

CHEMISTRY OF HIGH TEMPERATURE SPECIES AT LOW TEMPERATURE

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Hydrocarbon positive ions in low temperature media, such as liquid argon and liquid xenon, are particularly fascinating species. We have found that in concentrations of a percent or less, methane readily polymerizes when a solution in liquid argon is irradiated with cobalt 60 gamma radiation. It forms a polymer with general formula of $C_{20}H_{40}$ which is very similar to that found earlier in solid methane at liquid nitrogen temperatures. (1)

It is our present suggestion (2) that the mechanism of polymerization may involve the Auger transition in the argon atom, i.e. the polymer is formed only when an inner electron in argon is ionized. The resulting explosion caused by successive Auger transitions would produce a congregation of positive argon ions in the immediate vicinity of the original point of internal level excitation and each of the ions would then be neutralized by electron transfer from methane solute since the argon ionization potential is higher. Thus about 20 methane ions would be produced within a radius of a few 10's of Angstroms of the original site. The subsequent neutralization of these ions by electrons being a fast or vertical process (in the sense of the Franck-Condon Principle) would cause dissociation of the methane to form radicals and fragments such as CH, CH_2 and CH_3 . These then would subsequently recombine for there would be little else for them to do. This theory is still under experimental test. We are studying the effects on the isotopic composition of the polymer versus

that or the other principal product ethane, and we are further studying the small effect of diluting the methane on the molecular weight of the polymer.

The ability of hydrocarbon ions to react at low temperatures in the presence of ionizing gamma radiation has been well known for a long time in that the hardening of the plastic polymer polyethylene by gamma rays has been well studied. It is our present belief that this too is an ionic process in most part.⁽³⁾ Though once again, to say that the proof is complete would be an exaggeration. It would seem on balance that at low temperatures ionic processes may be dominant and that at ordinary temperatures they are very, very important in radiation chemistry in general.

Part B Carbon Vapor at Low Temperature

Our studies of the chemical reactions of carbon vapor with cold benzene and with diamond surfaces will be discussed. It is clear that carbon atoms are able to react with benzene even at 77°K. It is not certain that trace amounts of oxygen may not be involved in a critical way also.

Our attempts to prepare to grow diamonds by evaporating carbon vapor on to seed diamonds under high vacuum conditions will be described and any progress towards this goal discussed. It seems clear that the quality of the vacuum may be all important in this process. We indeed are using this as an example of the possible chemical value of the extremely high vacua that are attainable in the space chambers in the aerospace industry and in the laboratories such as Jet Propulsion Laboratory and, of course, in orbiting satellites. It seems to

us that we should be able to develop a chemistry of surfaces, which has been highly inhibited because of air, if we take the pains to eliminate air and this may be a chemical benefit of the space environment.

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THE CHEMISTRY OF ATOMIC CARBON

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A decade ago it was still said that the chemistry of atomic carbon was the first page of the book of organic chemistry, and that that page was blank. But even in the late forties and early fifties there were already some markings on the page.¹ The present rapid development of the field started about 1961 when it was proposed that the basic reaction mechanisms of atomic carbon with hydrocarbons was by insertion into C-H and C-C bonds.^{2,3} That blank first page is now quite well filled in as far as the basic outlines are concerned.⁴

The reason that the study of atomic carbon came so late is that this species is so reactive that it is difficult to produce in controlled conditions. Now, however, at least four techniques have been used: nuclear recoil⁴, photochemistry⁵, evaporation from graphite^{6,7,8}, and laser flash.⁹ Other methods have also been demonstrated but will not be reviewed here.

Nuclear Recoil Techniques

Nuclear recoil was the first technique used and it has supplied the bulk and the backbone of what we know at present of atomic carbon.⁴ Radioactive carbon is produced by a nuclear reaction. For instance on simply irradiating C^{12} with high energy gamma rays (> 20 Mev) the following process occurs



The C^{11} as initially produced may possess a very large amount of kinetic energy (~ 100 kev). This is lost in successive collisions. When the energy of the atom falls into the chemical energy range below 100 eV it may react to combine. Labelled molecules are formed by this means and may be assayed by radiogase chromatography.

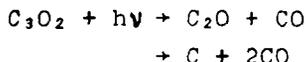
Considerations of atomic physics require, and experiment confirms, that as the carbon atoms reach the chemical energy range they are in a low-lying electronic state, either in 3P , 1D or 1S .^{10a,b} They may however react while they are still "hot",

i. e. have excess kinetic energy. This is rather an advantage, however, since one may control the energy of reaction by the use of moderators. In a system containing a large excess of a rare gas, essentially all reactions occur after the carbon atoms have been thermalized.

The nuclear method may be used with either C^{11} or C^{14} . However the half-life of C^{14} is so great that prolonged irradiation is required before enough is produced. This has led to serious difficulties with radiation damage effects. Most currently accepted data was obtained using C^{11} .

Photochemical Techniques

U.V. photolysis can be used to produce atomic carbon, e.g. with carbon suboxide.⁵



Atomic carbon is produced only if very short wave lengths ($\sim 1500 \text{ \AA}$) are used. This type of method has been employed both in the gas and solid phase. It is however severely restricted by the transparency of the medium to the needed radiation. For this reason methane is the only alkane whose reactions with atomic carbon have been studied by these means.

Evaporation Techniques

Several techniques have been developed in which carbon is evaporated from a heated graphite rod⁶, a carbon arc⁷, or an exploding filament⁸. The carbon vapor may be deposited on a surface on which it is allowed to react.

This technique tends to be restricted to the study of reactions of atomic carbon on solid surfaces. The interpretation of gas-phase reactions would present difficulties because of extensive pyrolysis and photolysis on the evaporating body.

Laser Flash Techniques

We have recently developed⁹ a variant of the evaporation technique in which a laser is used. A pulse is focused onto a carbon surface forming a small hot spot from which carbon evaporates. Reactions with a low-pressure gas can be studied because the hot spot is so small and short lived that extensive pyrolysis does not occur.

While the use of a laser flash represents an advantage in that reactions in the gas phase can be treated it still shares

with other evaporation techniques, the disadvantage that a range of carbon species C_1 , C_2 , C_3 etc. are formed.

