable liberation of energy) and high positive values of ΔS (*i.e.* increase in the entropy of the system). For many reactions which are not too complex, the first (energetic) factor reflects the usual increase in the stability of a system with decrease in its reserve of internal energy, manifested in a tendency towards greater aggregation of the substance, increase in the size of the species, etc., whereas the second (entropy) factor reflects the tendency towards intensification of all processes involving dissociation to simpler species under the influence of the thermal motion of the species [26]. In reactions which bring the system towards an equilibrium state, these two factors operate in opposite directions, and the overall course of the reaction is determined by the influence of whichever factor predominates until the influences of the two factors become equal, when the equilibrium state is reached. Since the heat of reaction ΔH usually depends little on the concentrations of the reactants, the attainment of equilibrium is almost entirely governed by the dependence of the entropy on concentration [27].

Eqns. (1) and (2) show that, other conditions being equal, the relative importance of the entropy factor increases with increase in temperature. Under standard conditions at low temperatures, the term $T\Delta S^\circ$ is small since the values of T are small, but at high temperatures this term shows a corresponding increase. For many types of gas reactions, ΔH° and ΔS° change relatively slowly with temperature, particularly when compared with the change in T, so that in these cases $T\Delta S^\circ$, and hence ΔG°, can often be roughly thought of as linear functions of temperature. In these cases $\ln K$ is a linear function of the reciprocal of the temperature $(1/T)$. Fig. 1 shows the relationships between these quantities for the thermal dissociation of I_2 to free atoms. For this reaction under standard conditions, the influence of the energy factor predominates up to 1455°K and that of the entropy factor above 1455°K. At T = 1455°K the influences under standard conditions are of equal magnitude but opposite sign. At this temperature $\Delta G^\circ = 0$, so that $\ln K_a = 0$ and $K_a = 1$. At the same temperature but with concentrations of the components different from the standard values, ΔG differs from zero and may be either positive or negative, depending on the ratio of the concentrations and hence on the value of ΔS. Independently of this, however, at T = 1455°K for this reaction $\ln K_a = 0$ and $K = 1$. At this temperature the dissociation process

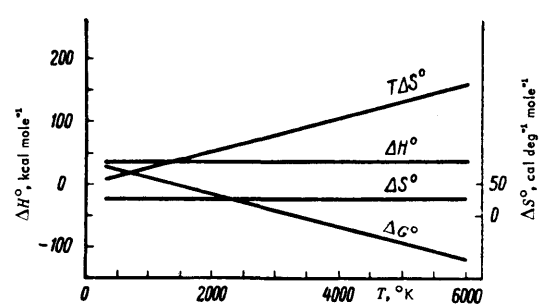


Fig. 1. Thermodynamic parameters of the reaction $I_2 \rightleftharpoons 2I$ at temperatures up to 6000°K.

undergoes a steep change. Dissociation begins at much lower temperatures and increases with increase in temperature to 1455°K and above. At this temperature the equilibrium constant passes through a value equal to unity, which for this reaction at p = 1 atm corresponds to a degree of dissociation x = 0.447 (and to corresponding different values of x for other pressures).

The most characteristic distinguishing feature of the influence of high temperatures at constant pressure is an increase in the rates of decomposition, dissociation, and disaggregation, associated with the increased importance of the entropy factor reflecting the influence of the thermal motion of the species.

As a result, the processes which become typical are those involving a decrease in the number of atoms per molecule, often associated with a change in the valence state (degree of oxidation) of the element, with further decomposition of the molecule to free atoms and then successive removal of the least firmly held electrons from the atoms to yield a plasma. It should be emphasised that this thermal ionisation of atoms, unlike ionisation under the influence of light and high-energy species, is characterised by a definite equilibrium state whose position depends on temperature and pressure. It is described by the usual thermodynamic relationships and, in particular, can be calculated by the methods of statistical thermodynamics.

A characteristic example of the influence of increase in temperature is provided by the sequence of changes:

$$MgCl_2 \longrightarrow MgCl \longrightarrow Mg \longrightarrow Mg^+ \longrightarrow Mg^{2+},$$

corresponding, for example, to the successive processes

$$MgCl_2 \rightleftharpoons MgCl + Cl, \quad (a)$$

$$MgCl \rightleftharpoons Mg + Cl, \quad (b)$$

$$Mg \rightleftharpoons Mg^+ + e, \quad (c)$$

$$Mg^+ \rightleftharpoons Mg^{2+} + e. \quad (d)$$

Fig. 2 shows the change in the degree of dissociation x with change in temperature for the first two reactions, for the particular case where the total pressure P is equal to 1 atm. The calculation was carried out from the values of K recommended [28] for the reactions

$$MgCl_2 \rightleftharpoons Mg + 2Cl \text{ and } MgCl \rightleftharpoons Mg + Cl,$$

assuming

$$x = \sqrt{\frac{K_P}{K_P + P}}.$$

The correspoinding values of x for the process of ionisation to Mg^+ were calculated by a similar conventional method.

The increase in the part played by the entropy factor leads to simpler relationships between the corresponding parameters for reactions and processes of the same type (see below), since for these we observe smaller differences in ΔS_T°, similar changes in ΔS° with temperature, etc. [29-31]. Table 1 gives the chief thermodynamic quantities for the dissociation of diatomic molecules of the alkali metals and halogens from published data [32,33].

The more atoms in the original molecule, the greater the variety of different species in the dissociation products and, correspondingly, the complexity of the relationships between the composition of the dissociation products at different temperatures. The compositions of the dissociation products of H_2O and CO_2 at different temperatures are shown in Figs. 3 and 4. Fig. 3 is based on calculations [34] in which allowance was made for the concentration of the following species: H_2O, OH, H_2, O_2, H, and O. The composition of the products of the thermal dissociation of H_2O in this case is expressed in terms of the concentration of these

TABLE 1. Basic thermodynamic parameters for the dissociation of the diatomic molecules of the alkali metals and of the halogens at 298.15°K (ΔH° kcal mole^{-1}, ΔS° cal deg^{-1} × × mole^{-1}).

Substance	ΔS°_{298}	ΔH°_{298}	$\log K_d$	$\Delta S^\circ_{1800} - \Delta S^\circ_{298}$
Li_2	−19.29	26.41	−15.16	−1.42
Na_2	−18.43	18.00	− 9.17	−1.20
K_2	−16.93	12.26	− 5.29	−1.02
Rb_2	−16.56	11.65	− 4.92	−1.09
Cs_2	−16.08	10.71	− 4.35	−0.91
F_2	−27.35	37.81	−21.72	−3.21
Cl_2	−25.63	57.88	−36.63	−3.15
Br_2	−24.97	53.52	−28.88	−1.91
I_2	−24.08	50.96	−24.58	−1.55

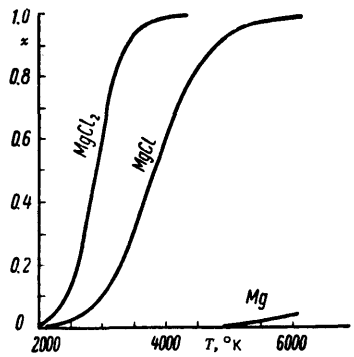


Fig. 2. Temperature dependence of the degree of dissociation of magnesium dichloride and monochloride according to reactions (a) and (b) and of the ionisation of magnesium atoms according to reaction (c).

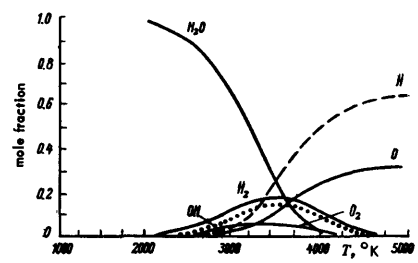


Fig. 3. Relative concentration (in mole fractions) of various species (OH, H_2, O_2, H, and O) in the products of the thermal dissociation of water vapour at various temperatures.

