Thermodynamics of Selected Trace Elements in the Jovian Atmosphere

BRUCE FEGLEY, JR. AND JOHN S. LEWIS

Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received October 10, 1978; revised November 30, 1978

The thermochemistry of several hundred compounds of twelve selected trace elements (Ge, Se, Ga, As, Te, Pb, Sn, Cd, Sb, Tl, In, and Bi) has been investigated for solar composition material along a Jupiter adiabat. The results indicate that AsF₃, InBr, TlI, and SbS, in addition to CO, PH₃, GeH₄, AsH₃, H₂Se, HCl, HF, and H₃BO₃ proposed by Barshay and Lewis (1978), may be potential chemical tracers of atmospheric dynamics. The reported observation of GeH₄ is interpreted on the basis of new calculations as implying rapid vertical transport from levels where $T \geq 800\,^{\circ}$ K. Upper limits are also set on the abundances of many gaseous compounds of the elements investigated.

INTRODUCTION

The spectroscopic observations of PH₃, CO, and possibly GeH₄ in Jupiter's atmosphere (Ridgway, 1974; Ridgway et al., 1976; Beer, 1975; Larson et al., 1977; Larson et al., 1978; Beer and Taylor, 1978; and Fink et al., 1978) have opened up a new area of research dealing with the use of chemical species as tracers of atmospheric motions. The presence of PH3 and possibly GeH₄ is attributed to rapid vertical transport of these high-temperature, high-pressure species to cool levels in the atmosphere, a process which is faster than the reactions which destroy these gases in the hot lower atmosphere. Prinn and Barshay (1977) have presented a quantitative treatment of the rapid transport model for CO which indicates that the vertical mixing rates previously estimated from heat flux considerations are rapid enough to quench the reduction of CO and make it observable. However, the observed differences in the CO rotational temperature (Beer and Taylor, 1978; Larson et al., 1978) indicate that a stratospheric CO source such as meteoritic infall (Prather et al., 1978) may also be required. It will be difficult if not impossible to assess the relative magnitudes of different proposed CO sources until data on the vertical distribution profile of CO in the Jovian atmosphere is obtained from a Jupiter entry probe such as Galileo.

The considerations outlined above and the somewhat distressing fact that kinetic data appear to be lacking for the relevant PH₃ oxidation reaction which has been postulated to destroy PH₃ in the Jovian atmosphere (Lewis, 1969; Prinn and Lewis, 1975) have led us to initiate this study. We have investigated in detail the thermochemistry of 12 selected moderately volatile elements (Ge, Se, Ga, As, Te, Pb, Sn, Cd, Sb, Tl, In, and Bi) along a nominal Jovian adiabat in order to suggest possible chemical tracers in addition to those already proposed by Barshay and Lewis (1978). Seven of these elements have not been previously studied, and five were investigated by Barshay and Lewis (1978) but

TABLE I
ASSUMED ELEMENTAL ABUNDANCES
FROM CAMERON (1973)

Element	Abundance	Figure No
Н	$31.8 imes 10^{9}$	
O	$21.5 imes10^6$	
N	$3.74 imes10^6$	
\mathbf{s}	$500 imes 10^3$	
P	9600	
Cl	5700	
\mathbf{F}	2450	
Ge	115	1
Se	67.2	1, 3, 4, 6
Ga	48	2
Br	13.5	
$\mathbf{A}\mathbf{s}$	6.6	2
${ m Te}$	6.42	1, 3, 4, 5
${ m Pb}$	4	3
Sn	3.6	4
Cd	1.48	3
I	1.09	
$\mathbf{S}\mathbf{b}$	0.316	5
\mathbf{Tl}	0.192	5
In	0.189	4
$_{ m Bi}$	0.143	6

are studied in substantially more detail here. Although the basic reasoning behind this approach has been discussed in detail by Barshay and Lewis (1978), we will briefly recapitulate it here.

The utility of equilibrium calculations rests on the assumption that rapid vertical transport of atmospheric gases from the deep lower atmosphere quenches all gas phase reactions thereby freezing in the high-pressure, high-temperature equilibrium configuration. Using our results it then becomes possible to interpret observed abundances of high-pressure, high-temperature species, e.g., GeH₄, in terms of rapid vertical transport from specific atmospheric levels and to suggest other possible tracers of atmospheric dynamics. In addition to suggesting possible tracers the present results are also used to place reasonably firm upper limits on the abundances of many gases, to describe the stability fields of condensates, and to list compounds which will not be detectable with significant concentration.

PROCEDURE

The construction of the nominal adiabat used in this study and the general calculational method used have been described in detail by Barshay and Lewis (1978) and will not be discussed here. The elements studied, their assumed abundances in a solar composition gas (Cameron, 1973), and the figure number (or numbers) in which they appear are listed in Table I.