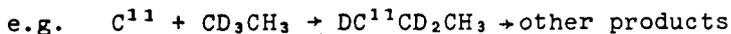
Comparison of Techniques

All techniques, though generally used under different conditions, tend to give very similar results in so far as a comparison can be made. However Skell has reported apparently significant differences in his evaporation techniques, which would tend to indicate that species of lower energy are involved⁷. In particular acetylene, a high energy product normally found when atomic carbon reacts with hydrocarbons is conspicuously absent when the particular method in question is used. This apparent discrepancy has not yet been resolved. One possible explanation¹⁰ stems from the fact that in this technique alone there is an appreciable delay between production and reaction of the carbon atoms. Conceivably this might allow complexing of the carbon atoms, reducing their reactivity, something that commonly happens to active species on aging in ordinary vacuums. Such complexed species could act as carbon atom donors, with reactions similar to but less energetic than those of free carbon atoms. Indeed a time dependence of reactivity is found in these experiments⁷, though this has been attributed to decay of spin states.

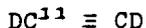
Summary of Findings

So much is now known of the reactions of atomic carbon that it is impossible to give a brief yet comprehensive review. Reactions with inorganic oxides¹¹, with nitrogen¹¹ and with hydrogen¹² are reviewed elsewhere. With hydrocarbons there are three principal modes of primary reactions.

1) Insertion into a C-H bond

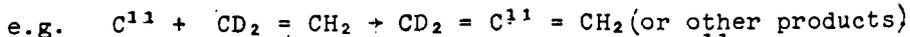


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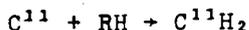
As expected the acetylene formed in such reaction with CD_3CH_3 is either $C^{11}D \equiv CD$ or $C^{11}H \equiv CH$ with little $C^{11}D \equiv CH$ being formed^{4a}.

2) Insertion into a C = C bond



As expected the allene formed by this reaction is C^{11} center labeled and has the hydrogen isotope distribution shown.^{4a}

3) Abstraction to form CH_2



Primary modes 1) and 2) yield an intermediate adduct which is highly excited due to the energy released in forming

the new bonds. The further fate of such complexes depends on their spin states and on how rapidly energy is moved by collisional deactivation. This topic is well understood and is fully discussed elsewhere.^{13,14}

Insertion in C-C and C-F bonds has not been observed. Instead in perfluorocarbons the dominant reaction appears to be abstraction to form C-F, fluoromethyne.⁹ The probable explanation for this pattern of primary insertion will be discussed.

Acknowledgement

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REACTIONS OF C₁, C₂, C₃, C₄

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Evaporation of graphite has been carried out producing the following species in proportions which vary with the method of vaporization and ageing.

C ₁	3 _p , 1 _p , 1 _s
C ₂	Triplet, Singlet
C ₃	Singlet, Triplet
C ₄	

The reactions of these species, with a range of substrates in condensed phase (low temperature) will be reported: alkanes, cycloalkanes, alkenes, alkynes, alcohols, aldehydes, ketones, epoxides, alkyl halides.

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Numerous examples of the carbene character of atomic carbon produced in a low intensity arc under high vacuum have recently been reported from this laboratory.

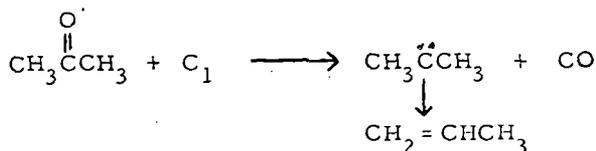
In an effort to find reactions of atomic carbon which might not be classified as normal carbene processes, the reactions of atomic carbon with carbonyl compounds were studied. The reaction of carbon atoms with acetone cocondensed on a liquid nitrogen cooled surface produced carbon monoxide and propylene in good yield (see Table I).

Table I

<u>Compound</u>	<u>Yield^a</u>
CO	59.6%
CH ₂ = CHCH ₃	54.2%

^a calculated as Mm product/MmC₁ vaporized

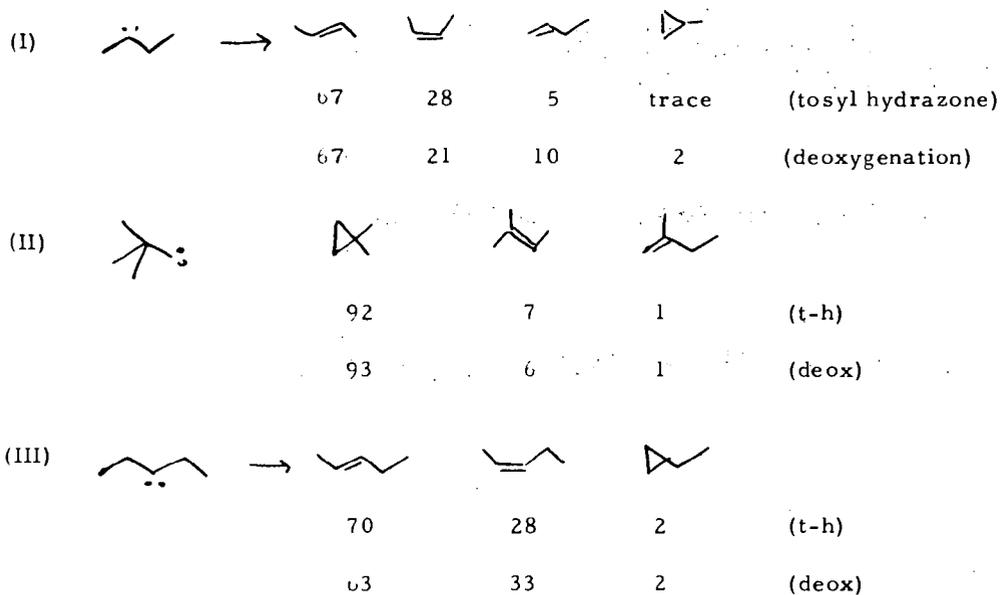
The production of Carbon monoxide and propylene in nearly equal amounts suggested the following reaction sequence:



If this scheme were operative, the reaction was novel deoxygenation process to produce the subvalent carbene species and would thus provide an opportunity to generate a wide variety of carbenes at low temperatures. To test the proposed scheme, the reaction of acetone with C¹⁴ enriched electrodes was examined. As

This method was found to be a general preparation of alkyl carbenes and the data gathered on product distribution from the deoxygenation method closely resemble those from tosyl hydrazone decompositions.

