FOREWORD

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ABSTRACT

Thermodynamic equations characterizing the chemical stability of heteronuclear diatomic molecules AB are presented. These equations permit one to predict the conditions in which yet unknown molecules can be observed. The chemical stability of the transition element chalcogenides is discussed.

A similarity in trend of the heat of vaporization of transition elements, the lattice energy and the dissociation energy of their chalcogenides is pointed out. AB molecules can be classified in groups for which the value of the ratio

$$\alpha = \Delta H^{\circ}\left[\text{at.AB}_{\text{solid}}\right] / D^{\circ}\ (\text{AB})$$

is characteristic. This parameter is important for predicting the chemical stability and available values are reviewed.

This technical documentary report has been reviewed and is approved.

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INTRODUCTION

The object of the present paper is to extend to heteronuclear diatomic molecules, symbolized by AB, considerations previously given for homonuclear diatomic molecules M_2 [1]. In addition to the usual concept of the stability of a given diatomic molecule, i.e., its dissociation energy, which is a measure of the bond strength of this molecule and which was called the "physical stability", a "chemical stability" was defined which is related to the possibility of observing this molecule. For homonuclear diatomic molecules, the chemical stability was defined as a free energy change which gives a measure of the relative concentration of diatomic to monoatomic species in thermodynamic equilibrium with the solid or liquid phase. This chemical stability was shown to depend on the parameter $\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2)$, which was correlated with the electronic structure of the ground state of the free atom and the atomic number; $\Delta H_o^o(\text{vap.M})$ is the heat of vaporization of the monoatomic species and $D_o^o(M_2)$ the dissociation energy of the diatomic molecule. Further, for the transition elements a correlation was given between $\Delta H_o^o(\text{vap.M})$ and the excitation energy of the free atom to well defined low lying electronic states [1,2].

In this paper, the chemical stability of AB molecules will be defined and again special focus will be put

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on certain molecules of the transition elements. It has been pointed out by Krikorian[3] that the bonding energies of solid carbides, silicides, nitrides and oxides of the transition elements follow a trend similar to that of the heats of vaporization of the elements. It is shown here that this is also the case for gaseous monoxides of the transition elements. Finally a parameter $\alpha = \Delta H^{\circ}(at.AB)/D^{\circ}(AB)$ similar to the one defined previously for homonuclear diatomic molecules appears to be important for the classification of the chemical stability of AB molecules; $\Delta H^{\circ}(at.AB)$ is the energy required to transform one half molecule gram of solid AB compound into atoms and $D^{\circ}(AB)$ the dissociation energy of the gaseous AB molecule. The available α values are reviewed.

THE CHEMICAL STABILITY OF AB MOLECULES.

In the case of homonuclear diatomic molecules, the highest concentration of M_2 molecules relative to M atoms is obtained in the saturated vapor. It was therefore proposed to define the "chemical stability" of M_2 molecules as the free energy change ΔG_T° corresponding to the equilibrium

$$M + (M) \rightleftarrows M_2$$

$$\Delta G_T^{\circ} = -RT \ln p(M)/p(M_2) = D_o^{\circ}(M_2) - \Delta H_o^{\circ}(vap.M) - T\Delta\{-G_T^{\circ}-H_o^{\circ}/T)\}_{\{(M)+M-M_2\}}$$

$$= \Delta H_o^{\circ}(vap.M)\{(1-\alpha)/\alpha\} - T\Delta\{-(G_T^{\circ}-H_o^{\circ}/T)\}_{\{(M)+M-M_2\}}$$

Square bracketts ( ) denote the condensed phase, symbols without bracketts are used for gaseous species. In a similar manner it is now proposed that the chemical stability of a heteronuclear diatomic molecule be defined as some measure of the concentration of AB molecules above condensed (AB) relative to the most abundant of the other gaseous species. Therefore its definition will depend on the vaporization process of (AB). In addition to the process leading to AB molecules

$$(AB) \rightleftarrows AB \qquad (0)$$

four other processes will be considered

$$(AB) \rightleftarrows A + B \qquad (1)$$

$$(AB) \rightleftarrows (A) + B \qquad (2)$$

$$(AB) \rightleftarrows A + 1/2\ B_2 \qquad (3)$$

$$(AB) \rightleftarrows (A) + 1/2\ B_2 \qquad (4)$$

Besides these four processes a comprehensive list should comprise numerous other modes of vaporization such as the formation of stoichiometric or non-stoichiometric solid compounds A_xB_y, solutions or alloys; solids andliquids should be distinguished; higher polymeric species than B_2 and AB as well as gaseous molecules A_xB_y should also be considered. The detailed discussion of these cases will not be given as the relevant equations may be found easily using the same principles as applied here.