The thermodynamic data used in the present calculations came from approximately 100 sources which are listed in Appendix II. In many cases the equilibrium constant for formation of an element or compound from the constituent elements in their designated reference states had to be calculated from the literature data. If at all possible this calculation was done by a third-law method and double-checked using data from a separate source. In some cases. a second-law method which is less accurate was used and the results were still doublechecked with data from a separate source. Details of the second- and third-law treatments of equilibrium data are available in the JANAF tables or any standard thermodynamic text.

RESULTS

The results of the calculations are discussed element by element in order of decreasing abundance. Compounds which do not appear in the figures due to extremely low abundances or activities less than 1 are listed in Appendix I.

Germanium. The calculated equilibrium abundances of germanium-bearing gases and the stability fields of germanium condensates are displayed in Fig. 1. These results, which differ from those of Barshay and Lewis (1978), illustrate several important points. First, at temperatures less than 1000°K the major gas phase species

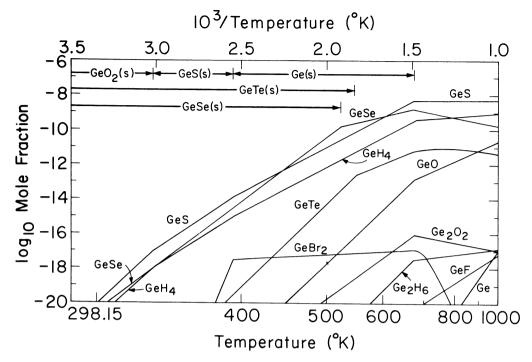


Fig. 1. Equilibrium abundances of germanium-bearing gases and stability fields of germanium condensates along the Jupiter adiabat. The temperature scale is linear in 1/T. The mole fraction X_i of a species i is defined as its partial pressure p_i divided by the total pressure P. The heavy lines which indicate the stability fields of the five condensates have nothing to do with their abundances. The abundances of the different condensates may be estimated from the adundances and rates of disappearance of the gases which constitute them. Notice that solid GeTe and GeSe are always stable once they appear but that Ge(s) becomes unstable relative to GeS(s) which in turn is replaced by $\text{GeO}_2(s)$.

are the germanium chalcogenides (GeS, GeSe, and GeTe) and GeH₄. Germane is at best only the second most abundant Gebearing gas, and is the third most abundant gas over a wide temperature range. Digermane (Ge₂H₆) is seen to be negligible at all temperatures less than 1000°K along the adiabat.

Second, the condensates are Ge(s), GeTe(s), GeSe(s), GeS(s), and $GeO_2(s)$. Solid GeO does not condense as previously indicated because the thermodynamic data source used by Barshay and Lewis (1978) for GeO(s) (Dean, 1973) is incorrect (the tabulated ΔG_f° , ΔH_f° , and S° values at 298.15°K do not satisfy the relation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$). This error coupled with

the inclusion of the important chalcogenide compounds GeSe and GeTe into the data set accounts for the differences between the results.

The reported observation of GeH₄ with a mole fraction about 6×10^{-10} (Fink *et al.*, 1978) is seen from Fig. 1 to imply rapid vertical transport of GeH₄ from the $T \geq 800^{\circ}$ K level. At this level there is approximately 10 times as much GeS as GeH₄ and about an equal amount of GeSe. However, since the condensation of GeS(g) and GeSe(g) is probably faster than the conversion of GeH₄ to either of these two gases, GeH₄ may be the most abundant Ge bearing gas at temperatures lower than $T \sim 520^{\circ}$ K if equilibrium is not exactly

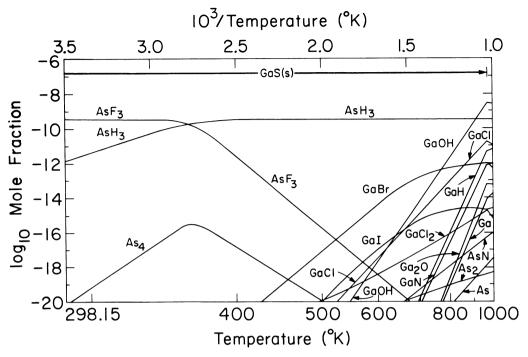


Fig. 2. Equilibrium abundances of arsenic- and gallium-bearing compounds along the Jovian adiabat. As F_3 is the dominant arsenic-bearing gas at low temperatures. The stability of this gas inhibits the condensation of solid arsenic. The abundances of all gallium-containing gases are rapidly reduced by the appearance of solid GaS at about 970 °K. Less than 1% of all gallium is still in the gas phase 100 °K below this point.

attained. Because of direct condensation of GeS and GeSe, we do not include them on our list of potential tracers.

Selenium. The results of the calculations on selenium-bearing gases and condensates are presented in Figs. 1, 3, 4, and 6. Hydrogen selenide is the most abundant selenium bearing gas at temperatures less than 1000° K, with GeSe being the second most abundant selenium gas. Condensation of GeSe(s) at $T \sim 520^{\circ}$ K severely depletes the abundance of H_2 Se(g).