Three such comparisons are given below:



Thus, it appears that deoxygenation produces an intermediate very similar to the process generally assumed to be a carbene preparation. It is quite striking that the similarities between reaction at a liquid nitrogen cooled surface and a decomposition performed at $\sim 160^\circ$ are so great. We feel this indicates a low activation energy for the intramolecular, carbene reactions.

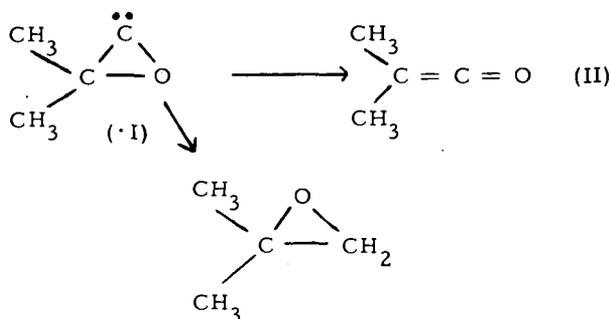
Deoxygenation was extended to other materials. It was observed that propylene oxide deoxygenated to propylene and carbon monoxide:

From the above data, we feel that oxygen abstraction is a convenient method for the generation of carbenes and radicals, free of complexing at low temperatures.

would be expected from the scheme, the propylene gave a molar activity 0.039 while the Carbon monoxide was found have a molar activity 0.91. This established that Carbon monoxide did indeed arise from a deoxygenation process involving C_1 and that the propylene was formed in a process not involving carbon from the electrodes.

As a second check, the reaction forming propylene should also be intramolecular if a carbene were involved since simple hydrogen transfer is all that is required for product formation. A mixture of acetone $d_6/d_o = 1.25$ was subjected to the reaction conditions and the resultant propylene analyzed by mass spectroscopy. The ratio propylene $d_6/d_o = 1.32$, confirming the intramolecular character of the process.

The dimer of the carbene, 2,3-dimethyl-2-butene, was not observed. This may be attributed to the relative rapidity of hydrogen transfer as opposed to the rate of diffusion of dimethyl carbene through the acetone matrix. It also appears that the process of Carbon atom insertion into carbon-carbon double bonds does not take place into carbonyl functions since such an adduct (I) would be expected to give either dimethyl ketene (II) or isobutylene oxide (III).



Neither of these products were formed.

RECENT SPECTROSCOPIC STUDIES OF HIGH-TEMPERATURE
MOLECULES

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ABSTRACT

Molecules that are important in high temperature studies of gases may be studied spectroscopically not only in absorption at high temperature but also in emission or absorption in electric discharges or their afterglows, or in absorption in flash photolysis of various parent compounds. Recent spectroscopic work on high-temperature molecules by all of these methods will be described. This work includes studies of diatomic hydrides (BH, AlH, CH, SiH,) of several homonuclear diatomic molecules and ions (H_2 , C_2 , C_2^- , N_2^+ , O_2 , Mg_2 , Si_2) and a few heteronuclear non-hydride molecules (BF, CF, NF, NCl, SO). A good deal of work on spectra of triatomic free radicals has been done and will be briefly described.

SPECTROSCOPY OF HIGH TEMPERATURE MOLECULES

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High temperature furnaces, flames, arcs, and similar sources of high excitation are the conventional sources of spectra of high temperature molecules. However, spectra from such sources are often difficult to resolve because of the high electronic, vibrational, and rotational excitation resulting in extensive overlapping of spectral bands. Excitation of impurity molecules increases the complications due to overlapping.

It is important to obtain complete analyses of the band systems of high temperature molecules to establish the spectroscopic constants needed for calculation of the high temperature thermodynamic properties. In particular the establishment of the degeneracies and energies of all low lying electronic states is very important.

The failure of conventional methods to produce the needed information has stimulated a variety of new approaches. This paper will discuss the potential advantages and handicaps of the new methods and will suggest other approaches.

A rather widely applied method in the last few years involves the entrapment of high temperature molecules in a rare gas or other inert matrices at liquid hydrogen or helium temperatures. This method offers a simplification of the analysis of the spectrum in that one would expect the entrapped molecules to be in their lowest electronic and vibrational states. The absorption spectrum of S_2 in a matrix is found to consist of a simple progression arising from the $v''=0$ level of the ground electronic state. When there are almost degenerate electronic states around the ground state energy, it is possible that interactions with the matrix might invert their order and thus indicate the incorrect gas ground state. A more severe disadvantage of matrix absorption spectra is the lack of sharpness and detail such that electronic spectra can not be unambiguously

identified without knowledge of the gas spectra. A most serious disadvantage of matrix absorption spectra is that information is not obtained for low lying electronic states.

Another fruitful approach to simpler high temperature spectra is through use of molecular beams from a Knudsen cell or some other high temperature source of vapor. During the typical transit times of 10^{-4} to 10^{-5} seconds, one would expect the excited electronic states to decay to the lowest state of each multiplicity for light molecules and to the ground state for heavier molecules for which the spin change prohibition is not rigid. Thus the molecular beam should provide simpler spectra. A variety of spectral measurements can be made on a beam. For example, electric-resonance and magnetic deflection experiments by Klumperman and his coworkers have been used to establish an O^+ ground electronic state for SrO and BaO. Also for triatomic and more complicated molecules, they have shown that electric-deflection experiments can be used to determine the symmetry of the molecules. The combination of a Stern-Jerlach experiment with a mass spectrometer detector offers to be a useful way of distinguishing singlet from triplet ground states or of determining the splitting of triplet ground states of heavier molecules. For example, Scarcy and Maschl have used this method to confirm that the 1 sublevel of the $^3\Sigma$ ground state of Te_2 lies so far above the O^+ sublevel that the beam of Te_2 shows no deflection. Optical absorption or fluorescent experiments may also be carried out on molecular beams. In this manner Brewer and Welch have established the ground state of LaO and Brewer and Green have shown that the lowest singlet and triplet states of ScF are virtually degenerate since both states persist in a molecular beam for longer than 10^{-4} sec. Although these various applications of molecular beams have been useful in establishing the very lowest electronic states, they do not provide information about the low-lying excited states which are important with respect to their contribution to the high temperature partition function since these states will have usually decayed in the

transit time of the beam.