For the simplest decomposition process (process(1)), the chemical stability of AB is obtained by combining reactions

(0) and (1) yielding the evaporation equilibrium

$$AB \rightleftarrows 1/2(AB) + 1/2\ A + 1/2\ B$$

for which the free energy change given in Table I is related to the relative abundance of AB molecules and is taken as its chemical stability. A similar treatment of processes (2), (3) and (4) lead to the evaporation equilibria and chemical stabilities given in Table I. As the change in free energy function $-\{(G^{\circ}_T-H^{\circ}_o)/T\}$ in all the evaporation equilibria is not very considerable, the chemical stability is mainly determined by the enthalpy change (except at very high temperature). Further, Table I (enthalpy conditions) gives the conditions for the predominance of respectively process 2, 3 or 4 compared to process 1, using for the sake of simplicity in the table, again the approximation which consists in neglecting the entropy term. Thus the condition $\Delta H^{\circ}_o(1\therefore 2)=\Delta H^{\circ}_o(\text{vap.A})-\Delta H^{\circ}_o(\text{at.AB})>0$ means that process (2) is predominant compared to (1); the condition $\Delta H^{\circ}_o(1\therefore 3)= D^{\circ}_o(B_2)-\Delta H^{\circ}_o(\text{at.AB})>0$, that process (3) is predominant compared to (1), and so forth, or vice versa if the corresponding $\Delta H<0$. Further due to these conditions, the chemical stability for a given $\Delta H^{\circ}_o(1)$ value is the largest for process (1) and the smallest for process (4).

A distinction, important in practice for heterogenous equilibria, results from the predominance of the enthalpy terms in $\Delta G^{\circ}_T(1)$, (2), (3) and (4). If the corresponding $\Delta H>0$

high concentrations of AB will be found at low temperatures and, as in homogeneous dissociation equilibria, the relative concentration of AB will decrease with increasing temperature. For $\Delta H>0$ the concentration will be low at low temperature and will increase with temperature, as has already been pointed out for dimers of halides by Brewer[4] and for homonuclear diatomic molecules[1]. The former may be called "low temperature molecules", the latter "high temperature molecules". For homonuclear diatomic molecules the distinction appears as $\alpha<1$ or $\alpha>1$. For heteronuclear molecules in case 1 (Table I), $\Delta H_o^o(1) = \Delta H_o^o(\text{at.AB})(1-\alpha)/\alpha$ and the two types of molecules are distinguished in the same manner. For cases 2-4 if $\alpha>1$, AB is also necessarily a high temperature molecule; $\Delta H_o^o(2)$ or (3) or (4) may however be smaller than 0 even if $\alpha<1 (\Delta H_o^o(1)>0)$.

A simple and useful approximation and a satisfactory general picture of the chemical stability, i.e., of the experimental possibilities of observing a given molecule, is obtained from a plot of $\Delta H^o(\text{at.AB})$, $\Delta H^o(\text{vap.A})$, $D^o(B_2)$ and $D^o(AB)$ as shown as an example in fig.1 to 4, for the first row of transition element oxides, sulfides, selenides and tellurides. Of course free energy plots give a more accurate picture and the exact concentration ratios; in that case however sets of plots for each temperature would be necessary.

Since the reduction to 0°K is uncertain in many

cases the practically equivalent values for 298°K are given. Also the $D^{\circ}(AB)$ values even for gaseous oxides are not all as reliable and accurate as would be desired. For the purpose of this paper an estimation of $D^{\circ}(AB)$ values for some transition elements chalcogenides was made on the basis of a parallel trend in D° values for oxides, sulfides, selenides and tellurides.

Where the $\Delta H^{\circ}(at.AB)$ curve in fig.1-4 lies above the $\Delta H^{\circ}(vap.AB)$ and $D^{\circ}(B_2)$ curve process (1) occurs rather than (2), (3) or (4), and this is, as easily seen, most favorable for observing gaseous AB molecules. Therefore for gaseous oxides of Sc, Ti and V the relative concentrations will be highest; those of Ca, Cr and Mn are considerably less stable partly due to the fact that the dissociation equilibrium of oxygen is shifted towards O_2. A relatively favorable situation was expected for CaS and MnS, due to the low value of $\Delta H^{\circ}(vap.A)$; this was confirmed by a mass spectrometric study [18]. TiS[17] has also been observed. It would be of interest to check the presence of ScS and VS. For the selenides and tellurides, the chemical stability is usually very low. It seems very improbable that the gaseous molecules can be observed with the methods presently available, except perhaps CaSe, CaTe, ScSe, ScTe and MnSe. The gaseous group IV_B-group VI_B molecules are stable[14].

Representation similar to fig.1 to 4 can easily be made for

other groups of compounds. Heats of vaporization are reasonably well known for all elements, as well as the dissociation energies of homonuclear diatomic molecules B_2, as far as their presence has to be considered here. Standard heats of formation for many simple compounds are known, making data on ΔH°(at.AB) available in many cases.

It is also easy to see from such representations that in some instances conditions for studying given types of molecules may be improved by changing the activity of a component by forming an alloy or by maintaining gaseous components at pressures different of the equilibrium decomposition pressure (oxidizing or reducing conditions).

THE PHYSICAL STABILITY OF TRANSITION ELEMENT OXIDES.