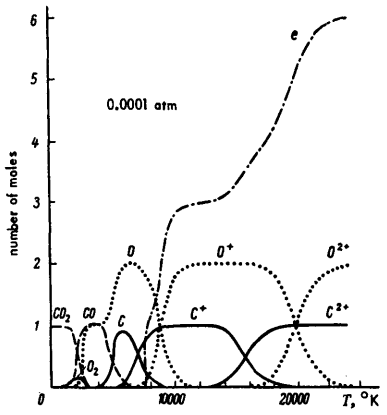


Fig.4. Concentration of various species (CO, C, O_2, O, C^+, C^{2+}, O^+, and O^{2+}) in the products of the thermal dissociation of CO_2 at $P = 0.0001$ atm, expressed as the number of moles of each species formed from 1 mole of CO_2.

species (in mole fractions) for a total pressure $P = 1$ atm. (Data for other pressures were also published [34].) For the same system, other authors [35,36] carried out calculations covering higher temperatures, at which ionisation of hydrogen and oxygen atoms and hydroxyl radicals occurs. An interesting feature is that in this system, at temperatures in the region of 4000°K (at $P = 1$ atm) (Fig. 2), the concentration of free hydroxyl radicals OH in the mixture is higher than the concentration of H_2O molecules. This is due to the fact that removal of the second hydrogen atom requires a slightly greater expenditure of energy than removal of the first.

Fig. 4 gives the product composition for the thermal dissociation of CO_2 at different temperatures ($P = 10^{-4}$ atm), expressed as the number of moles (or gramme-atoms or gramme-ions) of species of different type obtained from one mole of the original CO_2. [37] Here the calculation was carried out up to 24 000°K, *i.e.* it covers the range of the first and second ionisations of oxygen and carbon atoms at this pressure, but no allowance was made for the formation of carbon suboxide C_3O_2 or for the polymerisation of carbon vapour, *i.e.* the formation of C_2, C_3, etc. molecules. Data for other pressures up to $P = 100$ atm were also published [37]. The calculation was carried out in connection with a study of the possible state of the atmosphere of Venus.

Various data relating to the thermodynamic functions of substances in the gaseous state have also been given for a number of other systems such as the ionisation of alkali metal vapours [38], etc. [39-43].

The values of the main thermodynamic functions for the gaseous state under standard conditions at high temperatures have now been calculated for a large number of substances with molecules of the simplest type. Most of these calculations have been carried out for diatomic molecules of the type AB (the monoxides, monohalides, and monosulphides of various elements), many of them simply on the basis of the corresponding molecular constants in the rigid rotator–harmonic oscillator approximation, *i.e.* with the assumption that the rotation of the molecule can be regarded as the rotation of a completely rigid system and that the anharmonicity of the vibrations can be neglected. This assumption restricts appreciably the applicability of this method of calculation for temperatures above 1500–2000°K, since for many substances the results are appreciably different when allowance is made for the anharmonicity of the vibrations, let alone that for excited states (excitation of atoms and electronic excitations) which requires appropriate data on the spectra of the molecules and other methods of calculation.

For most elements in the monatomic-gas state and also for many elements in the state of diatomic or more complex molecules, the main thermodynamic functions and the thermodynamic parameters of the reactions of their formation from the ordinary simple elements for temperatures up to 3000°K have been tabulated [32]. Data have been given [40] on the high-temperature components of the enthalpy and entropy up to 5000–8000°K for many elements in the monatomic-gas state and for certain diatomic molecules. The main thermodynamic functions for the monatomic-gas state have been calculated for most elements up to 8000°K [44-48] and also for positive ions (singly-, doubly-, triply-, and quadruply-charged) up to 50 000°K. [49] The experimental basis for all this work is provided by appropriate spectroscopic data taken for the most part from reference tables [50]. It has become possible to carry out these complex and tedious calculations on a large scale through the use of electronic computers.

Table 2 gives as an example the values of the function $(H_T^\circ - H_0^\circ)/T$ for the singly-charged positive ions of certain elements at different temperatures up to 50 000°K. [49] For monatomic species the specific heat and internal energy do not have vibrational and rotational components and are determined entirely by the translational movement of the species and (at higher temperatures) by the excitation of higher electronic energy levels. Before these excitations take place, the specific heat C_P° and the function $(H_T^\circ - H_0^\circ)/T$ have a constant value of 4.9682 cal deg^{-1} $mole^{-1}$ for species of a given type. In this series of species the change from the structure of He atoms to those of Ne, Ar, Kr, Xe, and Rn is accompanied by a lowering of the first excited electronic state from 21.0 eV for helium atoms to 6.8 eV for radon atoms [50]. The influence of excited states does not yet manifest itself at 45 000°K for Li^+ ions, 20 000°K for Na^+ ions, 10 000°K for K^+ and Rb^+ ions, and 9000°K for Cs^+ ions. Similar relationships should also hold for F^-, Cl^-, Br^-, and I^- ions and for Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions, etc.; for isoelectronic species, increase in the charge on the nucleus is also associated with a rise of the first excited electronic state and hence with an increase in the temperature at which it begins to influence the thermodynamic functions.

TABLE 2. Enthalpy function $(H_T^\circ - H_0^\circ)/T$ for the singly-charged ions of certain elements at high temperatures (cal × × deg^{-1} g-$atom^{-1}$). [49]

T, °K	Ne^+	Li^+	Na^+	C^{2+}	Mg^+	Ba^+	Al^+	Tl^+
298.15	5.0533	4.9682	4.9682	4.9682	4.9682	4.9682	4.9682	4.9682
2000	5.2160	4.9682	4.9682	4.9682	4.9682	5.7143	4.9682	4.9682
4000	5.1213	4.9682	4.9682	4.9682	4.9684	6.5849	4.9685	4.9682
6000	5.0774	4.9682	4.9682	4.9682	4.9779	6.5090	4.9881	4.9686
8000	5.0528	4.9682	4.9682	4.9682	5.0334	6.3795	5.1098	4.9769
10 000	5.0372	4.9682	4.9682	4.9684	5.1503	6.3406	5.3983	5.0170
20 000	5.0041	4.9682	4.9682	5.4013	6.9102	7.7444	7.9331	6.4657
30 000	4.9972	4.9682	4.9700	8.8021	9.6147	8.6237	11.320	9.6355
40 000	5.0614	4.9682	5.0138	11.383	10.281	8.4389	12.312	11.182
50 000	5.3676	4.9689	5.2807	11.531	9.9249	8.0438	11.767	11.100

The values of C_P° and $(H_T^\circ - H_0^\circ)/T$ mentioned above are likely to stay unchanged with increase in temperature for the longest time for species with an eight-electron shell in the outer layer (Ne, Ar, Kr, Xe, and Rn atoms and the isoelectronic Na^+, K^+, Rb^+, and Cs^+ ions), followed by species containing only *s* electrons in the outer layer (Be, Mg, Ca, Sr, and Ba atoms and the isoelectronic B^+ and Al^+ ions, but not Sc^+, Y^+, or La^+).

Fig. 5 shows the temperature dependence of specific heat C_P° for certain gases with monatomic and diatomic molecules up to 6000°K. For atoms which are difficult to excite and for ions with similar electronic structures, C_P° throughout the whole of this temperature range retains its constant (minimum) value of 4.97 cal deg^{-1} mole^{-1} corresponding to the specific heat of translational motion. Halogen atoms have a slightly higher specific heat, that of bromine passing through an indistinct maximum at about 2000°K, while that of iodine increases appreciably in the range 2000–4000°K, after which it remains almost constant up to 6000°K. It can readily be seen that Li, Na, K, and Cs differ sharply from the halogens and make up a group with a similar temperature dependence of C_P°, but appreciably different position of the C_P° curves. Atoms with different structures (Mg, Fe, Pb) show a different type of relationship. All this shows that the change in the specific heat C_P°, and hence in S_T°, $H_T^\circ - H_0^\circ$ and other thermodynamic functions with change in temperature is not completely smooth or, more precisely, the derivatives of these quantities with respect to temperature are not monotonic. This of course applies not only to very high temperatures. The introduction of new degrees of freedom (in particular, new vibrational levels in polyatomic molecules) produces a similar effect, albeit generally less marked, even at moderately high temperatures. The widely-used methods of expressing thermodynamic functions in analytical form in power series with respect to absolute temperature in many cases leads to excessive smoothing out of significant variations. This is true not only of thermodynamic functions. Fig. 6 shows the change in the number of species in 1 cm^3 of the products of the thermal dissociation of CO_2 with change in temperature at constant pressure.