There is a possibility of eliminating the limitation of absorption spectra of molecular beams and matrices through use of fluorescent spectra. By exciting to very high electronic states, one can observe cascading through the lower electronic states. The matrix spectra offer the advantage of relatively rapid vibrational deactivation and the fluorescent spectra often consist of simple progressions arising from the $v' = 0$ level of the upper electronic state. The matrix method offers the other advantage of enhancement of forbidden transitions which could allow the fixing of the energies of singlet and triplet states relative to one another. Meyer, Phillips, and Smith have applied this method recently to SO_2 .

A new method has been suggested that might be able to provide direct information about the energies of all of the low-lying electronic states of a molecule. For example, the first excited $^1\Sigma^+$ state of CaO is perturbed by six different low-lying states or sublevels. From the perturbations observed for $Ca^{16}O$, the vibrational and rotational constants of these states can be established, but their energies are not known. A similar analysis of the perturbations for $Ca^{18}O$ may allow fixing of the energies of each of the states from the isotope shift.

The application and potential future applications of the above methods will be discussed. This work has been supported by the Research Division of the Atomic Energy Commission.

MATRIX ISOLATION INFRARED SPECTROSCOPY
OF HIGH TEMPERATURE SPECIES

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Matrix isolation in rare gases has been widely used for infrared studies of reactive species. An advantage of matrix isolation for infrared studies of high temperature species is apparent if one compares the usual band widths of gas phase absorption spectra to those obtained in matrix isolation spectra. In fact the narrow band widths often make possible accurate isotope shift measurements of vibrational bands which in turn can be used to calculate accurate force constants. For XY_2 triatomic molecules isotope shifts of the antisymmetric stretch (ν_3) can often set close limits on the bond angle. Alternatively, isotope shifts of the ν_1 and ν_2 can be used in combination to determine the bond angle but the measurements are sometimes made difficult because of their relatively low absorption intensities.

A simple use may be made of the isotope shifts of some diatomic molecules to determine their anharmonicity. A comparison of the measured anharmonicity of a molecule trapped in a rare gas matrix to its gas phase value serves as an indication of the effect of the matrix on the shape of the potential energy curve. The following table lists $\omega_e x_e$ for matrix isolated, using Ne or Ar, and gas phase molecules.

	$\omega_e x_e$ (cm^{-1})	
	matrix isolated	gas phase
LiF	9.4 ± 1	8.0
LiCl	3.1 ± 1	4.2
SiO	7.8 ± 3	6.0

It is clear from the above table that anharmonicities are affected only a very small amount, if at all, by a rare gas matrix. This is true for LiF even though the ν_e value shifts about 50 cm^{-1} from the gas phase to an argon matrix.

Isotope shift measurements of the ν_3 for symmetric triatomic XY_2 molecules may be exactly related to the bond angle by the following equation:

$$\sin \alpha = \frac{\left[\frac{M_x (M_y w_3^2 - M_y^i w_3^{i2})}{2M_y M_y^i (w_3^{i2} - w_3^2)} \right]^{1/2}}$$

where 2α equals the bond angle and w_3 is the zero-order antisymmetric stretch frequency. In practice one uses measured ν_3 values and estimates the anharmonic effect which in most cases has little influence on the measured bond angle.

It also follows from the above equation that a $\pm 0.1 \text{ cm}^{-1}$ error in the isotope shift measurement of ν_3 will cause a bond angle close to 180° to be less well determined than one close to 90° . The effect is such that with present instruments it becomes difficult to distinguish between bond angles of 160° and 180° . Although for these cases an isotope shift measurement can clearly establish a lower limit. The triatomic molecules listed in the following table have been studied in our laboratory and for the few cases (eg. NiF_2 , CuF_2 and ZnF_2) where these molecules have also been studied by other investigators the agreement with our work is very good.

	Bond Angles (degrees)		
	<u>This work</u>	<u>Microwave</u>	<u>This work</u>
SO_2	117 ± 2	119.3	ZnF_2 160 - 170
SeO_2	110 ± 3	113.5	CuF_2 163 - 170
TeO_2	110 ± 2	-	NiF_2 154 - 167
SiF_2	100.5 ± 2	100.9	FeF_2 155 - 170
GeF_2	94 ± 2	-	CrF_2 160 - 180

	Bond Angles (degrees)		
	<u>This work</u>	<u>Microwave</u>	<u>This work</u>
SnF ₂	92 [±] 3	-	MnCl ₂ 180
TiF ₂	120 [±] 4	-	VCl ₂ 180

It is apparent from the above data that the bond angle decreases slightly as the central atom size is increased down a column of the periodic table. One also notes that all of the isoelectronic 18 valence-electron molecules listed above are bent as predicted by Walsh rules. The bent configuration of TiF₂ indicates that its d-electrons are involved in the bonding to a considerable extent.

Infrared absorption data obtained for Group IV difluorides, SiF₂, GeF₂, SnF₂, and PbF₂ are given in the following table along with other molecular parameters. The force constants for GeF₂, SnF₂ and PbF₂ were calculated with the assumption of a zero stretch-bend interaction. The force constant values for CF₂ are taken from Milligan and Jacox J.C.P. 48, 2265, (1968) and for SiF₂ from V. M. Khanna et al J.C.P. 47, 5031 (1967).

mdyn/Å	CF ₂	SiF ₂	GeF ₂	SnF ₂	PbF ₂
k ₁	6.0	5.02	4.07	3.52	3.02
k ₁ /l ²	1.40	0.44	0.32	0.16	0.11
k ₁₂	1.45	0.31	0.22	0.17	0.10
r _{X-MX} (Å)	1.30	1.595	(1.73)	(1.92)	(2.01)
bond angle	104.9	100.9	94 [±] 4	92 [±] 3	(90)
D _{X-MX} (kcal/mole)	108	153	115	114	104
k ₁ r _{X-MX} / D _{X-MX} (x 100)	7.2	5.2	6.1	5.9	5.8

It is apparent from the above table that k₁ varies rather smoothly through the Group IV series this is not the case however for the D_{X-MX} energies. The ratio of k₁r_{X-MX} / D_{X-MX} might be expected to remain constant through the Group IV

series and in fact does for Ge, Sn, and Pb difluorides. The deviation of the ratio from an average value of 6 for SiF₂ and CF₂ seems to indicate a strengthening of the F-SiF bond by approximately 20 kcal and a weakening of the F-CF bond by approximately 20 kcal. A strengthening of the F-SiF bond might be attributed to some type of d-orbital involvement in the bonding. The weakening of the F-CF bond might well be due to strong fluorine-fluorine or fluorine-lone pair repulsion. It has been pointed out by others that the quite high value of the bond-bond interaction force constant for CF₂ is good evidence for strong fluorine-fluorine interaction.