The low temperature condensation of $H_2Se(g)$ as solid ammonium hydroselenide (NH₄HSe) has also been studied. If equilibrium is not attained at $T \sim 500^{\circ}$ K, H_2Se may be present at essentially solar abundance ($X_{H_2Se} \sim 3.7 \times 10^{-9}$) until NH₄HSe condensation occurs at $T \sim 219^{\circ}$ K. As the H₂Se abundance decreases the condensation of NH₄HSe is delayed until lower temperatures and higher altitudes.

The photolysis of H₂Se in the Jovian upper atmosphere has also been briefly investigated in connection with the possible depletion of H₂Se in the upper atmosphere. The results of calculations made using H₂Se absorption coefficients from Goodeve and Stein (1931), the radiative transfer model of Prinn (1970), and solar flux data from Schultz and Holland (1963) are presented in Fig. 7. Although the results are only approximate they indicate that rapid photolysis of H₂Se around the 200 to 250°K region will deplete the gas on the time scale of 2 days to 2 weeks. Thus, even if equilibrium is not attained in the lower atmosphere, H₂Se may still be unobservable due to depletion by NH₄HSe condensation and solar uv photolysis. Thus in several ways H_2Se behaves similarly to H_2S .

Gallium. The chemistry of gallium is illustrated in Fig. 2. Lewis (1969) briefly mentioned that gallium's chemical behavior

in the Jovian atmosphere at high temperatures was unknown, although oxides and gallium metal are involatile at 300°K. At high temperatures ($T\sim 1000$ °K) Fig. 2 shows that gallium hydroxide is present at solar abundance $X_{\rm GaOH}\sim 2.7\times 10^{-9}$. Condensation of solid GaS at $T\sim 970$ °K rapidly reduces the abundances of all Ga bearing gases to less than 1% of the gallium solar abundance within 100°K of its condensation temperature, and no Ga bearing gas is expected to be observable.

Arsenic. Figure 2 also displays the relatively simple gas phase chemistry of arsenic. As F_3 , which was not included in the calculations of Barshay and Lewis (1978), is seen to be the major As bearing gas at $T \leq 360$ °K if equilibrium is attained.

The large stability of AsF₃ also inhibits arsenic precipitation, which may still occur

if arsine is not converted to the trifluoride. Low temperature calculations indicate that $AsF_3(s)$ should saturate around the tropopause. However, the presence of this condensate in Jupiter's atmosphere must be considered a moot topic until it is known if the conversion of arsine to the trifluoride occurs readily.

Tellurium. The equilibrium chemistry of tellurium is displayed in Figs. 1, 3–5. Although tellurium has been investigated by Barshay and Lewis (1978), their results are incorrect because of incorrect data on the thermodynamic functions of $H_2Te(g)$ from Rossini et al. (1952). The ΔH_f° (298.15) value from the compilation of Rossini and co-workers does not agree with a more recent determination (Gunn, 1964) which makes $H_2Te(g)$ more stable with respect to other Te-bearing gases. Thus, if the forma-

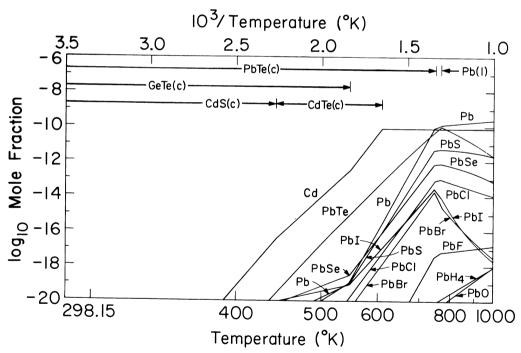


Fig. 3. Equilibrium abundances of lead- and cadmium-bearing compounds along the Jupiter adiabat. The chemistry of lead contains one of the few instances where a liquid condensate is stable. Lead telluride is more stable then solid lead which never condenses. Plumbane (PbH₄) is seen to be very unstable. The condensation of solid CdTe and later solid CdS dramatically reduces the Cd(g) abundance. Thermodynamic data could not be found for any other cadmium-containing gases. Refer to Barshay and Lewis (1978) to relate the temperature scale to pressure and depth scales.