Accumulation of multiplicity of data on the thermodynamic properties of species (atoms, ions, and molecules) is not necessarily accompanied by a corresponding increase in information on the parameters of the reactions between them: only the entropy change for the reaction can be calculated from the values of the entropies of its components.

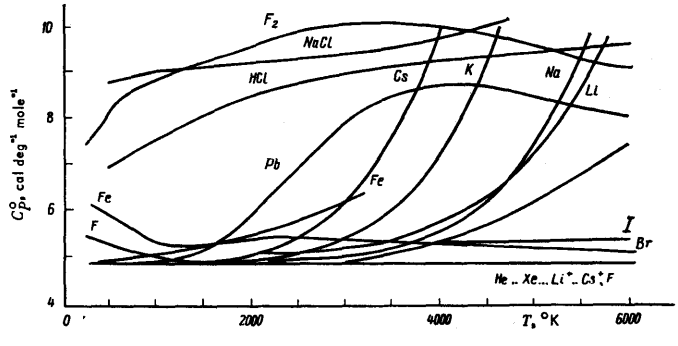


Fig.5. Temperature dependence of the specific heat C_P° for certain substances in the ideal-gas state.

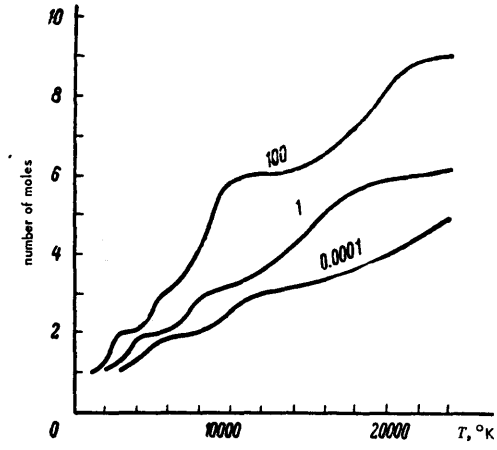


Fig.6. Temperature dependence of the total number of species per unit volume in the products of the thermal dissociation of CO_2 at pressures of 100, 1, and 0.0001 atm, expressed as the number of moles in 1 cm^3 (reduced to normal conditions).

In order to determine the corresponding enthalpy change ΔH, Gibbs free energy change ΔG, equilibrium constant K_a, and other related quantities, a knowledge of the heat of reaction or equilibrium state for at least one temperature is necessary. The methods of statistical thermodynamics cannot yet be used for this purpose. The value of ΔH for the formation of the simplest molecules from the free atoms can in many cases be calculated from the dissociation energy determined from spectroscopic data. For this, the ground states adopted in calculations from spectroscopic and thermochemical data must be identical, but this has not always been the case in the past.

Mass-spectrometric determinations on vapours at different temperatures are now beginning to provide a new source of information on thermodynamic parameters (see below).

III. THERMODYNAMIC DETERMINATIONS BASED ON THE CHEMICAL SIMILARITY OF SUBSTANCES AND REACTIONS

Much of the new information on the thermodynamic properties of different substances and the thermodynamic parameters of reactions has come from the use of the chemical similarity between substances on the basis of various methods of comparative calculation. The rapid increase in the demand for thermodynamic data as a result of the extension of the range of substances acquiring practical importance and the tedious and often time-consuming nature of the experimental determination of some of these quantities have stimulated the development of methods of comparative calculation. By making use of the analogy in the chemical properties of appropriate substances, it is possible by these methods to estimate the thermodynamic properties of the required substances and the reaction parameters on the basis of experimental data for other substances and reactions chemically similar to the first.

Thus the method of related compounds and reactions is based on a comparison of the analogous compounds of elements in the same subgroup of the Periodic System, present in these compounds in the same valence (oxidation) state and showing a sufficiently complete analogy between one another in this state. Such related compounds as, for example, the alkaline earth metal carbonates have values of the chief thermodynamic functions which are related to one another in regular fashion; their temperature dependences do not usually differ markedly and any difference is regular. Different degrees of related character can be considered. Thus the compounds of lithium, beryllium, and to some extent boron, are not infrequently less similar to the corresponding compounds of their analogues than the latter are to one another. This is apparently due to the absence from their ions of the eight-electron shell present in the ions of their higher analogues. A two-row difference is less favourable than a one-row difference, and in the case of a three-row difference the method generally cannot be recommended. The conditions are also unfavourable if the differing atoms predominate with respect to mass or dimensions in the molecule, as in the hydrogen halides, for example.

Without dealing at this stage with the reasons for the simpler relationships between thermodynamic properties for substances of the same type, we would merely point out that internal structures of the same type entail in the first place simpler relationships between the values of the entropy, the entropy changes in reactions of the same type (see below), and their temperature dependence, since the magnitude of the entropy is sensitive to all the characteristic features of the internal structure of substances. At the same time, in the high-temperature range, the methods of comparative calculation are often particularly valuable because calculations by the methods of statistical thermodynamics become more complex and experimental determinations more difficult. It is therefore necessary to get to know the extent and the temperature limits to which the various methods of comparative calculation (established for the most part for ordinary or moderately high temperatures) remain applicable at high temperatures, and what restricts their applicability under these conditions.

For the ideal-gas state, the changes in the high-temperature components of the entropy ($S^\circ_T - S^\circ_{T_1}$) with change in temperature for substances of strictly the same type should be related to one another in regular fashion [29-31,51,52]. For the most part the ratio of, or the difference between, these changes for two substances of the same type X and Y

$$\frac{(S^\circ_T - S^\circ_{T_1})_Y}{(S^\circ_T - S^\circ_{T_1})_X} = \alpha_S \qquad (3)$$

or

$$(S^\circ_T - S^\circ_{T_1})_Y - (S^\circ_T - S^\circ_{T_1})_X = c \qquad (4)$$

can be regarded as approximately constant quantities over a more or less extensive temperature range. Similar expressions also relate the high-temperature components of the enthalpy [51,53,54]

$$\frac{(H^\circ_T - H^\circ_{T_1})_Y}{(H^\circ_T - H^\circ_{T_1})_X} = \alpha_H \qquad (5)$$

or

$$(H^\circ_T - H^\circ_{T_1})_Y - (H^\circ_T - H^\circ_{T_1})_X = a. \qquad (6)$$

It is convenient to take as temperature T_1 the value 298.15°K = 25°C, from which the values of the high-temperature components of the thermodynamic functions are given in reference literature [40]. The use of slightly higher temperatures for this purpose, however, sometimes improves the applicability of relationships (3)–(6). For substances of sufficiently similar type, the high-temperature components of the entropy at a given temperature are for the most part similar to one another, so that for such substances Eqns. (3) and (4) apply approximately and simultaneously. The same is true of Eqns. (5) and (6).

In the most favourable cases the various equations (3)–(6) apply also in the low-temperature range, so that it is then possible to take 0°K as the temperature T_1 without introducing any appreciable errors. Comparison of the quantities $S^\circ_T - S^\circ_{298}$ and $H^\circ_T - H^\circ_{298}$ has the advantage over comparison of the quantities S°_T and $H^\circ_T - H^\circ_0$ in that the low-temperature values of the enthalpy and entropy need not be known.

Table 3 gives the values of S°_T for sodium and potassium fluorides and chlorides in the ideal-gas state under standard conditions at different temperatures up to 6000°K from published data [28]. These four substances suitably paired exhibit fairly rigorous common-type character. For these substances, throughout the whole of this temperature range, the ratios α and differences c remain fairly constant. When compared with sodium or potassium fluorides and chlorides, however, the analogous lithium compounds show a more marked variation in the values of α and c with change in temperature.