The similarity in trend of the heat of vaporization of transition elements, of the heat of atomization of the solid AB compounds and the dissociation energies of the gaseous oxides appeared in figs.1 to 4. On the other hand, the highly irregular trend of the heats of vaporization of transition elements especially in the first transition period disappears and a practically smooth curve is obtained[1,2] from Ca to Cu if, instead of the heat of vaporization to atoms in the ground state, the heat of vaporization to a promoted configuration is represented. This promoted configuration includes d^n, $d^{n-1}s$ and $d^{n-2}sp$ states where n is the difference between the atomic number Z of the element and the

atomic number of the preceding rare gas. Therefore, it appears that these states play an important part not only in the bonding of the pure elements but also in the solid and gaseous compounds of these elements. It is beyond the scope of this paper to draw further conclusions from this fact. It is believed however that these considerations may form a basis for a more thourough theoretical treatment.

THE RATIO OF HEAT OF ATOMIZATION OF SOLID AND GASEOUS AB COMPOUNDS

It has been mentionned above that the quantity $\alpha = \Delta H_o^o(at.M)/D_o^o(M_2)$, which appeared to be important parameter for the classification of homonuclear molecules[1] has a parallel for the heteronuclear diatomic AB molecules in the quantity $\alpha = \Delta H_o^o(at.AB)/D_o^o(AB)$. Here again the values of α fall into different categories (Table II):

1) the smallest values of $0.5<\alpha<1$ are found for the molecules where A and B are a group IV and a group VI or a group III and a group VII elements. These molecules are isosteric with group V homonuclear molecules and the values of α of these isosteric molecules show a close relationship.

2) it is interesting to note for the typically ionic alkali halides $\alpha = 0.76$ is practically constant, although some trends appear. Qualitatively this is easily understood by an ionic model; accurate calculations could of course be made only by solving the well known difficulties about the

exact shape of the "repulsive" interaction. For I_B halides α is somewhat larger but still in general <1.

Thus the molecules isosteric with group V and the ionic molecules are definitely "low temperature molecules". Most other AB molecules seem to have value of $\alpha>1$. This is the case for the halides HgX for which α = 1.24; 1.53; 1.95 and 3.94 is found. For the only known III_B/V_B molecule InSb α = 1.9 (for the isosteric Sn_2 molecule: α = 1.5) and high values of α are the reason why other molecules of this group as well as II/VI could not be observed.

3) again it is interesting to note the values of approximately 1 or more for the transition metal oxides with a smooth increase from TiO and NiO, CuO seems to be a low temperature molecule. However the dissociation energy is uncertain[8]. For the two known transition metal sulfides, the α values are higher than those of the corresponding oxides.

4) an increase in α when going from oxides to sulfides appears also for the II_A molecules for which $\alpha>1$ with the exception of BaO.

OUTLOOK

The use of the definition of the chemical stability has already facilitated the search for certain previously unknown molecules. In numerous cases reasonably satisfactory predictions can be made as to the possibility and experimental conditions in which such molecules may be found; estimates

of entropies must of course be included. The temperature dependence of the chemical stability can be foreseen and as has been shown earlier can be changed systematically if convenient for the aimed object[23].

These considerations can also be easily extended to polyatomic molecules. Dimers or polymers of molecules can be treated in a similar manner to dimers of elements[24].

The main point in all these cases is that since the highest concentrations of gaseous molecules as compared to dissociation products are observed at the highest pressures, the chemical stability is defined in the saturated vapor. At a given temperature therefore, pressure is not an independent variable and the chemical stability is given by a pressure ratio.

Finally, the interesting parallelism between heats of atomization of solids and dissociation energies of gaseous molecules as expressed by the α values are valuable in using the thermodynamic equations given and may be accessible to fundamental theoretical considerations. In fact, such regularities exist also for polyatomic molecules and for polymers. A similarity in trend was observed recently[26] between the dissociation energies of the oxides of the lanthanides and the vaporization energies of the corresponding elements. As for the transition elements, minima were observed for the half filled and totally filled f shell.

TABLE I. CHEMICAL STABILITY OF AB MOLECULES

Main Evaporation Process	Evaporation Equilibrium	Chemical stability*	Enthalpy conditions
1. $(AB) \rightleftarrows A+B$	$AB \rightleftarrows \frac{1}{2}(AB)+\frac{1}{2}A+\frac{1}{2}B$	$\Delta G_T^o(1)=-RT\ln p(B)/p(AB$ $=\Delta H_o^o(1)-T\Delta\{-(G_T^o-H_o^o/T)\}(1)$ $\Delta H_o^o(1)=D_o^o(AB)-\Delta H_o^o(at.AB)$	
2. $(AB) \rightleftarrows (A) +B$	$AB \rightleftarrows (A)+B$	$\Delta G_T^o(2)=-RT\ln p(B)/p(AB)$ $=\Delta H_o^o(2)-T\Delta\{-(G_T^o-H_o^o/T)\}(2)$ $\Delta H_o^o(2)=\Delta H_o^o(1)-\Delta H_o^o(1\therefore 2)$	$\Delta H_o^o(1\therefore 2=\Delta H_o^o(vapA)-\Delta H_o^o(atAB)>0$
3. $(AB) \rightleftarrows A+\frac{1}{2}B_2$	$AB \rightleftarrows \frac{1}{3}(AB)+\frac{2}{3}A+\frac{1}{3}B_2$	$\Delta G_T(3)=-RT\ln p2^{\frac{2}{3}}p(B_2)/p(AB)$ $=\Delta H_o^o(3)-T\Delta\{-(G_T^o-H_o^o/T)\}(3)$ $\Delta H_o^o(3)=\Delta H_o^o(1)-\frac{1}{3}\Delta H_o^o(1\therefore 3)$	$\Delta H_o^o(1\therefore 3)=D_o^o(B_2)-\Delta H_o^o(atAB)>0$
4. $(AB) \rightleftarrows (A)+\frac{1}{2}B_2$	$AB+(AB) \rightleftarrows 2(A)+B_2$	$\Delta G_T^o(4)=-RT\ln p(B_2)/p(AB)$ $=\Delta H_o^o(4)-T\Delta\{-G_T-H_o^o/T)\}(4)$ $\Delta H_o^o(4)=\Delta H_o^o(1)-\Delta H_o^o(1\therefore 3)-2\Delta H_o^o(1\therefore 2)$	$\Delta H_o^o(1\therefore 2)+\Delta H_o^o(1\therefore 3)>0$ $3\Delta H_o^o(1\therefore 2)+2\Delta H_o^o(1\therefore 3)>0$