Infrared data obtained for the first row transition metal dihalides are given in the following table. The gas phase frequencies have been estimated by arbitrarily adding $0.7\Delta(\text{Ne-Ar})$ to the measured frequency in a Neon-matrix. The force constants have been calculated using a three constant valence force field.

	Transition Metal Difluorides		$\Delta(\text{Ne-Ar})$ cm ⁻¹	$\nu_3(\text{Ne})+0.7(\Delta)$ cm ⁻¹	k_1-k_{12} md/A
	$\nu_3(\text{Most Abundant})$ Isotope cm ⁻¹	Neon			
Ca ⁴⁰	581 ^a	561 ^a	20	595	2.17
Sc ⁴⁵	700.2	685.5	14.7	710.6	3.34
Ti ⁴⁸	753.3	740.6	12.6	762.1	4.03
V ⁵¹	743.3	733.7	9.6	750.0	3.80
Cr ⁵²	680.5	654.8	25.7	698.5	3.18
Mn ⁵⁵	722.6	700.6	22.0	740.0	3.67
Fe ⁵⁶	753.3	731.8	21.5	768.3	4.00
Co ⁵⁹	746.3	723.6	22.7	762.2	4.02
Ni ⁵⁸	801.2	780.6	20.6	815.6	4.57
Cu ⁶³	767.0	744.4	22.6	782.8	4.33
Zn ⁶⁴	782.0	764.0	18.0	794.6	4.48
Ge	655 ^b	648 ^b	7	660	3.82

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The stretch force constants for the difluorides, dichlorides and their ratio are listed in the following table. The dichlorides of Mn, Fe, Co, Ni, Cu and Zn have been taken from Leroi et al J.C.P. 36, 2879 (1962).

	MF_2 $k_1(\text{mdyn./\AA})$	MCl_2 $k_1(\text{mdyn./\AA})$	$\frac{k_1(\text{MF}_2)}{k_1(\text{MCl}_2)}$
Ca	2.17	-	-
Sc	3.34	(1.88)	-
Ti	4.03	(2.27)	-
V	3.80	2.19	1.74
Cr	3.18	(1.79)	-
Mn	3.67	1.99	1.84
Fe	4.00	2.23	1.79
Co	4.02	2.30	1.75
Ni	4.57	2.51	1.82
Cu	4.33	2.43	1.78
Zn	4.48	2.67	1.68
Ge	3.82	2.17	1.76

The ratio of stretch force constants is almost invariant and provides a convenient means of estimating the unmeasured dichloride force constants. The estimated values are bracketed in the above table.

Infrared spectra obtained for SeO_2 , TeO_2 and TeO are listed in the following table.

	$\frac{\nu_3-1}{\text{cm}}$	$\frac{\nu_1-1}{\text{cm}}$	$\frac{k_1-k_1^2}{\text{mdyn./\AA}}$
SeO_2	974	924	7.00
TeO_2	845	827	5.75
TeO	791		5.25

Polymeric forms of these species have also been identified in the matrices.

Mass spectrometric studies have indicated that the polymeric species **also**

exist in the high temperature vapors. However for the SiO system where the vapor species is almost completely monomeric SiO, matrix isolation leads to extensive polymerization even at relative SiO to rare gas concentrations of 1/1000. Similarly the electronically similar high temperature species, BF is difficult to isolate in these matrices.

Reactions of NaF and SiF₂ and Na + SiF₂ have been studied by co-condensation of both species. New absorption bands were observed and are tentatively assigned to NaSiF₃ and NaSiF₂. These products decomposed when the condensate was warmed to room temperature to form elemental Si and Na₂SiF₆.

DICHLOROCARBENE FROM CHLOROFORM PYROLYSIS

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Although cyclopropane formation from photolysis of suitable diazo compounds in the presence of an olefin is generally regarded to proceed through a free divalent carbon intermediate, there is much question as to the nature of the intermediate when alpha-elimination reactions are carried out in the presence of olefins to form cyclopropanes. Some species as ICH_2ZnI and LiCHCl_2 have been postulated as directly transferring the CXY moiety to olefin forming cyclopropanes without the intermediacy of a free carbene, but rather a carbene complex or carbenoid. On the other hand, indications are that the action of base on CHF_2X ($\text{X} = \text{Cl}, \text{Br}$) yield a free carbenic species, CF_2 .

In the instance of dichlorocarbene produced through alpha-elimination, there is much controversy as to whether the intermediate carbene is a free or a complexed species. The aim of this work was to resolve this conflict by comparing the reactivity of an unambiguously free dichlorocarbene with that of the species from alpha-elimination.

Unambiguously free dichlorocarbene was produced via chloroform pyrolysis: chloroform was passed through a pyrolysis zone ($\sim 1400^\circ$) which led into a high vacuum system, allowing molecular flow to a cooled solution of substrate. The substances leaving the pyrolysis chamber experienced a 10^{-5} second free flight before encountering the stirred liquid solution of olefin and hydrocarbon solvent. The dichlorocyclopropanes formed under these conditions are the products derived from the reaction of free dichlorocarbene with the olefin substrate. This variety of dichlorocarbene was found to add stereospecifically to the 2-butenes as does the dichlorocarbene from base and chloroform.

Reactions were run in which olefin pairs were allowed to compete for the free dichlorocarbene. Results of these competitions were compared with those for dichlorocarbene systematically generated by a number of alpha-elimination reactions in a variety of solvents, and over an extensive temperature range.

The reactivity of trichloromethylithium, a dichlorocarbene precursor stable at low temperatures ($\sim -80^\circ$) was also studied. The mode of reaction of this compound with olefins is of great interest, since it can conceivably react by both a carbene and an organometallic route.

Arrhenius plots were made for the relative reactivities of pairs of olefins. A common line was obtained independent of the mode of generation of the dichlorocarbene, with alpha-elimination or pyrolysis of chloroform.