Similar relationships are observed for the enthalpies of lithium, sodium, and potassium halides. The temperature dependences of the quantities

$$\alpha_H = \frac{(H^\circ_T - H^\circ_0)_Y}{(H^\circ_T - H^\circ_0)_X}$$

and

$$a = (H^\circ_T - H^\circ_0)_Y - (H^\circ_T - H^\circ_0)_X$$

are slightly more marked than those for α_S and c.

These relationships make it possible to calculate otherwise unavailable data sufficiently reliably by this method of comparison. Thus by using the values of S°_T for sodium chloride at different temperatures it is possible to calculate S°_T for potassium chloride at high temperatures (with an accuracy of up to ±0.5 e.u. up to 6000°K) if the values of S°_T for these compounds at some single temperature are known.

The double-comparison method (see below) makes the last condition superfluous. Comparison of compounds with different anions (particularly complex anions) usually gives somewhat worse results than comparison of compounds in which only the cations differ.

TABLE 3. Values of the entropy S°_T (cal deg^{-1} mole^{-1}) of the gaseous fluorides and chlorides of sodium and potassium [28] and the ratio between them at various temperatures.

T, °K	S°_T				α			c	
	NaF	NaCl	KF	KCl	$\frac{NaCl}{NaF}$	$\frac{KCl}{KF}$	$\frac{KF}{NaF}$	NaCl—NaF	KF—NaF
298.15	51.872	54.882	54.079	57.102	1.059	1.056	1.043	3.01	2 21
1000	62.289	65.587	64.610	67.920	1.052	1.051	1.037	3.30	2.32
2000	68.454	71.920	70.785	74.332	1.051	1.050	1.034	3.47	2.33
3000	72.073	75.714	74.407	78.226	1.051	1.051	1.032	3.64	2.33
4000	74.643	78.487	76.978	81.143	1.052	1.054	1.031	3.84	2.34
5000	76.638	80.726	78.972	83.488	1.053	1.057	1.030	4.09	2.33
6000	78.268	82.639	80.603	85.414	1.056	1.060	1.030	4.37	2.34

An important factor limiting the applicability of these relationships at high temperatures is the thermal excitation of new vibrational or electronic energy levels, since this often takes place at temperatures which differ appreciably even for molecules, atoms, or ions of the same type (see Fig. 5). In this respect the most stable species at high temperatures are naturally atoms and ions which in the free state or in the given state have a closed electron shell like that of the inert gas atoms. These include the Li^+, Na^+, K^+, F^-, and Cl^- ions making up the above halides of lithium, sodium, and potassium.

Comparison of beryllium and magnesium monofluorides and monochlorides gives equally good results, up to 4000–5000°K at least, since the influence of excited states in the Be^+ and Mg^+ ions manifests itself only from 4000°K (see Table 2). In the comparison of S°_T for the nitrides of boron and aluminium BN(gas) and AlN(gas), the ratio α_S varies from 1.07 to 1.05 and the difference c from 3.86 to 3.41 (for values of S°_T from 54 e.u. to 80 e.u.); as for $H^\circ_T - H^\circ_0$ for these substances, the difference a up to 5000°K amounts up to 0.65 kcal mole^{-1}, but at 6000°K it reaches 1.4 kcal mole^{-1} (for values of $H^\circ_T - H^\circ_0$ from 2 kcal mole^{-1} to 53 kcal mole^{-1}).

When insufficient data are available for compounds which are strictly of the same type as the compounds for which information is required, it is sometimes necessary in practice to compare substances which are less similar, for example, the compounds of lithium, beryllium, and to some extent boron, mentioned above, or the analogous compounds of elements belonging to a different group or subgroup of the Periodic System, or the first members of a homologous series of organic compounds, or substances which are less rigorously of the same type for other reasons. In such cases good results are given by the double-comparison method[56], which requires a large number of initial data for the calculation, but which makes it possible to obtain more accurate results than from the comparison of compounds which are less rigorously of the same type. The method is based on the introduction into the calculation of another pair of compounds analogous to those under consideration and the assumption that the temperature dependence of the quantities α or c is the same for both these pairs of compounds. As an example, for four such compounds of the type AX, BX, AY, and BY (say lithium and sodium fluorides and chlorides), it may be assumed that the ratio

$$\frac{(S^\circ_T - S^\circ_{T_1})_{AX}}{(S^\circ_T - S^\circ_{T_1})_{BX}} : \frac{(S^\circ_T - S^\circ_{T_1})_{AY}}{(S^\circ_T - S^\circ_{T_1})_{BY}} = \frac{\alpha_X}{\alpha_Y} \quad (7)$$

and the difference

$$[(S^\circ_T - S^\circ_{T_1})_{AX} - (S^\circ_T - S^\circ_{T_1})_{BX}] - [(S^\circ_T - S^\circ_{T_1})_{AY} - (S^\circ_T - S^\circ_{T_1})_{BY}] = c_X - c_Y \quad (8)$$

do not change with temperature.

In practice it is often sufficient to assume that $\frac{\alpha_X}{\alpha_Y} = 1$ or that $c_X - c_Y = 0$, *i.e.* that

$$\frac{(S^\circ_T - S^\circ_{T_1})_{AX}}{(S^\circ_T - S^\circ_{T_1})_{BX}} = \frac{(S^\circ_T - S^\circ_{T_1})_{AY}}{(S^\circ_T - S^\circ_{T_1})_{BY}} \quad (9)$$

and

$$(S^\circ_T - S^\circ_{T_1})_{AX} - (S^\circ_T - S^\circ_{T_1})_{BX} = (S^\circ_T - S^\circ_{T_1})_{AY} - (S^\circ_T - S^\circ_{T_1})_{BY}. \quad (10)$$

Similar equalities have also been given for the enthalpy[55]. All these relationships can be used, for example, for compounds of elements in two different (preferably adjacent) groups of the Periodic System, with analogous formulae. Thus Table 4 gives the values of α and c for the monochlorides of sodium and lithium, magnesium and beryllium, *i.e.* normal molecules and species which in a certain temperature range exhibit unsaturated valency (radicals). Despite these severe comparison conditions, each of the quantities α and c remains fairly constant up to 6000°K, and this makes it possible, for each pair of substances, to determine unavailable values of S°_T with an accuracy of ~ 1.5% using α for the calculations, or of 1 e.u. using c, taking only one value at some temperature for the required substance. At the same time, for each temperature, the values of all three quantities α (and all three quantities c) are close to one another and change in approximately parallel fashion with change in temperature. The ratio of the two given quantities α_1/α_2 and the difference between the two given quantities $c_1 - c_2$ thus show even smaller changes with change in temperature, and this may be made the basis of calculations of higher accuracy (up to 0.3% in calculations using α_1/α_2 and up to 0.35 e.u. in calculations using $c_1 - c_2$). Moreover, all the ratios of the values of α differ little from unity and all the differences in the values of c differ little from zero. Thus when there are no data on S°_T for the required substance (for any temperature), it is possible to assume that α_1/α_2 equals unity or that $c_1 - c_2$ equals zero, and to calculate its S°_T values at different temperatures with an accuracy of up to 0.7% for calculations using α_1/α_2 and up to 0.5 e.u. for calculations using $c_1 - c_2$. This example is not the best, but in many cases the attainable accuracy will of course be less.