*The equations are written for congruent vaporization; therefore
in (1) $p(B) = p(A)$
and in (3) $p(A) = 2p(B_2)$

TABLE II

α value for known AB molecules

$$\alpha = \Delta H^{\circ}_{298}(\text{at.AB})/D^{\circ}_{298}(AB)^{*}$$

1. Molecules isosteric with Group V

V/V		IV/VI		III/VII	
N_2	0.50	CO	0.50	BF	0.51
		SiO	0.72	AlF	0.54
P_2	0.70	GeS	0.65		
		SiS	0.72		
As_2	0.77	SnS	0.74	InCl	0.64
		CeTe	0.75	GaBr	0.66
		SnSe	0.77		
		SnO	0.80		
		PbO	0.85	InBr	0.74
Sb_2	0.87	SnTe	0.83	InI	0.69
		PbS	0.83	TiCl	0.70
		PbSe	0.87	TiBr	0.75
		PbTe	1.07	TLI	0.82
Bi_2	1.1				

2. Group I_A and I_B halides

	F	Cl	Br	I
Li	0.74	0.71	0.74	0.80
Na	0.85	0.78	0.79	0.85
K	0.74	0.77	0.78	0.81
Rb	0.71	0.74	0.72	0.80
Cs	0.68	0.75	0.72	0.82
Cu	1.14	0.81	0.85	-
Ag	-	0.89	0.86	0.91
Au	-	0.96	-	-

3. Transition element

Oxides		Sulfides	
ScO			
TiO	0.94	TiS	1.04
VO	0.95		
CrO			
MnO	1.19	MnS	1.41
FeO	1.20		
CoO			
NiO	1.27		
CuO	0.85		

4. Group II_A

Oxides		Sulfides	
BeO	1.32	BeS	-
MgO	1.42	MgS	≥1.68
CaO	1.36	CaS	1.54
SrO	1.17	SrS	1.45
BaO	0.95	BaS	1.19

* $\Delta H^{\circ}_{298}(\text{at.AB})$ values were calculated from heats of formation given by Kubaschewski and Evans[5] and Freeman[13]. Heats of vaporization of (A) were taken from Part I[1]. Dissociation energies and heats of vaporization of B_2 halides were taken from Stull and Sinke[7] The best available value for $D^{\circ}_{298}(AB)$ were selected from Gaydon[8] and Herzberg[25]. Group IV-group VI AB molecules have been reviewed by Colin and Drowart[14].