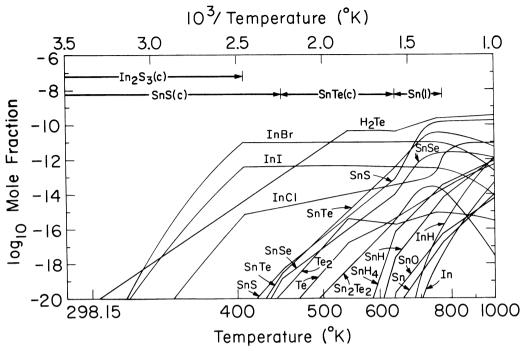


Fig. 4. Equilibrium abundances of tin-, indium-, and tellurium-bearing compounds along the Jupiter adiabat. The major tin-containing gases are SnS and SnTe. Liquid tin condenses at about 770°K but becomes unstable relative to tin telluride at about 633°K. Tin sulfide is stable at temperatures less than about 450°K. The dominant indium-bearing gases over a wide temperature range are InBr and InI. InCl is also important at high temperatures. The first stable indium condensate is indium sesquisulfide which appears at about 406°K. The hydrogen telluride abundance is decreased sequentially by the formation of PbTe(s), SnTe(s), CdTe(s), and GeTe(s). Other tellurium-bearing gases are graphed in Figs. 1, 3, and 5.

tion of group IV tellurides (GeTe, SnTe, PbTe) is excluded, H2Te is present at solar abundance $X_{\rm H_2Te} \sim 3.5 \times 10^{-10}$ down to $T \sim 440\,^{\circ}\mathrm{K}$ where solid Te condenses. If equilibrium is reached, the H₂Te abundance is reduced due to the successive condensation of PbTe(s), SnTe(s), CdTe(s), and GeTe(s). Calculations on the low temperature stability of solid ammonium hydrotelluride (NH4HTe) indicate that even at $X_{\rm H_2Te} \sim 3.5 \times 10^{-10}$ the solid NH₄HTe will not condense until the $T \sim 130$ °K level is reached. Depending on the degree to which equilibrium is achieved at higher temperatures, NH₄HTe may not be a stable condensate in the Jovian upper atmosphere.

Lead. The behavior of lead is illustrated in Fig. 3. At equilibrium monatomic Pb and

PbTe are the major gases. Plumbane (PbH₄) is highly unstable and never achieves a mole fraction larger than 10^{-18} at temperatures of 1000° K and lower. An interesting feature of the equilibrium chemistry displayed is the stability of liquid Pb. Solid Pb is unstable relative to PbTe(s) and does not condense.

Tin. Figure 4 depicts the chemistry of tin. The major gases are SnS and SnTe. Stannane (SnH₄) never reaches a mole fraction greater than 10^{-12} ($\sim 0.5\%$ of the Sn solar abundance) at temperatures of 1000°K and below. Analogous to Pb, liquid Sn is stable over a narrow temperature range, but solid Sn is never stable.

Cadmium. The chemistry of cadmium is presented in Fig. 3. Monatomic Cd gas is

the only Cd-bearing gas for which data are available. Its abundance is depleted by CdTe(s) condensation at $T\sim605^{\circ}\mathrm{K}$ and then by CdS(s) condensation at $T\sim440^{\circ}\mathrm{K}$.

Antimony. Figure 5 presents the results of calculations on Sb bearing gases and condensates. Stibine (SbH₃) and SbS which have similar abundances and Sb₄ are the major gases. Solid Sb condenses at $T \sim 600$ °K because Sb₂Te₃(s) is unstable owing to the prior depletion of H₂Te by PbTe(s), SnTe(s), and CdTe(s) condensation.

Thallium and indium. The equilibrium chemistry of thallium and indium is displayed in Figs. 5 and 4, respectively. In both cases at temperatures less than $T \sim 800\,^{\circ}\mathrm{K}$ the major gases are the monochloride, monobromide, and monoiodide. Indium condenses as the sesquisulfide

 $\rm In_2S_3(s)$ at $T\sim 406\,^{\circ}K$, whereas thallium condenses as the monoiodide TlI(s) at $T\sim 390\,^{\circ}K$.

Bismuth. Figure 6 illustrates the behavior of bismuth along the adiabat. At temperatures greater than approximately 550°K monatomic and diatomic bismuth are the major gases, while BiI and BiBr are the dominant Bi-bearing gases below this temperature. Liquid Bi first condenses at $T \sim 680$ °K and solid Bi becomes unstable relative to Bi₂S₃(s) at $T \sim 360$ °K. Bismuthine (BiH₃) is seen to be very unstable and it never reaches a mole fraction larger than 10^{-16} at 1000°K and below.

CONCLUSIONS

Potential chemical tracers of atmospheric dynamics revealed by this study [excluding those already mentioned by Barshay and Lewis (1978)] are AsF₃, InBr, TII, and

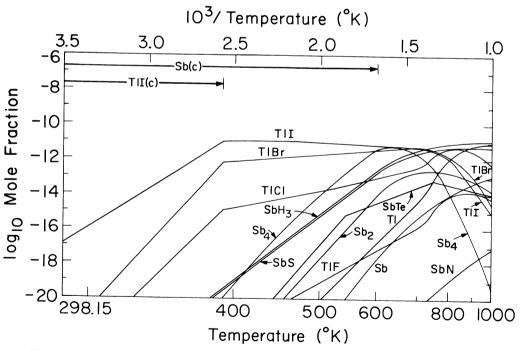


Fig. 5. Equilibrium abundances of thallium- and antimony-bearing compounds along the Jupiter adiabat. Major thallium-containing gases are TII, TlBr, and TlCl. Abundances of all three gases drop when TlI condenses at about 390°K. At high temperatures stibine (SbH₃) and SbS are the major antimony-bearing gases. As the temperature drops Sb₄ gas rapidly becomes dominant. Antimony condenses at about 600°K and is always more stable than Sb₂Te₃(s).