TABLE 4. Ratio between the values of the entropy S°_T of the monochlorides of sodium and lithium, magnesium and beryllium, and aluminium and boron, at various temperatures.[28]

T, °K	$\frac{\alpha_1}{NaCl}$ / $\frac{}{LiCl}$	$\frac{\alpha_2}{MgCl}$ / $\frac{}{BeCl}$	$\frac{\alpha_3}{AlCl}$ / $\frac{}{BCl}$	α_1/α_2	$\frac{c_1}{NaCl}$—$\frac{}{LiCl}$	$\frac{c_2}{MgCl}$—$\frac{}{BeCl}$	$AlCl\frac{c_3}{}—BCl$	$c_1 - c_2$
298.15	1.080	1.073	1.069	1.0070	4.08	3.78	3.52	0.30
1000	1.074	1.070	1.066	1.0037	4.50	4.31	4.04	0.19
2000	1.068	1.064	1.062	1.0036	4.60	4.39	4.13	0.21
3000	1.066	1.062	1.059	1.0035	4.68	4.48	4.19	0.23
4000	1.065	1.060	1.058	1.0046	4.79	4.47	4.26	0.32
5000	1.065	1.059	1.057	1.0056	4.92	4.51	4.32	0.41
6000	1.066	1.058	1.057	1.0070	5.09	4.55	4.43	0.54

Similar relationships exist for the enthalpy, but here the discrepancies are greater. Table 5 gives an example of the calculation of the enthalpy $H^\circ_T - H^\circ_0$ for magnesium monochloride from the data for gaseous lithium, sodium, and beryllium monochlorides using the two equations

$$(H^\circ_T - H^\circ_0)_{MgCl} = \frac{(H^\circ_T - H^\circ_0)_{NaCl}}{(H^\circ_T - H^\circ_0)_{LiCl}} (H^\circ_T - H^\circ_0)_{BeCl} \quad (11)$$

and

$$(H^\circ_T - H^\circ_0)_{MgCl} = (H^\circ_T - H^\circ_0)_{NaCl} - (H^\circ_T - H^\circ_0)_{LiCl} + (H^\circ_T - H^\circ_0)_{BeCl}. \quad (12)$$

The calculated values begin to deviate appreciably from the published data at temperatures above 3000°K.

Table 6 gives the high-temperature component of the entropy ($S^\circ_T - S^\circ_{298}$) for MgCl calculated from the equations

$$(S^\circ_T - S^\circ_{298})_{MgCl} = \frac{(S^\circ_T - S^\circ_{298})_{NaCl}}{(S^\circ_T - S^\circ_{298})_{LiCl}} (S^\circ_T - S^\circ_{298})_{BeCl} \quad (13)$$

$$(S^\circ_T - S^\circ_{298})_{MgCl} = (S^\circ_T - S^\circ_{298})_{NaCl} - (S^\circ_T - S^\circ_{298})_{LiCl} + (S^\circ_T - S^\circ_{298})_{BeCl}. \quad (14)$$

With the exception of the entropy at 6000°K, the deviations between the calculated and published values do not exceed 0.12 e.u.

TABLE 5. Enthalpy $(H_T^\circ - H_0^\circ)$ of the gaseous monochlorides of lithium, sodium, beryllium, and magnesium (kcal mole^{-1}) from published data[28] and $(H_T^\circ - H_0^\circ)$ for magnesium monochloride, calculated from Eqns. (11) and (12).

T, °K	$H_T^\circ - H_0^\circ$			$(H_T^\circ - H_0^\circ)$ MgCl				
	LiCl	NaCl	BeCl	published data	from Eqn. (11)	Δ	from Eqn. (12)	Δ
298.15	2.16	2.30	2.12	2.23	2.26	+0.03	2.26	+0.03
1000	8.19	8.54	8.00	8.38	8.34	−0.04	8.35	−0.03
2000	17.19	17.69	16.89	17.38	17.38	0.00	17.39	+0.01
3000	26.35	27.05	25.91	26.50	26.60	+0.10	26.61	+0.11
4000	36.64	36.70	35.04	35.77	36.08	+0.31	36.10	+0.33
5000	45.06	46.74	44.33	45.25	45.98	+0.73	46.01	+0.76
6000	54.65	57.23	53.84	54.98	56.38	+1.40	56.42	+1.44

TABLE 6. High-temperature components of the entropy $(S_T^\circ - S_{298}^\circ)$ of the gaseous monochlorides of lithium, sodium, beryllium, and magnesium (cal deg^{-1} mole^{-1}) from published data[28] and $(S_T^\circ - S_{298}^\circ)$ for magnesium monochloride, calculated from Eqns. (13) and (14).

T, °K	$S_T^\circ - S_{298}^\circ$			$(S_T^\circ - S_{298}^\circ)$ MgCl				
	LiCl	NaCl	BeCl	published data	from Eqn. (13)	Δ	from Eqn. (14)	Δ
1000	10.28	10.71	9.99	10.53	10.41	−0.12	10.42	−0.11
2000	16.52	17.04	16.15	16.76	16.66	−0.10	16.67	−0.09
3000	20.23	20.83	19.78	20.46	20.37	−0.09	20.38	−0.08
4000	22.90	23.61	22.43	23.12	23.13	+0.01	23.14	+0.02
5000	25.00	25.84	24.50	25.24	25.32	+0.08	27.34	+0.10
6000	26.75	27.86	26.24	27.01	27.32	+0.31	27.35	+0.34

In a similar comparison of S_T° for the gaseous trifluorides of nitrogen and phosphorus NF_3 and PF_3 with the radicals CF_3 and SiF_3, the quantity α_1/α_2 changes from 0.007 to 0.011 [presumably 1.007 to 1.011 (Ed. of Translation)] and $c_1 - c_2$ changes from 0.49 to 1.1 e.u., that is, when Eqns. (9) and (10) are used, in which $T_1 = 0$°K, the possible error does not exceed about 1.1 e.u. for an absolute value of S_T° up to 120 e.u.; for $S_T^\circ - S_{298}^\circ$ it decreases to 0.6 e.u. In the calculation of $H_T^\circ - H_0^\circ$ the error amounts to not more than 0.5 kcal mole^{-1} for an absolute value of $H_T^\circ - H_0^\circ$ of 113 kcal mole^{-1}.

Chemical *reactions* of the same type, *i.e.* analogous changes in compounds of the same type (with identical stoichiometric coefficients in the reaction equations), show simple relationships between the corresponding thermodynamic parameters at the same temperature or under other comparable conditions. The temperature dependences of the thermodynamic parameters of reactions of the same type are as a rule even closer. With increase in temperature the influence of the entropy factor $T\Delta S^\circ$ on the position of equilibrium becomes more pronounced. As a result, the simpler relationships observed for it in reactions of the same type make this method of common-type reactions particularly fruitful in the examination of various thermodynamic relationships in the high-temperature range.

One characteristic feature of reactions of the same type is that the standard entropy changes ΔS° in the reactions at the same temperature do not differ significantly from one another. In favourable cases this makes it possible to assume as a first approximation that for two common-type reactions X and Y the standard entropy changes at a given temperature are equal, *i.e.* that

$$\Delta S_{X,T}^\circ = \Delta S_{Y,T}^\circ \qquad (15)$$

A second approximation, which makes allowance for the fact that the difference in the entropy change

$$\Delta S_{Y,T}^\circ = \Delta S_{X,T}^\circ = c \qquad (16)$$

is not equal to zero, but which assumes that it does not change with temperature (c = const) is more rigorous and has a wider use.

For reactions which are of the same type to a sufficient degree, this assumption usually shows good agreement with experimental data over a wide temperature range. At very high temperatures the agreement becomes less satisfactory when temperatures corresponding to the population of new vibrational levels or new levels of electronic excitation are approached. This assumption may not apply to reactions involving a change in the valence state of the elements being compared, since in the high-temperature range this may lead to a change in the nature of their chemical similarity. In many cases the results of the calculations can be improved by the double-comparison method. In the comparison of reactions of the same type, as in the comparison of substances of the same type, this method takes account of the fact that the difference c may change with temperature, but assumes that in two analogous pairs of reactions of the same type AX, AY and BX, BY the corresponding differences

$$\left.\begin{aligned} \Delta S_{AX,T}^\circ - \Delta S_{BX,T}^\circ = c_X \\ \Delta S_{AY,T}^\circ - \Delta S_{BY,T}^\circ = c_Y \end{aligned}\right\} \qquad (17)$$

change with temperature in the same way, *i.e.* that the difference $(c_X - c_Y)$ can be taken as constant within a certain temperature range. Referring this constant to the values of S° at the temperature T_1, we obtain

$$(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AX} - (\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{BX} = (\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AY} - (\Delta S_T - \Delta S_{T_1}^\circ)_{BY}. \qquad (18)$$

This method requires a large number of data for the calculation, but it extends the applicability considerably and leads to a corresponding increase in the accuracy of the results; it can be regarded as a third approximation. It is possible in a similar fashion to compare the high-temperature components of the entropy change $(S_T^\circ - S_{298}^\circ)$.