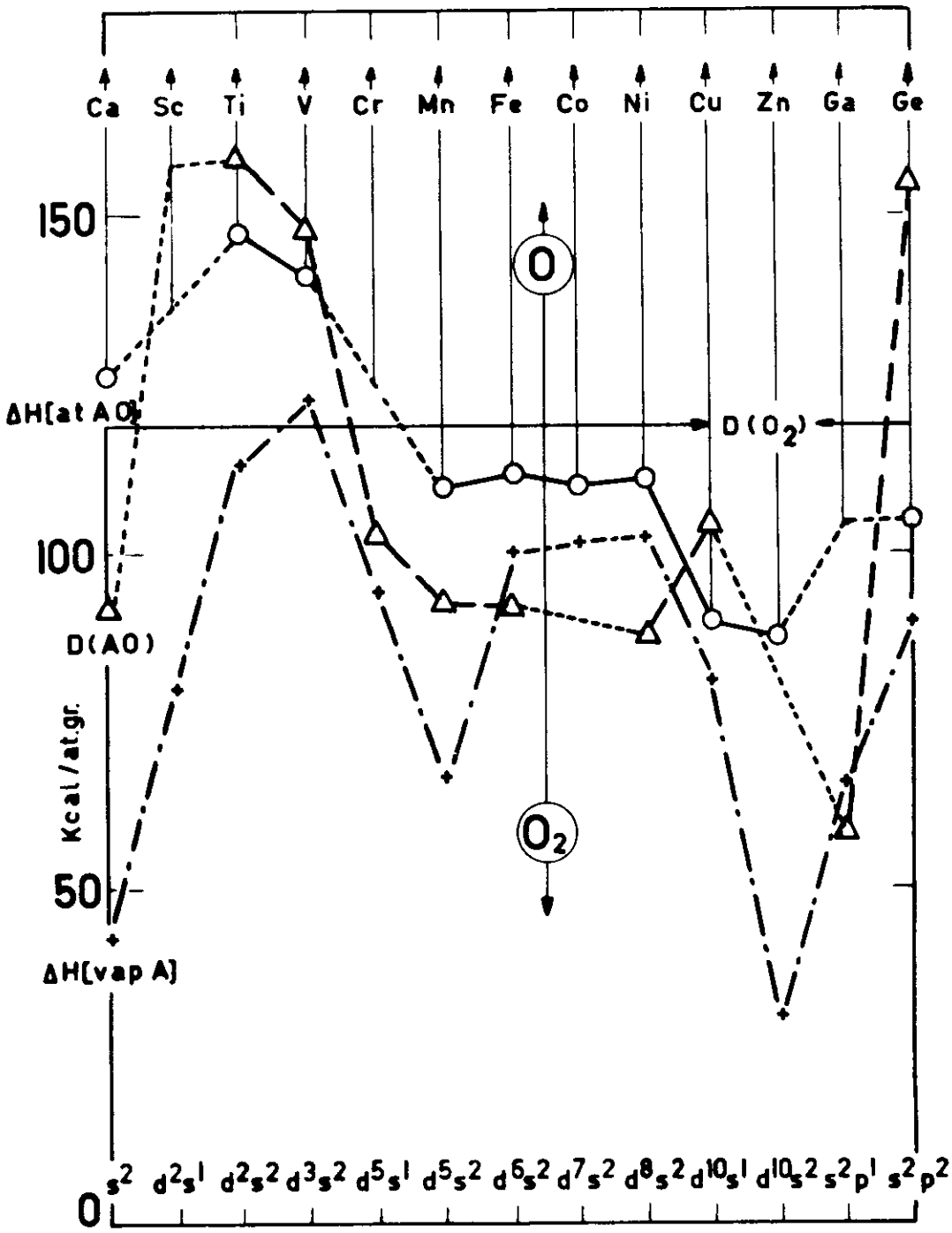

Fig.1 Chemical Stability of Transition Metal Oxides

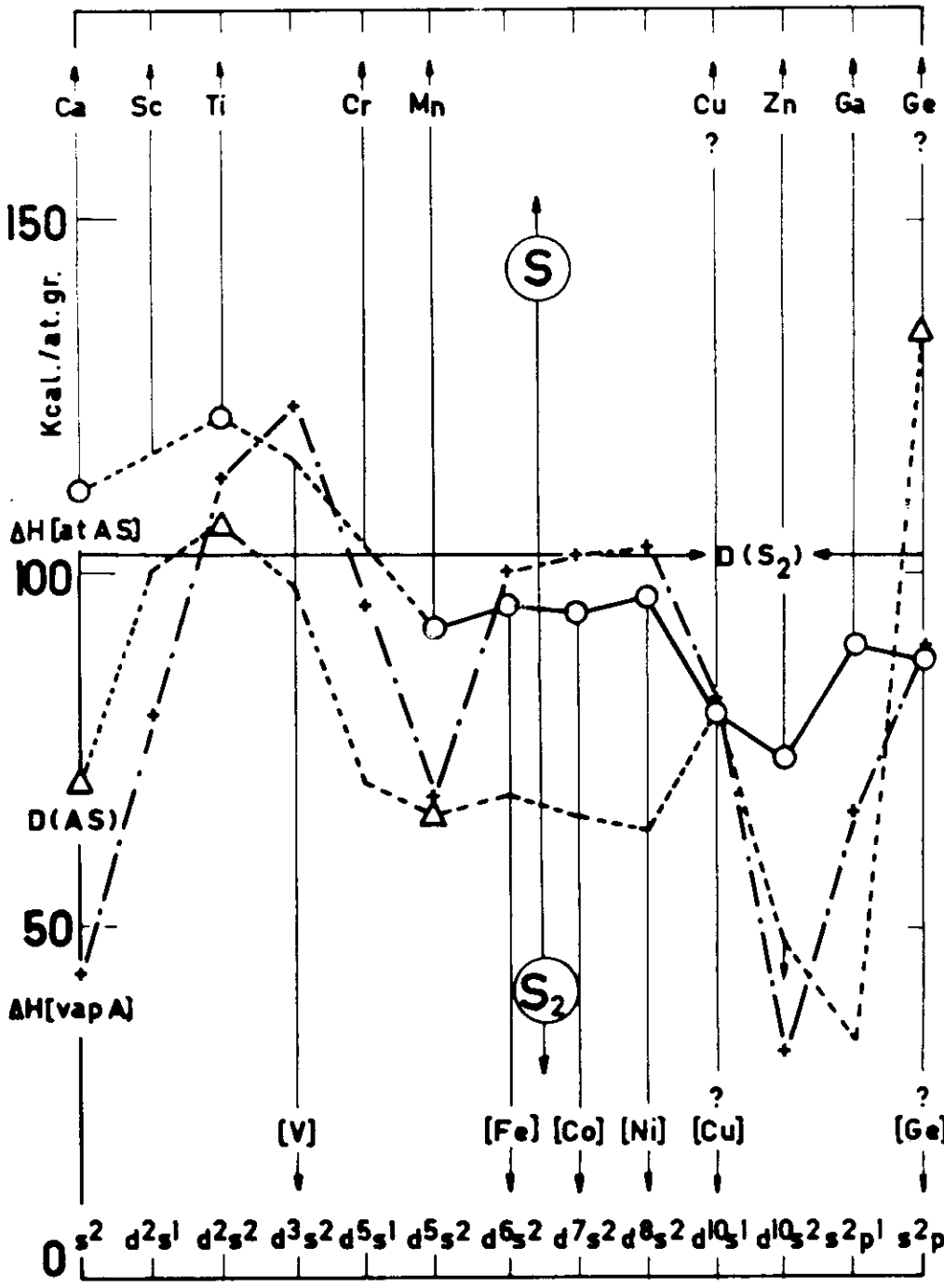

Fig.2 Chemical Stability of Transition Metal Sulfides

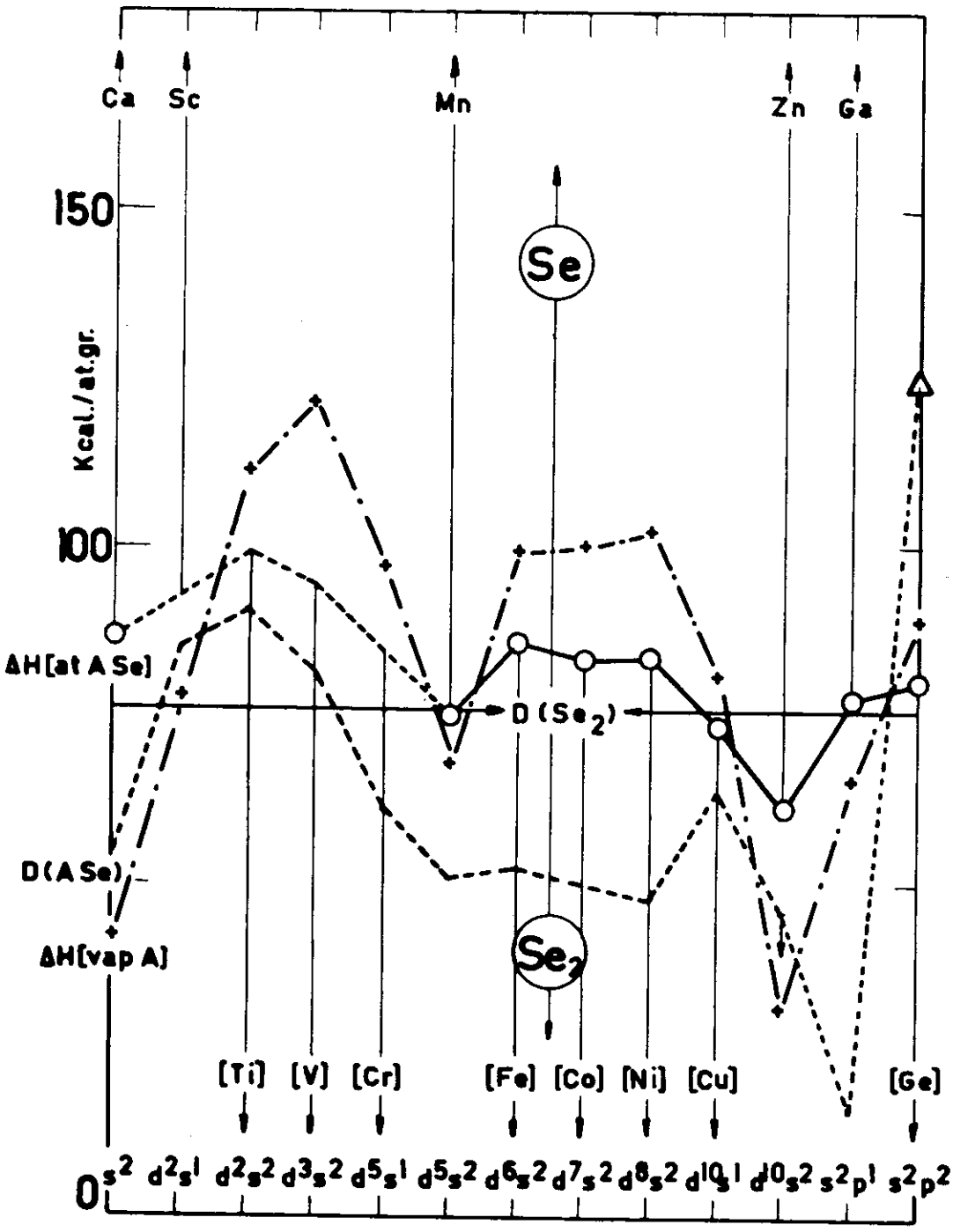

Fig.3 Chemical Stability of Transition Metal Selenides

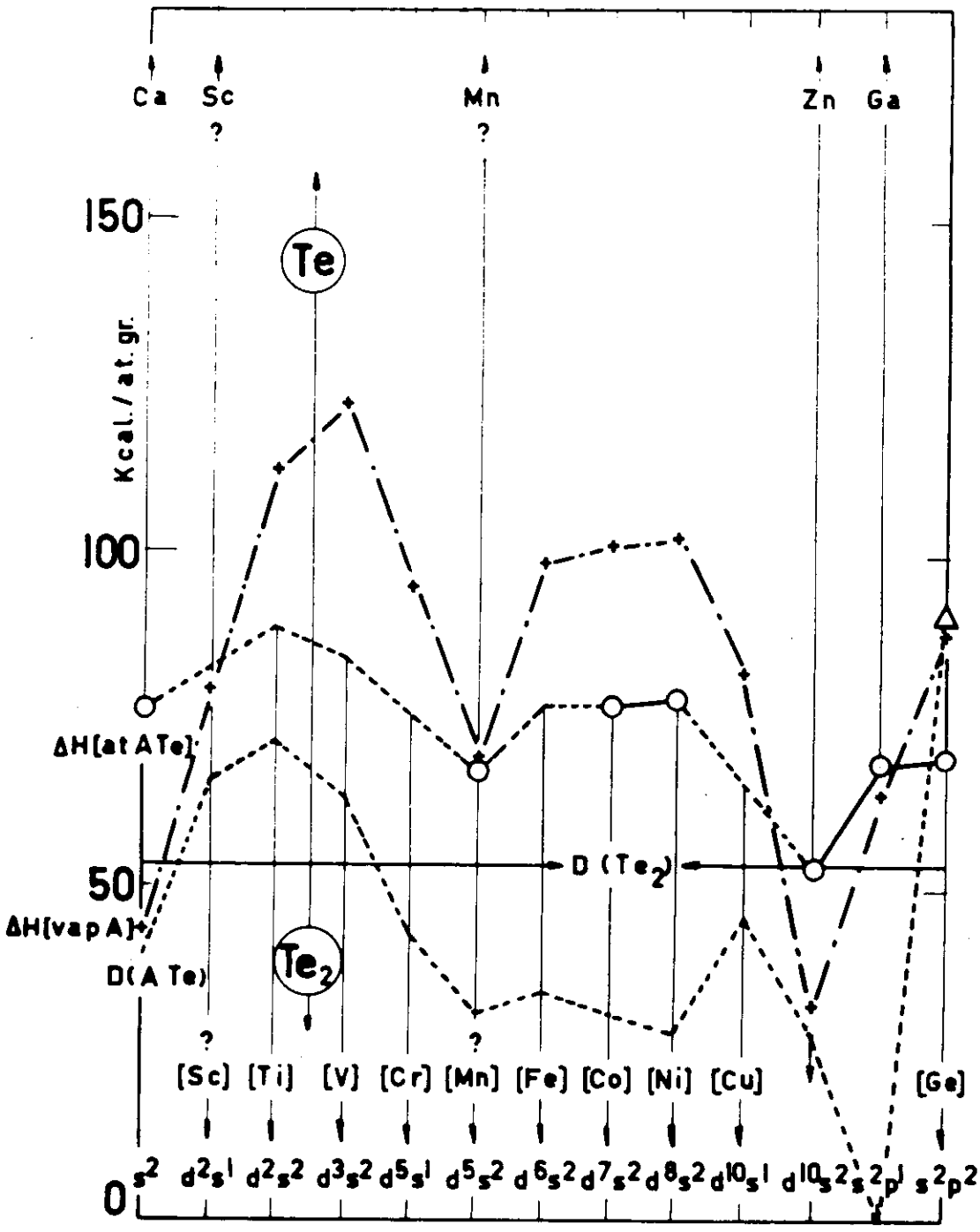

Fig.4 Chemical Stability of Transition Metal Tellurides

Legend to fig.1, 2, 3 and 4.

Fig.1 Chemical Stability of Transition Metal Oxides

$\Delta H^{\circ}_{298}(\text{at.AO}) = \frac{1}{2}\{-\Delta H^{\circ}_{298f}(\text{AO}) + \Delta H^{\circ}_{298}(\text{vap.A}) + \frac{1}{2}D^{\circ}_{298}(O_2)\}$

ΔH°_{298f} values were all taken from Kubaschewski and Evans[5], except that of (GeO)[6]; $D^{\circ}_{298}(O_2) = 119.10 \pm 0.05$ kcal/mole[7]; ΔH°_{298}(vap.A) were taken from Part I[1]; D°_{298}(AO) for ScO, MnO, FeO, CuO and GaO are those given by Gaydon[8]; $D^{\circ}_{298}(CaO)$[9]; $D^{\circ}_{298}(TiO)$ and $D^{\circ}_{298}(VO)$[10] $D^{\circ}_{298}(CrO)$[11]; $D^{\circ}_{298}(NiO)$[12]; $D^{\circ}_{298}(GeO)$[6].