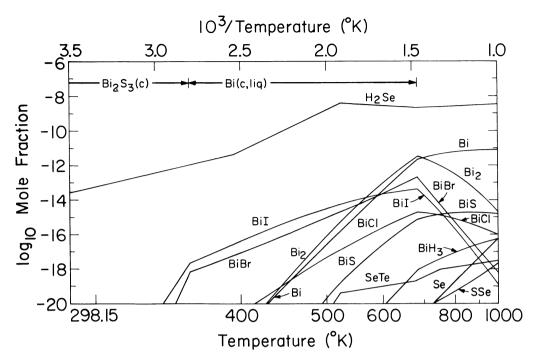


Fig. 6. Equilibrium abundances of bismuth-bearing compounds and of hydrogen selenide along the Jovian adiabat. Monatomic and diatomic bismuth are the major gases at high temperatures and BiI and BiBr are the most abundant bismuth-containing gases at lower temperatures. Bismuth condenses while it is still a liquid at about 680°K. At about 360°K Bi₂S₃ becomes stable relative to solid Bi. The abundance of H₂Se is relatively constant until solid GeSe condenses at about 520°K. Other selenium-bearing compounds are graphed in Figs. 1, 3, and 4.

SbS. Although H₂Se [proposed as a tracer by Barshay and Lewis (1978) and H₂Te are both present at solar abundances at $T \sim 1000$ °K, their depletion by the condensation of group IV selenides and tellurides may render them unobservable. Furthermore, additional considerations such as the condensation of NH4HSe around the 220°K level and rapid photolysis of H₂Se in the 200 to 250°K region may also decrease the H₂Se abundance and make its observation above the NH₃ cloud layer even more unlikely. Of course these same considerations also mean that H₂Se is a potential tracer of dynamics both in the deep atmosphere where selenide condensation occurs and also in the upper atmosphere where solar uv photolysis is important. Similar reasoning applies to H₂Te which is both highly photolabile (Goodeve and Stein, 1931) and susceptible to telluride condensation in the lower atmosphere.

The reported observation of GeH₄ in Jupiter's atmosphere (Fink et al., 1978) can be explained by the present calculations if rapid mixing from the $T \sim 800^{\circ}$ K region of the Jovian atmosphere occurs. This explanation is in accord with the postulated rapid vertical transport of PH₃ from the $T \sim 800$ –1000°K region and of CO from the $T \sim 1100^{\circ}$ K level of Jupiter's atmosphere (Barshay and Lewis, 1978; Prinn and Barshay, 1977). A more precise explanation of the presence of GeH₄ must await confirmation of the observations and an investigation of the kinetics of relevant reactions.

Of the potential tracers identified in the present study, three have mole fractions close to 10⁻¹¹. Quenching of SbS from the

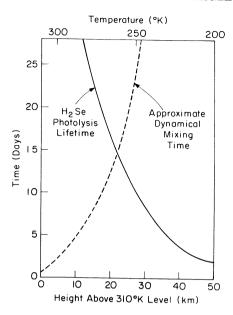


Fig. 7. The lifetime of hydrogen selenide against depletion by photolysis. Condensation of H₂Se as solid NH4HSe and rapid depletion of the H2Se gas phase abundance by photolysis both occur in the same region of the atmosphere around the 220°K level. The graph was calculated assuming a solar abundance of H₂Se below this level (higher temperatures), a H₂Se abundance fixed by the vapor pressure of NH4HSe(s) above this level (lower temperatures), and complete clearing of high-altitude cloud cover (the Belts). Approximate dynamic mixing times are indicated for $K = 10^8 \text{ cm}^2 \text{ sec}^{-1}$ (300°K) level), 106 (220°K), and 104 (140°K): Mixing probably cannot maintain a near-solar H2Se abundance against photolysis above the about 250°K level. Thus NH₄HSe condensation probably is limited to regions of NH₃(s) cloud cover (the Zones).

 $T\sim 700\,^{\circ}\mathrm{K}$ level could provide one such tracer, while the abundances predicted for InBr and TlI near the 400°K level are about 10^{-11} without the need for high-temperature quenching. The abundance of $\mathrm{AsF_3}$ if it forms readily from $\mathrm{AsH_3}$ can reach a mole fraction of 3×10^{-10} . We feel that the prospects for discovery of other tracers of deep mixing beyond those theoretically identified so far are not bright: The approximately 700 compounds of the 34 elements which have now been studied carefully include all the abundant and volatile elements.