Relationships based on the assumption that the ratio of the entropy changes in two reactions of the same type are constant

$$\frac{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_Y}{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_X} = \alpha \quad \text{or} \quad \frac{\Delta S_{Y,T}^\circ}{\Delta S_{X,T}^\circ} = \alpha, \qquad (19)$$

analogous to those above and, more particularly, relationships analogous to Eqns. (7) or (9), in particular

$$\frac{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AX}}{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{BX}} = \frac{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AY}}{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AY}}, \qquad (20)$$

also give on the whole quite satisfactory results. Their applicability is somewhat more restricted, however, and the accuracy of the calculation is usually lower than of that based on the assumption that c or the differences $c_X - c_Y$ are constant.

Similar equations can be derived for the enthalpy change for the reaction (the heat of reaction) ΔH.

Table 7 gives ΔS_T° (and the corresponding values of c and α) for the hydrolysis of CCl_4 and $SiCl_4$ in a reaction of the type $CCl_4 + 2H_2O = CO_2 + 4HCl$ and the corresponding reaction for $SiCl_4$, calculated from published data[28]. For the sake of comparison, the calculation for the hydrolysis reaction was carried out, nominally, for the gaseous state of SiO_2. (Recalculation for the crystalline and liquid states of SiO_2 for the corresponding temperatures can readily be

TABLE 7. Standard entropy changes ΔS°_T (cal deg^{-1} mole^{-1}) for the hydrolysis of carbon and silicon tetrachlorides as homogeneous gas reactions.

T, °K	Hydrolysis		c	a
	CCl_4	$SiCl_4$		
298.15	65.32	63.72	1.60	1.025
1000	63.98	63.24	0.74	1.012
2000	62.88	62.47	0.41	1.007
3000	61.64	61.24	0.40	1.007
4000	61.32	60.87	0.45	1.007
5000	60.70	60.17	0.53	1.009
6000	60.17	59.53	0.64	1.011

carried out from available data[28].) Here the possible error in the calculation of ΔS° from Eqn. (14) does not exceed 1 e.u. and is slightly higher in the calculation using α. The results cannot be improved by the double-comparison method using data for CF_4 and SiF_4. The calculation for the hydrolysis of CF_4 and SiF_4 itself gives approximately the same result, but the combination of these two pairs of reactions does not lead to any improvement, since the substances differ in four of the five atoms making up the molecule.

A similar picture is observed when comparing the values of $\Delta H^\circ_T - \Delta H^\circ_0$ and ΔH°_T and also the quantity a for the same reactions. For these reactions the method involving comparison of the ratios of the heats of reaction α cannot be used, since they have opposite signs and hence their absolute values change in opposite directions. The maximum error in the values calculated for 6000°K using a is here slightly greater than 1 kcal mole^{-1}.

No allowance was made here for the change in the heat of formation of SiO_2 (quartz) from ΔH°_{298} = 210 kcal mole^{-1}, given in standard tables[28] on the basis of published data[56], to the most recent value 217.7 kcal mole^{-1},[57,58] since this is not reflected in the results of the comparison.

For a very important class of reactions — formation from the elements (simple substances or free atoms) — however, the applicability of the above relationships at high temperatures is often very limited, since these reactions are always associated with a change in the valence state of the elements. For different valence states the analogy between the properties of given elements may not hold; in particular, the energies of the excited states and their temperature ranges are not the same. For many compounds of the same type the entropy of atomisation even at 6000°K shows simple relationships analogous to those described earlier[59-62] for less high and for ordinary temperatures.

A different kind of relationship is observed in the comparison of reactions of the same type not at the same temperature but at temperatures corresponding to equal values of the equilibrium constant K_a. With this method of comparison of any two chemical reactions X and Y (or phase changes), the difference in their standard entropy changes $\Delta S^\circ_X - \Delta S^\circ_Y$ is equal[63] to the difference in their entropy changes under equilibrium conditions $\Delta S_{X(equil)} - \Delta S_{Y(equil)}$ so that

$$\Delta S^\circ_X - \Delta S^\circ_Y = \frac{\Delta H^\circ_X}{T_X} - \frac{\Delta H^\circ_Y}{T_Y}. \qquad (21)$$

For reactions of the same type these differences are very small and affected little by temperature. Since the values of $\Delta H^\circ_X/T_X$ and $\Delta H^\circ_Y/T_Y$ are similar, their ratio $A = \Delta H^\circ_X T_Y / T_X \Delta H^\circ_Y$ also changes little with temperature. Thus for the dissociation of the diatomic molecules of the alkali metals at values of $\log K_a$ from -5 to +2 (corresponding to a temperature range of about 1000 deg for these reactions), the value of A for each pair of reactions changes by not more than 10%. At the same time the value of A in all these cases is close to unity. Hence one may assume that in comparing reactions of the same type, under conditions corresponding to identical values of the equilibrium constants, the parameters $\Delta H^\circ/T$ are numerically identical†.

$$\frac{\Delta H^\circ_X}{T_X} = \frac{\Delta H^\circ_Y}{T_Y} \qquad (22)$$

Table 8 gives, for several groups of reactions of the same type involving the dissociation of diatomic molecules to free atoms (and for certain reactions of this kind which are not of the same type), the values of $\Delta H^\circ/T$ for conditions corresponding to two values of the equilibrium constants ($\log K_{a,1}$ = -0.4771, corresponding to a degree of dissociation x_1 = 0.5, and $\log K_{a,2}$ = -5.0000, corresponding to x_2 = 0.00316), calculated from published data[28]. In each of these groups the values of $\Delta H^\circ/T$ in most cases are fairly close to one another but tend to increase slightly for reactions in which the given value of $\log K_a$ corresponds to a higher temperature. This manifests itself most markedly in the case of the hydrogen halides (here the degree to which the reactions are of the same type is also lower).

The ratio of the parameters $\Delta H^\circ/T$ corresponding to two values of the equilibrium constants naturally shows

TABLE 8. Ratio of the parameters of the dissociation of certain diatomic molecules to atoms under conditions corresponding to equal values of the dissociation constants ($\log K_{a,1}$ = -0.4771 and $\log K_{a,2}$ = -5.0000).