Fig.2 Chemical Stability of Transition Metal Sulfides

$\Delta H^{\circ}_{298}(\text{at.AS}) = \frac{1}{2}\{-\Delta H^{\circ}_{298f}(\text{AS}) + \Delta H^{\circ}_{298}(\text{vap.A}) + \frac{1}{2}\Delta H^{\circ}_{298}(\text{vap.}S_2) + \frac{1}{2}D^{\circ}_{298}(S_2)\}$

ΔH°_{298f} values were all taken from Freeman[13], except that of (GeS)[14]; $\Delta H^{\circ}_{298}(\text{vap.}S_2) = 30.8 \pm 1.5$ kcal/mole[7]; $D^{\circ}_{298}(S_2) = 102.0 \pm 2.0$ kcal/mole[13,15,16]; $D^{\circ}_{298}(CaS)$[15]; $D^{\circ}_{298}(TiS)$[17]; $D^{\circ}_{298}(MnS)$[18]; $D^{\circ}_{298}(ZnS)$[19]; $D^{\circ}_{298}(GeS)$[14]

Fig.3 Chemical Stability of Transition Metal Selenides

$\Delta H^{\circ}_{298}(\text{at.ASe}) = \frac{1}{2}\{-\Delta H^{\circ}_{298f}(\text{ASe}) + \Delta H^{\circ}_{298}(\text{vap.A}) + \frac{1}{2}\Delta H^{\circ}_{298}(\text{vap.}Se_2) + \frac{1}{2}D^{\circ}_{298}(Se_2)\}$

ΔH°_{298f} values were all taken from Kubaschewski and Evans[5] except that of (GeSe)[14]; $\Delta H^{\circ}_{298}(\text{vap.Se}) = 34.1 \pm 1.5$ kcal/mole[7]; $D^{\circ}_{298}(Se_2) = 75.4 \pm 2.0$ kcal/mole[20]; $D^{\circ}_{298}(ZnSe)$[19]; $D^{\circ}_{298}(GeSe)$[14].

Fig.4 Chemical Stability of Transition Metal Tellurides.

$$\Delta H^{\circ}_{298}(\text{at.ATe}) = \frac{1}{2}\{-\Delta H^{\circ}_{298f}(\text{ATe}) + \Delta H^{\circ}_{298}(\text{vap.A}) + \frac{1}{2}\Delta H^{\circ}_{298}(\text{vap.Te}_2) + \frac{1}{2}D^{\circ}_{298}(\text{Te}_2)\}$$

ΔH°_{298} values were all taken from Kubaschewski and Evans[5] except that of (GeTe)[14]; $\Delta H^{\circ}_{298}(\text{vap.Te}_2) = 39.6 \pm 1.5$ kcal/mole[7]; $D^{\circ}_{298}(\text{Te}_2) = 52.2 \pm 2.0$ kcal/mole[21,22]; $D^{\circ}_{298}(\text{ZnTe})$[19]; $D^{\circ}_{298}(\text{GeTe})$[14].

REFERENCES

(1) G. Verhaegen, F.E. Stafford, P. Goldfinger and M. Ackerman, Trans. Faraday Soc, 478, 1926 (1962).

(2) J.S. Griffith, J. Inorg. Nucl. Chem.,3, 15 (1956).

(3) O. Krikorian, University of California U.C.R.L. 9688 (1955).

(4) L. Brewer, Natl. Nucl. Energy Series, div.4, Vol.19B p.261 (1946) (McGraw Hill).

(5)O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry", (Pergamon Press, New York 1958).

(6) R. Colin, F. De Grève, J. Drowart and G. Verhaegen, to be published.

(7) D.R. Stull and G.C. Sinke, "Thermodynamic Properties of the Elements", Adv. Chem., 18 (1956).

(8) A.G. Gaydon, "Dissociation Energies", 2nd ed.(revised) (Chapman and Hall Ltd, London 1953).

(9) J. Drowart, G. Exteen and G. Verhaegen, to be published.

(10) R.J. Ackermann and R.J. Thorn, "Vaporization of Oxides" in "Progress in Ceramic Science", Vol.1 (Pergamon Press) New York 1961.

(11) R.T. Grimley, R.P. Burns and M.G. Inghram, J. Chem. Phys. 34, 664 (1960).

(12) R.T. Grimley, R.P. Burns and M.G. Inghram, J. Chem. Phys. 35, 551 (1961).

(13) R.D. Freeman, "Thermodynamic Properties of Binary Sulfides", Research Foundation Report n°60, Oklahoma State University 1962.

(14) R. Colin and J. Drowart, to be published.

(15)R. Colin, M. Jeunehomme and P. Goldfinger, Nature 187 408 (1960).

(16) D.G. Marsden, J.Chem.Phys.,31, 1144 (1959).
L. Brewer, J.Chem.Phys.,31, 1143 (1959).

(17) P.W. Gilles, private communication.

(18) R. Colin, M. Jeunehomme and P. Goldfinger, Nature 194, 282 (1962).

(19) M. Jeunehomme and P. Goldfinger, to be published.

(20) This laboratory, unpublished work.

(21) R.F. Porter, J. Chem. Phys.,34, 583 (1961).

(22) R. Colin, Ind.Chim.Belg.,26, 51 (1961).

(23) J. Drowart and P. Goldfinger, J.Chim.Phys.,55, 721 (1958).

(24) R. Colin and J. Drowart, J.Chem.Phys.,37, 1120 (1962).

(25) G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co Inc., Princeton, New Jersey, 2nd ed.(1950).

(26) D. White, P.N. Walsh, L.L. Ames and H.W. Goldstein, private communication.