Since all methods of generating dichlorocarbene gave an intermediate showing the same selectivity it follows that all generate the same intermediate, free dichlorocarbene.

PREPARATIVE PROSPECTS OF "HIGH TEMPERATURE" SPECIES

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Much of the emphasis of traditional high temperature chemistry in the past two decades has been placed on the elaboration of thermodynamic, kinetic, and structural features of chemical systems. Less attention, perhaps, has been given until quite recently to the implications of the results of high-temperature investigations for the synthetically oriented chemist. It has become increasingly evident, however, that the variety of unconventional and intrinsically interesting species accessible in significant concentrations under energetic regimes are potentially valuable reagents, and that these reactive intermediates can provide the means for syntheses of novel systems not yet achieved by more usual routes.

From the synthetic viewpoint, the availability of potential intermediates under energetic conditions is of primary importance, and the nature of the excitation employed is perhaps secondary. Accordingly, "high temperature" techniques in the literal sense are but one facet of a more general synthetic rationale, which also embraces alternate modes of excitation such as electric or microwave discharge procedures and photochemical syntheses. Even more generally, one may extend this synthetic viewpoint to the rational utilization of stable compounds, themselves formed by energetic routes, which provide sources of preformed

submolecular entities not otherwise available for synthetic exploitation. Thus, the energetic synthesis may provide the starting point for a derivative chemistry that might not be accessible by exclusively high energy procedures.

In this paper, we describe some recent activities in the authors' laboratories utilizing this somewhat permissive view of "high temperature" processes as a synthetic tool.

The preparation of catenated systems involving elements other than carbon is an area in which synthesis has traditionally relied heavily on the "energetic chemistry" approach. While conventional condensation reactions are applicable under some conditions, much of the synthetic progress in the area of catenated hydrides and halides of the representative elements, for example, has relied either on hydrolytic procedures using derivatives in which the catenation is "preformed" by high temperature preparative routes, or on thermal or discharge excitation. Thus, synthesis of catenated halides has been frequently achieved by discharge routes involving chlorides or compounds of the heavier halogens. Procedures involving fluorides have been generally unsuccessful, and it is frequently assumed that the reactive species in fluoride discharges are incompatible with retention of homoelemental bonding. In the course of investigations of the discharge reactions of covalent fluorides of elements such as boron, silicon, germanium, and phosphorus, we have demonstrated, mass spectrometrically and in bulk, the occurrence of catenation in fluoride-based systems. In more complex systems involving silicon, halogen redistribution and catenation to mixed halopolysilanes has been observed.

Some of these compounds have subsequently been prepared by alternate routes and investigated in detail by NMR double resonance techniques.

Of more general occurrence in microwave-excited fluoride plasmas is reaction with oxides or oxygen itself to produce oxyhalide species such as OBF and OSiF_2 which appear to undergo a series of secondary reactions to produce an array of simple and polymeric oxyfluorides. Progress made to date toward the elucidation of products and of principal reaction pathways suggests that relatively straightforward four-center addition reactions of the principal oxyfluoride intermediates are involved.

The well-known discharge synthesis of the boron subhalides provides a ready source of these compounds, which exemplify a class of reagents, accessible by energetic routes, for which an extensive derivative chemistry can be developed. A number of hitherto unreported organo derivatives have now been prepared. Reactions with a number of organic and organo-metallic reagents have been observed in which these compounds function as a formal source of BX groups. A comparison is suggested with the high-temperature boron-halogen chemistry investigated by others, including the possibility that the nominally stable subhalides may function under some conditions as low temperature sources of high temperature species.

Photochemical excitation is a particularly attractive source of a more selective energy input in systems, such as organometallics, that are potentially degradable by more rigorous high-temperature procedures. New synthetic results in organoboron photochemistry include the synthesis of an ethynyl derivative of three-coordinate boron. The relationship of photochemical and other energetic processes has been probed in studies of free radical chemistry of phosphorus. The radicals PCl_2 and PCl_4 have been characterized and their chemical consequences investigated.

THE USE OF SPECIES FORMED BY HIGH TEMPERATURE
EVAPORATION IN CHEMICAL SYNTHESIS

P. L. Timms

Over the last thirty years, there has been growing interest in the high temperature, vacuum evaporation of many solid elements and compounds to form thin films, special alloys and new solid phases. As a result, methods and apparatus now exist for the evaporation of at least a gram an hour of most materials at any temperature up to 3500°C at pressures of 10^{-6} torr or lower.

There has also been increasing study of vapor species formed when materials vaporize at above 1000°C. The species have mostly been identified by their mass spectra or ultra-violet spectra, and vapor equilibrium measurements have been made.

Atoms of the metals and metalloids, vapors of low valent compounds, and vapors of some normal valent compounds, formed at high temperatures, are all "high energy" species. They may be capable of chemical reactions not shown by the original material in the condensed phase at lower temperatures. Yet despite their physical characterization and commonplace generation for other purposes, the possible use of high temperature vapors as reagents in chemical synthesis has been overlooked until the last few years.

The purpose of this paper is to discuss the conditions necessary to use high temperature species in synthesis, to indicate the synthetic potentialities of such species, and to summarise the results of relevant research underway in the author's laboratory.

Conditions for using high temperature vapors in synthesis

Whenever a vapor is formed by heating a material in the condensed phase, the energy supplied overcomes the forces which hold the

molecules or atoms together. Relative to the condensed phase of the material at room temperature, the vapor is a species of higher energy. For a material with a normal boiling point of above 1500°C , the difference in free energy between the solid at room temperature and its vapor at room temperature will usually be above 30 Kcals per mole. The vapors of metals, with a few exceptions, will be atomic species with free energies of formation of +30 to +180 Kcals relative to the solid metal. Such atomic species may have a chemical reactivity far greater than that of the original metals.

Of course, the vapors formed by evaporation at high temperatures are not stable at ordinary temperatures and will immediately condense to reform the starting material. They can thus be made to undergo gas-phase reactions only with the relatively few other molecules which are stable at high temperatures. However, the potential reactivity of the high temperature vapors towards a wide range of compounds can be exploited by cocondensing the high temperature vapor and the vapor of another compound on a surface at -196° . This requires that the high temperature vapor is generated under high vacuum and passes by a collision free path to a cold surface, on to which another molecule is also being condensed. The high temperature species will either react with itself on the cold surface or with the other molecule. Which reaction is favored depends on both thermodynamic and kinetic factors. Only reactions with an activation energy less than about 5 Kcals can occur to a measureable extent at -196° , but fortunately the reactions of many high temperature species do have very low activation energies.