Substance	$\log K_{a,1} = -0.4771$		$\log K_{a,2} = -5.0000$		$\frac{T_1}{T_2}$	$\frac{\Delta H^\circ_2 T_1}{T_2 \Delta H^\circ_1}$	$\frac{\Delta H^\circ_2}{T_2} - \frac{\Delta H^\circ_1}{T_1}$
	T_1	$\frac{\Delta H^\circ_1}{T_1}$	T_2	$\frac{\Delta H^\circ_2}{T_2}$			
LiF	4881	29.53	2854	49.50	1.71	1.68	20.0
NaF	4199	28.57	2423	48.56	1.73	1.70	20.0
KF	4425	28.45	2535	47.86	1.75	1.68	19.4
LiCl	4246	27.87	2425	47.90	1.75	1.72	20.0
NaCl	3850	26.45	2155	46.73	1.79	1.77	20.3
KCl	4093	25.68	2260	45.94	1.81	1.79	20.3
CO	7147	37.50	4590	57.48	1.56	1.53	20.0
SiO	5681	35.46	3596	55.15	1.58	1.55	19.7
PbO	3428	29.64	1994	48.72	1.72	1.64	19.1
ZrO	5657	35.47	3532	54.03	1.60	1.52	18.6
BO	5648	33.91	3501	54.22	1.61	1.60	20.3
NO	4900	32.19	2972	52.33	1.65	1.63	20.1
SO	4019	31.98	2438	52.40	1.65	1.64	20.4
HF	4390	32.51	2676	52.65	1.64	1.62	20.1
HCl	3585	30.46	2129	50.53	1.68	1.66	20.1
HBr	3173	29.38	1853	49.56	1.71	1.69	20.2
HI	2687	28.09	1541	48.04	1.74	1.71	20.0
LiH	2356	25.21	1290	45.44	1.83	1.80	20.2

† This assumption is essentially analogous to Trouton's rule, but can be extended to any thermodynamic processes (phase transitions, chemical reactions, etc.) and to any case of identical values of the equilibrium constants, not merely those equal to unity. At the same time its use is restricted to reactions or processes of the same type, although it applies approximately to reactions and processes which are not strictly of the same type. Trouton's rule itself is also obeyed most closely in the comparison of substances of the same type and can also be extended[64-68] to pressures other than 1 atm. As for the dependence of Trouton's coefficient on boiling point, the same behaviour appears to apply to chemical reactions (see Table 8).

smaller variations. Since the values of ΔH° change more or less in parallel (and not very much in any case) with change in temperature, the above relationship leads to an approximate proportionality between the actual temperatures corresponding to the two values of the equilibrium constants. In Table 8 this corresponds to the result that the ratio T_1/T_2 is approximately constant for reactions which are to a sufficient degree of the same type. Constancy in the difference between the parameters $\Delta H^\circ/T$ corresponding to two values of the equilibrium constants is less affected by the degree to which the reactions are of the same type (see Table 8). Thus these relationships, previously established for ordinary and moderately high temperatures[63,69], are also applicable to high temperatures. Appreciable differences in excitation levels (for example for ZrO and PbO) may, however, lead to significant errors.

Many of the relationships and methods of calculation described by Karapet'yants[70,71] can undoubtedly be extended to the high-temperature range, probably with the same restrictions regarding the transition of atoms and molecules to excited states (for elements whose excitation levels differ appreciably) as those described above for the method of reactions of the same type.

IV. GASES AT VARYING PRESSURE

The degree of dissociation of gaseous substances decreases with increasing pressure if the dissociation process is accompanied by an increase in the number of molecules of gaseous substances.

For the dissociation of a molecule into two species (atoms, atomic groups, or ions), the dependence of the degree of dissociation x on the total pressure P for the case where the species formed are different, *i.e.* for reactions of the type AB = A + B, is given by the equation

$$x^2 = \frac{K_a}{K_a + P}, \qquad (23)$$

where K_a is the equilibrium constant; where the species are identical, *i.e.* for reactions of the type A_2 = A + A, the corresponding equation is

$$x^2 = \frac{K_a}{K_a + 4P}. \qquad (24)$$

The influence of pressure on the degree of atomisation of hydrogen at different temperatures is shown in Fig. 7.

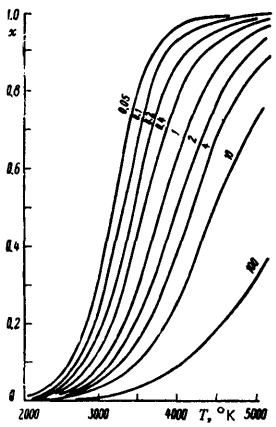


Fig. 7. Influence of pressure and temperature on the degree of dissociation x of hydrogen according to the reaction $H_2 = 2H$ at pressures of 0.05–100 atm.

V. PROCESSES OF VAPORISATION

Processes of vaporisation at high temperature have attracted considerable attention. This has been encouraged by the development of experimental methods for their study. Combining the technique of volatilisation from a surface or a Knudsen effusion chamber with mass spectrometry has made it possible to determine the masses of the species present in an equilibrium vapour and their relative concentrations. From the results of such determinations at several temperatures, it is possible to calculate the thermodynamic parameters for the vaporisation process. These methods have shown that vapours at high temperature often contain, in addition to simple species, various more complex species (see Table 9) whose number and concentration have been shown for many cases to increase with increasing temperature. Such data have been summarised[72].

These results have led to the view that at high temperatures the composition of vapours is complex and that the complexity of the species can increase with increase in temperature[1-3,10,23]. At the same time theoretical examination and factual material do not make it possible to assume that these conclusions are applicable to all systems (see below). The question as a whole has not yet been sufficiently studied. Increase in temperature always facilitates the dissociation of species to some extent, but for a saturated vapour increase in temperature is also associated with an increase in pressure, which suppresses the dissociation processes to a corresponding extent, which influence predominates in a given case and a given temperature range depends on the ratio of the heats of volatilisation and dissociation and on certain other parameters.

Processes involving an increase in the complexity of species (dimerisation, trimerisation, and polymerisation) at high temperatures may take place in the same temperature range as dissociation, and for processes which increase the complexity of the species, different directions and different degrees of displacement of the equilibrium composition of the saturated vapour with increase in temperature are possible, depending on the ratio of the corresponding parameters. Fig. 8 shows the influence of both

TABLE 9. Complex species in high-temperature vapours.

Condensed phase	Species in the gaseous phase*
LiF	LiF, $(LiF)_2$, $(LiF)_3$, $(LiF)_4$
LiOH	LiOH, $(LiOH)_2$, $(LiOH)_3$
NaOH+HCl	NaOH, $(NaOH)_2$, NaCl, $(NaCl)_2$, $Na_2(OH)Cl$
SiC	Si_2, Si_3, SiC_2, Si_2C, Si_3C, SiC, Si_2C_2, Si_3C_2
V_2O_5	V_4O_{10}, V_4O_8, V_6O_{14}, V_6O_{12}, V_2O_4
WO_3	$(WO_3)_3$, $(WO_3)_4$, $(WO_3)_5$
C	C, C_2, C_3, C_5, C_4, and a small number of more complex species
Ge	Ge, Ge_2 . . . . Ge_6
$LiAlF_4$	$LiAlF_4$, LiF, $(LiF)_2$, AlF_3

* Detected for the most part as positive ions in the mass-spectrometer.

factors on the degree of dissociation of dimeric Na_2 molecules. The detailed mechanism for the formation of the equilibrium vapour and the nature of the dynamic equilibrium between it and the crystal (or melt) have not yet been studied.

The most important factor responsible for the presence of complex species in the vapour is the fact that, at high temperatures, atoms or groups of atoms (radicals) with unsaturated valences may take part in vaporisation. Complex species may then be produced as a result of the formation of covalent bonds between the species. In other cases the cause may be dipole–dipole interaction, for example in $(LiF)_2$. In addition, the transition of species to an excited state leads to the possibility of forming bonds which do not occur at ordinary temperatures, for example in the Mg_2 molecule, formed at high temperatures.

In each temperature range, vaporisation takes place by the rupture of those bonds which can be overcome by the thermal motion of the species at these temperatures. At low and ordinary temperatures volatilisation of liquids and crystals with molecular structures takes place. Substances consisting of complex molecules often cannot be heated without decomposition below their boiling points at normal pressure, since even at lower temperatures the thermal motion becomes capable of causing partial rupture of the bonds between the atoms in the molecules. At high temperatures almost the only materials which can remain in the condensed state are metals and substances with an ionic structure or with covalent bonds between the species, since these substances vaporise only under stronger thermal excitation.