APPENDIX I

ADDITIONAL COMPOUNDS WHICH ARE NOT GRAPHED

This Appendix lists compounds which were investigated but not included in the figures. Unstable condensates (liquids and solids with less than unit activity) and minor gases (mole fractions always less than 10⁻¹⁵) are listed only if they were not already included in the list of unstable condensates and minor gases prepared by Barshay and Lewis (1978).

Ga $Ga(s, 1), Ga_2O_3(s), GaO(g), GaBr_3(s, 1, g), GaCl_3(s, 1, g), GaF_3(s, g), GaSb(s), Ga(OH)_3(s), GaI_3(g), GaN(s), GaAs(s), Ga_2Se_3(s), GaSe(s), GaTe(s).$

 $\begin{array}{c} A_8 \\ A_8(s), A_8O(g), A_8F(g), A_8F_2(g), A_8F_5(g), \\ A_8Cl(g), \quad A_8Cl_2(g), \quad A_8I_3(g), \quad A_8_2Se_3(s), \\ A_8_2Te_3(s). \end{array}$

Te Te(s, l).

Pb

Sn

Cd

 $\begin{array}{cccc} Cd(s,\ l),\ CdO(s),\ CdCl_2(s),\ CdF_2(s),\\ Cd(OH)_2(s),\ CdOHCl(s),\ CdSb(s,\ l),\\ CdBr_2(s),\ CdI_2(s),\ CdSe(s),\ CdCO_3(s),\\ CdSiO_3(s). \end{array}$

Sb

Tl

 $\begin{array}{c} Tl(s,\ l),\ Tl_2O(s,\ g),\ Tl_2Cl_2(g),\ Tl_2O_3(s),\\ TlF(s,\ l),\ TlCl(s,\ l),\ TlBr(s,\ l),\ Tl_2Se(s),\\ TlOH(s),\ Tl_2S(s),\ Tl_4S_3(s),\ TlS(s),\ TlSe(s),\\ Tl_2Te(s),\ TlTe(s),\ TlI(l). \end{array}$

In

 $\begin{array}{ll} InO(g), & In_2O_3(c), & InBr(c), & InI_2(g), \\ InI_3(g), InS(c), InSe(c), In_2Se_3(c), InTe(c), \\ InP(c), InAs(c), InSb(c, l), In(c, l). \end{array}$

Bi

 $BiO(g), Bi_2O_3(c), BiCl_3(c, l, g), BiBr_3(c, l, g), BiI_3(c, l, g), BiF_3(c, l), BiF(g), Bi_2Se_3(c), Bi_2Te_3(c).$

APPENDIX II

Thermodynamic Data Sources

- Anderson, T. J., and Donaghey, L. F. (1977). Solid-state electrochemical study of the standard Gibbs energy of formation of indium sesquioxide. J. Chem. Thermo. 9, 617–628.
- Anisimov, M. P., Stenin, Yu. G., and Paukov, I. E. (1974). The low-temperature heat capacity, entropy, and enthalpy of tin(IV) iodide. Russ. J. Phys. Chem. 48, 1116.
- Anisimov, M. P., Zhamskaya, N. N., and Paukov, I. E. (1974). The low-temperature heat capacity, entropy, and enthalpy of tin(II) iodide. Russ. J. Phys. Chem. 48, 1116.
- Battat, D., Faktor, M. M., Garrett, I., and Moss, R. H. (1974a). Modified entrainment method for measuring vapour pressures and heterogeneous equilibrium constants. Part 2. Equilibria in the water/gallium system. J. Chem. Soc. Faraday Trans. I 70, 2280-2292.
- Battat, D., Faktor, M. M., Garrett, I., and Moss, R. H. (1974b). Modified entrainment method for measuring vapour pressures and heterogeneous equilibrium constants. Part 4. The