Synthetic possibilities of high temperature species

Two types of uses are seen for cocondensation reactions of high temperature species with ordinary molecules at low temperatures. In the first, the high temperature atom or molecule will become incorporated in another molecule with which it reacts. This use has been well illustrated by published work on carbon and silicon vapor, and by reactions of other high temperature species such as boron monofluoride, silicon difluoride, and silicon dichloride¹. It is to be expected that atoms and homonuclear molecules of almost all metals and metalloids, and molecules like BC_2 , SiC , SiO , etc., will all react with other molecules to form new compounds which contain the species.

In the second use, the high temperature species may be used as powerful and selective reagents for removal of halogens and other active atoms from molecules. Although nearly all metals might serve in this role, it is to be expected that the greatest selectivity will be shown by the later transition metals, for which intermediates may be governed by particular complexing ability.

Present work in the author's laboratory

A. Methods of Evaporation

Two main methods are being used to evaporated metals and other materials inside a chamber with liquid nitrogen cooled walls, at a pressure less than 10^{-6} torr.

The first is electron bombardment heating using a Varian "e-Gun", which permits downward evaporation from a rod of material. For those materials which melt before evaporation, a molten drop is held on the end of

the rod by surface tension. The rod can be advanced as material vaporises from the tip. The method gives a rate of evaporation of about one gram an hour for most metals boiling below 3000°C , and for carbon, silicon, and boron. The method has the disadvantage that it does not allow evaporation of very large quantities of metals. There is also some uncertainty about the temperature at which evaporation is occurring, and the electronic state of the vapor species formed. Occasionally there have been problems due to stray electrons inside the vacuum chamber exciting the vapor which is being cocondensed with the high temperature species.

The second method is simple evaporation from resistively heated molybdenum boats or baskets, with or without alumina linings. It is easy to evaporate 1 to 3 g. an hour of metals like copper or silver, and it will probably prove the best method for most metals boiling below 3000°C . It can be scaled up to permit evaporation of many grams of a metal.

B. Reactions of atoms being studied

Boron Atoms

The reactions of boron with hydrogen halides, boron trichloride, phosphorus trichloride, and some organic compounds have already been reported by the author². Further reactions being carried out all tend to confirm the idea that boron atoms react destructively with most compounds. Free radical polymerisation occurs, and the yields of products in which boron has undergone simple insertion into a bond or any similar process, are always low.

Silicon Atoms

One reaction of silicon atoms, their insertion into the Si-H bond

of trimethylsilane, has already been reported by Skell³. In this work, silicon has been reacted with B_2F_4 in an effort to make compounds in the series $SiF_{4-n}(BF_2)_n$ (the first two members of this series, SiF_3BF_2 , and $SiF_2(BF_2)_2$, have resulted from the action of SiF_4 on boron at $2000^\circ C$). The only new volatile material obtained from the cocondensation of B_2F_4 and Si atoms, has been characterised as $SiF(BF_2)_3$. This structure was assigned from its mass spectrum, ^{11}B and ^{19}F nmr spectrum, and infrared spectrum. The compound $Si(BF_2)_4$ was not formed.

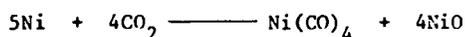
Iron Atoms

Iron has been cocondensed with a large excess of benzene in an effort to make the as yet unknown compound dibenzeneiron, $Fe(C_6H_6)_2$. On warming the cocondensate to about -50° under vacuum, most of the benzene could be pumped off. On warming further to 0° , the cocondensate exploded liberating benzene, and a little diphenyl and hydrogen. The residue was metallic iron. If the cocondensate was allowed to warm from -50° to room temperature in the presence of one atmosphere of hydrogen, there was no explosion. The volatile material which could be pumped off was then mostly cyclohexane. The results suggest that a very unstable iron benzene compound was being formed. The reactivity of benzene in the compound was far higher than usual as it would be reduced to cyclohexane under very mild conditions. The formation of dibenzeneiron would be consistent with the data so far obtained, but more work is necessary to prove its existence.

This work with iron atoms does demonstrate that cocondensation reactions may be a useful route to unstable zero-valent transition metal complexes.

Nickel Atoms

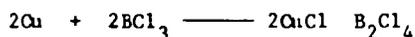
Nickel was cocondensed with carbon dioxide. On warming the cocondensate a little above -196° some carbon monoxide was evolved. About 15% of the nickel deposited was recovered as nickel carbonyl, the rest remained as a black nickel oxide, approximating to NiO in composition. The yield of $\text{Ni}(\text{CO})_4$ was about 75% of that required by the equation



Nickel was also condensed with boron trifluoride to try to obtain $\text{Ni}(\text{BF})_4$. Reaction occurred but the product seemed to be a mixture of a nickel boride and the known complex $\text{NiF}_2 \cdot \text{BF}_3$. No evidence of stepwise reduction of the boron trifluoride was obtained.

Copper and Silver Atoms

Copper has been found to be a very effective reagent for removing chlorine from B-Cl bond and coupling the boron atoms. When copper atoms and BCl_3 were cocondensed in a 1:6 mole ratio, B_2Cl_4 was formed in 40% of the yield required by the equation



Using copper atoms and CH_3BCl_2 , a similar yield of the new compound 1,2-dimethyl-1,2-dichlorodiboron was obtained. This was characterised by its mass spectrum and its ^{11}B and proton nmr spectrum, and by its quantitative reversion to CH_3BCl_2 on treatment with chlorine at -80° . The cocondensation reaction of copper with $(\text{CH}_3)_2\text{BCl}$ was very complex, although an unstable compound $(\text{CH}_3)_4\text{B}_2$ may have been among the products.

Cocondensation of copper atoms generated by electron bombardment heating with a mixture of BCl_3 and SiCl_4 , gave B_2Cl_4 and $\text{SiCl}_3\text{BCl}_2$. Cocondensation of copper evaporated from a molybdenum boat at 1400° with the same mixture, gave B_2Cl_4 but no $\text{SiCl}_3\text{BCl}_2$. This is an example of electronic excitation either of the copper vapor or of the SiCl_4 which can occur with electron bombardment heating.