The formation of complex species in the vapour is often observed in the volatilisation of individual metals (Li_2, Na_2, Cu_2, Ag_2, Mg_2, Ba_2, Pb_2, Sn_2–Sn_5, etc.). In ionic crystals and their melts and in crystals with covalent bonds, vaporisation may be associated with an increase in the complexity of the species or with chemical dissociation (in the case of compounds). Different groups of compounds show characteristic behaviour in this respect. Thus in the vapour of crystals consisting of singly-charged ions (alkali metal halides), thermal dissociation of the molecules takes place only at very high temperatures, whereas at lower temperatures the species increase in complexity as a result of dipole–dipole interaction. The increased complexity is restricted for the most part to the formation of dimers of the type $(LiF)_2$, and more complex species are formed only to a comparatively small extent[73-75]. Less frequently (CuCl) the preferential formation of trimers‡ of the type $(CuCl)_3$ and $(AgCl)_3$ is observed[76-78].

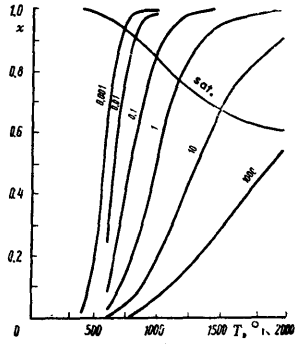


Fig.8. Influence of pressure and temperature on the degree of dissociation x of diatomic Na_2 molecules to atoms at pressures of 0.001–100 atm and the degree of dissociation of Na_2 molecules in the saturated vapour at different temperatures.

In lithium fluoride vapour at 900–1600°K the relative concentration of the dimer decreases[28] with increase in temperature (from calculated data) from 60–40 mole % above crystalline LiF to 20 mole % above the melt close to its boiling point, the concentration of the trimer decreasing at the same time. The decrease in the relative concentration of the dimer in LiCl vapour with increase in temperature follows approximately the same course[28]. With increase in temperature the concentration of the dimer in sodium chloride vapour increases above crystalline NaCl and decreases above the liquid. The particular nature of these relationships depends on the relationships between the values of the heats of sublimation, evaporation, and dimerisation, and other process of parameters.

The halides of metals of the lithium subgroup have heats of sublimation ΔH°_{298} equal to 47–66 kcal mole^{-1}, heats of dimerisation of the molecules ΔH°_{1000} equal to 32–62 kcal × × mole^{-1} and heats of dissociation of the diatomic molecules into atoms equal to 82–140 kcal mole^{-1}. With the exception of LiI, their boiling points lie above 1500°K.

Crystals consisting (formally) of doubly-charged cations and anions are naturally less volatile, because of the stronger interionic attraction. Out of the oxides of metals in the beryllium subgroup, only barium oxide vaporises to form BaO molecules (at 1530–1758°K) with almost no decomposition, plus a small quantity of Ba_2O, Ba_2O_2, and Ba_2O_3. Moderate decomposition accompanies the volatilisation of calcium oxide (65% at 1600–1750°K). The oxides of beryllium, magnesium, and strontium, however, are almost completely decomposed into atoms at about 2000°K. At the same time species such as $(BeO)_3$, $(BeO)_4$, $(BeO)_5$, $(BeO)_2$, and $(BeO)_6$ (in order of decreasing concentration) have been observed in small quantities in beryllium oxide vapour, the relative concentration of the more complex species increasing with increase in temperature. The heats of sublimation of these oxides ΔH°_0 decrease from 171.9 kcal mole^{-1} for BeO to 102 kcal mole^{-1} for BaO.[28] The heats of dissociation of the molecules into atoms ΔH°_0 increase from 100 kcal mole^{-1} for MgO to 137 kcal mole^{-1} for BaO.

Among the sesquioxides of the elements in the third group of the Periodic System, the rare-earth metals, and other metals, only boric oxide forms a vapour consisting chiefly of molecules B_2O_3. In the other cases[79-81] vapour formation is accompanied by chemical decomposition according to reactions of the type

$$M_2O_3(\text{solid}) \rightarrow 2MO(\text{gas}) + \frac{1}{2}O_2(\text{gas}), \quad (a)$$

or

$$M_2O_3(\text{solid}) \rightarrow M_2O(\text{gas}) + O_2(\text{gas}), \quad (b)$$

or

$$M_2O_3(\text{solid}) \rightarrow 2M(\text{gas}) + \frac{3}{2}O_2(\text{gas}). \quad (c)$$

‡ The earlier generally-held idea that copper monohalides are dimeric was based on the determination of their vapour densities, which characterise merely the average mass of the vapour species. Mass-spectrometric measurements showed, however, that in reality the vapour of copper(I) chloride consists chiefly of CuCl and $(CuCl)_3$ species, with a small concentration of $(CuCl)_2$.

Thus at about 2000°K, vaporisation takes place chiefly according to reactions of type (a) for Li_2O_3, Nd_2O_3, and Pr_2O_3; type (c) for Eu_2O_3; types (a) and (b) for Ti_2O_3 and Al_2O_3; and types (a) and (c) for Sm_2O_3.

A number of studies have been made of carbon in the vapour state [2,28]. It has been shown [82,83] on the basis of mass-spectrometric measurements that in the range 2000–2700°K the saturated vapour above graphite consists chiefly of species C_3, C_2, C_1, C_5, and C_4. Extrapolation of the experimental data leads to the conclusion that the ratios of the concentrations of these species in the saturated vapour at about 4000°K $C_3 : C_2 : C_1 : C_5 : C_4$ equals 4.5 : 2.8 : 1 : 0.5 : 0.35. A slight preponderance of species with an odd number of carbon atoms had already been established in several earlier studies. Pitzer and Clementi [84] carried out an approximate calculation of the basic thermodynamic functions up to 4000°K for these and more complex species on the assumption that they are made up of carbon atoms which are arranged linearly and joined by double bonds, using as a model carbon suboxide O=C=C=C=O. Although some of the conclusions reached in their work (in particular the result that the relative concentration of monatomic species increases at high temperatures) require confirmation, the work has revealed essentially the overall picture. It is undoubtedly true that a similar use of the molecules of di-, tri-, and poly-acetylenes and the corresponding cumulenes [85,86] as models, after experimental determination of their structural parameters and spectral data, will make it possible to obtain more complete information on the state of carbon species in the vapour. Mass-spectrometric measurements also give similar results for the nearest analogues of carbon, for which the vapours have been shown to contain polymeric species $Si_1 \ldots Si_7$, $Ge_2 \ldots Ge_8$, $Sn_2 \ldots Sn_5$, and Pb_2. The process of formation of complex species not from identical but from different monomeric species is of considerable interest. The formation of $Na_2(OH)Cl$ species in the volatilisation of NaOH and NaCl and of $LiAlF_4$ species in the volatilisation of LiF and AlF_3 have been described earlier [3,10,74]. The use of mass-spectrometry for the systematic study of the thermodynamic parameters of various processes occurring in related complex systems is, however, only just beginning. Thus Akishin and Sidorov [87–89] have determined various thermodynamic parameters for vaporisation in the $NaF–ZrF_4$ system, where, in addition to the simple species NaF and ZrF_4, the vapour also contains Na_2F_2 and $NaZrF_5$ species. The enthalpy of their dissociation into the component species NaF and ZrF_4 had the values 54.9 ± 2.2 kcal mole^{-1} for Na_2F_2 and 62.2 ± ± 4.6 kcal mole^{-1} for $NaZrF_5$. The use of mass-spectrometry should undoubtedly be extremely fruitful in studying the vapour composition of individual substances and also of more complex systems and solutions, not only at high temperatures but also at moderate and ordinary temperatures, particularly in examining association and chemical interaction in vapours.

Here we have given results from only a few of the papers devoted to the study of high-temperature vapours [2]. We have not dealt with the study of the structure of species in the vapour phase [2,28] or, in particular, with the work of Akishin and coworkers [90,91], which occupies a leading position in this field. Of the thermodynamic relationships for vaporisation, we have not considered the conclusions [1,2] reached by assuming that the entropy change is constant both for the volatilisation of different species and for corresponding dissociation processes of dimeric and more complex species. These assumptions make it possible to express approximately, in simple form, the relationship between temperature, the heat of the process, and the equilibrium pressure in processes of dimerisation, polymerisation, sublimation, and volatilisation. However, the limits of applicability of these relationships have not yet been adequately defined.

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HALIDES OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

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