- gallium arsenide/hydrogen chloride system. J. Chem. Soc. Faraday Trans. I 70, 2302–2312.
- Behrens, R. G., and Rosenblatt, G. M. (1972). Vapor pressure and thermodynamics of octahedral arsenic trioxide (arsenolite). *J. Chem. Thermo.* 4, 175–190.
- Behrens, R. G., and Rosenblatt, G. M. (1973). Vapor pressure and thermodynamics of orthorhombic antimony trioxide (valentinite). *J. Chem. Thermo.* 5, 173–188.
- Bevolo, A. J., Shanks, H. R., and Eckels, D. E. (1976). Molar heat capacity of GeTe, SnTe, and PbTe from 0.9 to 60K. *Phys. Rev.* **13B**, 3523–3533.
- BLACHNIK, R., AND IGEL, R. (1974). Thermodynamicsche eigenschaften von IV-VI verbindungen: Bleichalkogenide. Z. Naturforsch. 29B, 625-629.
- BLACHNIK, R., AND SCHNEIDER, A. (1971). High-temperature enthalpies of As₂Te₃, Bi₂Se₃, GeAs, GeAs₂, Sb₂Se₃, and SnAs. *J. Chem. Thermo.* 3, 227–233.
- BLACHNIK, R., IGEL, R., AND WALLBRECHT, P. (1974). Thermodynamische Eigenschaften von Zinnchalcogeniden. Z. Naturforsch. 29A, 1198–1201.
- Brekow, G., Meissner, M., Scheiba, M., Tausend, A., and Wobig, D. (1973). Specific heat of thallium monoselenide between 3 and 600K. J. Phys. C 6, L462–L464.
- Brekow, G., Meissner, M., Scheiba, M., Tausend, A., and Wobig, D. (1975). Specific heat of Tl₂Se between 3 and 640K. J. Phys. C 8, L456–L460.
- Bugden, W. C., and Shelton, R. A. J. (1970). Thermodynamic properties of PbCl₂, SnCl₂ and CuCl from emf measurements of galvanic cells with a solid electrolyte. *Inst. Min. Metall. Trans. Sect. C* 79, C215–C220.
- Bugden, W. G., and Shelton, R. A. J. (1973). Thermodynamic properties of PbBr₂, SnBr₂, and CuBr from emf measurements on galvanic cells with a solid electrolyte. *Inst. Min. Metall. Trans. Sect. C* 82, C132–C134.
- Cartwright, M., and Woolf, A. A. (1976). Heats of formation of tin and titanium iodides. *J. Chem. Soc. Dalton Trans.* 829–833.
- Chase, M. W., Curnutt, J. L., Hu, A. T., Prophet, H., Syverud, A. N., and Walker, L. C. (1974). JANAF Thermochemical Tables, 1974 Supplement. J. Phys. Chem. Ref. Data 3, 311-480.
- CHASE, M. W., CURNUTT, J. L., PROPHET, H., McDonald, R. A., and Syverud, A. N. (1975). JANAF Thermochemical Tables, 1975 Supplement. J. Phys. Chem. Ref. Data. 4, 1-175.
- CLARK, R. J. H., AND RIPPON, D. M. (1974). The vapor phase Raman spectra, Raman band contour analyses, Coriolis constants, force constants, and

- values for thermodynamic functions of the trihalides of group V. J. Mol. Spectrosc. 52, 58–71.
- Colin, R., Drowart, J., and Verhaegen, G. (1965). Mass-spectrometric study of the vaporization of tin oxides. *Trans. Faraday Soc.* **61**, 1364–1371.
- Cubicciotti, D. (1967). The dissociation energy of bismuth chloride. J. Phys. Chem. 71, 3066–3068.
- Cubicciotti, D. (1968a). The thermodynamic properties of bismuth(I) bromide and bismuth(III) bromide *Inorg. Chem.* 7, 208–211.
- Cubicciotti, D. (1968b). The enthalpy of formation of bismuth (III) iodide and the dissociation energy of bismuth (I) iodide. *Inorg. Chem.* 7, 211-213.
- Cubicciotti, D. (1968c). Thermodynamic properties of bismuth trifluoride. J. Electrochem. Soc. 115, 1138–1143.
- Cubicciotti, D. (1969a). Some thermodynamic properties of the thallium oxides. *High Temp. Sci.* 1, 11–17.
- Cubicciotti, D. (1969b). Some thermodynamic properties of antimony trifluoride. *High Temp. Sci.* 1, 268–276.
- Cubicciotti, D. (1970). The thermodynamics of vaporization of thallous oxide. *High Temp. Sci.* 2, 213–220.
- Cubicciotti, D., and Eding, H. (1965). Enthalpies, entropies, and free energy functions of TlF, TlBr, and TlI above room temperature. *J. Chem. Eng. Data* 10, 343–345.
- Cubicciotti, D., and Eding, H. (1967). Enthalpy and entropy increments above 298K for BiBr₃, Bi₂O₃, Tl₂O₃, and Tl₂O. J. Chem. Eng. Data 12, 548–551.
- Cubicciotti, D., Eding, H., Keneshea, F. J., and Johnson, J. W. (1966). The saturation thermodynamic functions for bismuth chloride from 298°K to the critical point. J. Phys. Chem. 70, 2389–2393.
- Demaria, G., Malaspina, L., Bardi, G., and Gigli, R. (1973). Simultaneous determination by Knudson effusion-microcalorimetric technique of the vapour pressure and sublimation enthalpy of antimony trifluoride. Vapour pressure of bismuth trifluoride. Rev. Roum. Chim. 18, 367–375.
- Drake, M. C., and Rosenblatt, G. M. (1976). Raman spectroscopy of gaseous GaCl₃ and GaI₃. J. Chem. Phys. **65**, 4067–4071.
- Drowart, J., and Smoes, S. (1977). Determination by the mass spectrometric Knudsen cell method and discussion of the dissociation energies of the molecules Se₂(g), SSe(g), and SeTe(g). J. Chem. Soc. Faraday Trans. II 73, 1755–1767.
- Faktor, M. M., Garrett, I., Lyons, M. H., and Moss, R. H. (1977). Thermodynamic study of the chemical vapour transport system GaAs-HBr