Silver atoms, formed by evaporation from molybdenum boats, react with B-Cl compounds in a similar way to copper atoms, but the yields are much poorer. The bulk of the silver is recovered as metal from the surface where cocondensation takes place.

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THE OXIDATION OF HYDROGEN CHLORIDE IN ELECTRODELESS
RADIOFREQUENCY DISCHARGES

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A study of the oxidation of Hydrogen Chloride in electrodeless glow discharges between 3.75 and 150 torr is described. A cylindrical quartz reactor was used at 2450 MHz in a tapered waveguide section. Other work done at 7 and 20 MHz used cylindrical vessels with external sleeve electrodes and pillbox-shaped reactors with external electrodes painted onto the flat top and bottom surfaces. Power at 20 MHz was coupled from a self-excited oscillator through a coupling coil in the tank and at 7 MHz a helical resonator was used.

For sufficiently high driving frequencies there is not sufficient time during a cycle for electrons to be swept to the walls of a discharge reactor. Electron loss is then controlled, in a non-attaching gas, by diffusion. For a constant electron momentum collision frequency ν_m , the average power input per unit

$$P = \frac{n_e e^2 E_o^2}{2m\nu_m} \frac{\nu_m^2}{\omega^2 + \nu_m^2}$$

and likewise the electron energy is given by

$$E = E_{dc} - \frac{k\nu_m}{2\omega} E_{dc} \sin 2\omega t$$

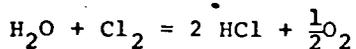
where

$$E_{dc} = \frac{e\mu E_o^2}{2k\nu_m}$$

is that energy obtained in a d.c. electric field of magnitude equal to the a.c. R.M.S. value and where ω is the frequency of the applied field, k is the average fraction of energy lost per collision and is assumed constant, m is the electron mass, and E_o is the peak applied field, and μ is the mobility.

The behavior is explained by the balance between electron attachment and detachment processes in the different regions of the discharge.

Limited data were also obtained on the reverse reaction



which gave some evidence that at moderate pressures the reaction approached an asymptotic composition at long residence time.

Finally it is shown that a major method of energy loss for electrons is vibrational excitation of HCl and subsequent infrared radiation.

FREE ENERGY CHARTS FOR HIGH TEMPERATURE CHEMICAL CALCULATIONS

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To calculate the degree of chemical reaction for



at any temperature, it is necessary to know the Gibbs free energy change

$$\Delta G(T) = \Delta H(T) - T\Delta S(T) \quad (2)$$

One can then find the concentrations of the reactants and products from the equilibrium constant K

$$\Delta G = -RT \ln K \equiv -RT \ln \frac{p_M^m p_N^n}{p_A^a p_B^b} \quad (3)$$

where p is the activity of each reactant. For reactants whose standard state is gaseous at the reaction temperature, p is approximately equal to the partial pressure.

The heat capacities, and other thermodynamic properties of elements and compounds, are not simple functions of temperature and are usually presented in extensive tabulations such as JANAF Tables. However, in forming ΔG from these properties, the non-linear terms largely cancel so that to a very good approximation

$$\Delta G(T) = \Delta \bar{H} - T\Delta \bar{S} \quad (4)$$

where now $\Delta \bar{H}$ and $\Delta \bar{S}$ are respectively the asymptote and slope of a plot of ΔG vs T , and may differ by 5-10% from $\Delta H(T)$ and $\Delta S(T)$. For instance, the free energy of formation of Al_2O_3 varies from the straight line $\Delta G = -402.3 + 77.2T$ by at most 0.08% between 1,000 and 2,300°K, while $\Delta H(T)$ varies by 1.5% and $\Delta S(T)$ varies by 5% over this range.

It is possible to summarize a great deal of the data on chemical reactions in the form of families of straight lines on plots of ΔG vs T . Free energies of reactions for the formation of the chalcogenides, halides and hydrides, disassociation of polyatomic gases and ionization of elements are assembled here as a convenient summary of the thermodynamic data on these reactions. The straight line values of $\Delta \bar{H}$ and $\Delta \bar{S}$ are tabulated.

*Operated with support from the U. S. Air Force.

A plot of ΔG vs T has a number of advantages in the presentation of free energy data. It enables the relative reactivity of various materials to be easily visualized over a wide range of temperature. Phase changes are marked by changes in slope so that melting points and boiling points of reactants are recorded. The charts become simple nomograms in several ways. A fixed value of K lies on a line passing through the origin so that by adding one scale it is possible to read K or p for reactions involving only one gas. Other scales can be constructed to give the results of compound reactions such as hydrogen reduction of oxides. The free energy change is proportional to the emf of electrochemical reactions so that a separate scale gives this conversion.

At temperatures above $2,000^{\circ}\text{K}$ many of the diatomic gases begin to dissociate. Above $10,000^{\circ}\text{K}$ most molecules have dissociated to atoms and the atoms begin to ionize thermally to give electrons and ions. For dissociation and ionization at one atmosphere total pressure, it is possible to read on the free energy charts the degree of dissociation or ionization and the partial pressures of molecules, atoms, ions, and electrons. By moving the scale it is possible to read these quantities at any other total pressure. The use of the charts in measuring very high temperature is discussed.

The major source of entropy change in chemical reactions involving at least one gaseous species is the production or consumption of gas, since the entropy of a mole of gas is much higher than that of the corresponding solid or liquid. It becomes apparent on examining the charts that the entropy change is given approximately by $\pm \Delta \bar{S} = \pm k \Delta n$, where Δn is the increase in the number of moles of gas for the reaction. For the formation of the chalcogenides and halides, the constant k is approximately 40-50 e. u./mole, but is smaller for reactions involving dissociation or ionization. Provided that the reactions are all written for one mole of gas, the free energy charts then show a series of parallel lines of slope $\Delta \bar{S}$. From this it is seen that the relative magnitude of ΔG is determined primarily by $\Delta \bar{H}$ and the relative stability of oxides, sulfides, etc. stays constant over a wide range of temperatures.

The oxygen pressure at equilibrium between a metal and its oxide or between an oxide and a higher oxide provides a scale of stability toward oxidation similar to the EMF or electronegativity scale. We define "pO" as the negative log of oxygen pressure, $-\log p_{\text{O}_2}$ (analogous to the definition of pH as the negative log of hydrogen