- using a modified entrainment method. J. Chem. Soc. Faraday Trans. I 73, 1446–1453.
- Faure, F. M., Mitchell, M. J., and Bartlett, R. W. (1972). Vapor pressure study of stibnite (Sb₂S₃). *High Temp. Sci.* **4**, 181–191.
- Feather, D. H., Büchler, A., and Searcy, A. W. (1972). The vapor pressures of gallium trifluoride monomer and dimer. *High Temp. Sci.* 4, 290–300.
- Galasso, V., Bigotto, A., and dealti, G. (1966). Normal vibrations and thermodynamic properties of GeH₃CN, Ge₂H₆, and GeH₃CH₃. Z. Phys. Chem. **50**, 38–45.
- Gordon, J. S. (1969). Thermodynamic functions of hydrogen selenide. J. Chem. Eng. Data 14, 460.
- Grinberg, Ya. Kh., Boryakova, V. A., and Shevel'kov, V. F. (1976). Thermodynamic properties of indium iodides. *Inorg. Mater.* 12, 348–352.
- GROSS, P., HAYMAN, C., AND BINGHAM, J. T. (1966). Heats of formation of germanium tetrafluoride and of the germanium dioxides. *Trans. Faraday* Soc. 62, 2388-2394.
- Gunn, S. R. (1964). The heats of formation of H₂Se and H₂Te. Correlations of simple covalent hydrides. J. Phys. Chem. **69**, 949–952.
- Gunn, S. R. (1972). The enthalpies of formation of arsine and biarsine. *Inorg. Chem.* 11, 796–799.
- Gunn, S. R., and Green, L. G. (1961). The heats of formation of some unstable gaseous hydrides. J. Phys. Chem. 65, 779–783.
- Hajiev, S. N. (1970). Advances in experimental thermochemistry. 1. The determination of enthalpies of formation of binary semiconducting compounds by direct synthesis in a bomb calorimeter. J. Chem. Thermo. 2, 765-773.
- HANSEN, E. E., MUNIR, Z. A., AND MITCHELL, M. J. (1969). Sublimation pressure and sublimation coefficient of single-crystal lead selenide. J. Amer. Ceram. Soc. 52, 610-612.
- Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., and Kelley, K. K. (1973). Selected Values of the Thermodynamic Properties of Binary Alloys. Amer. Soc. Metals.
- Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, D. D. (1973). Selected Values of the Thermodynamic Properties of the Elements. Amer. Soc. Metals.
- Jeffes, J. H. E., and McKerrell, H. (1964). The thermodynamics of hydrides. J. Iron Steel Inst. 202, 666–676.
- KARBANOV, S. G., ZLOMANOV, V. P., AND NOVO-SELOVA, A. V. (1969). Saturated vapor pressures of solid and liquid germanium monosulfide and monoselenide. *Inorg. Mater.* 4, 1634–1637.
- Kelley, K. K. (1960). Contributions to the Data on Theoretical Metallurgy, XIII., High-Temperature Heat-Content, Heat-Capacity, and Entropy Data

- for the Elements and Inorganic Compounds. U.S. Bur. Mines Bull. No. 584, Washington, D.C.
- Kelley, K. K., and Christensen, A. U. (1961). High-temperature heat content and entropies of crystalline and glassy germanium dioxide. U.S. Bur. Mines Rept. Invest. No. 5710.
- KELLEY, K. K., AND KING, E. G. (1961). Contributions to the Data on Theoretical Metallurgy, XIV. Entropies of the Elements and Inorganic Compounds. U.S. Bur. Mines Bull., No. 592, Washington, D.C.
- Kerimov, I. G., Mamedov, K. K., Kostryukov, V. N., and Mekhtiev, M. I. (1971). Heat capacity of some A^{III}B^{VI}-type semi-conductors. In *Teplofiz. Svoistva Tverd Tel, Mater. Vses. Teplofiz. Konf. Svoistvam Veshchestv Vys. Temp.* (G. V. Samsonov, Ed.), 3rd ed., 1968. Naukova Dumba, Kiev, USSR.
- Krasnov, K. S., and Solomonik, V. G. (1973). Thermodynamic functions and molecular constants for dimer forms of monohalides of the gallium subgroup metals. *Teplofiz. Vys. Temp.* 10, 973–978. [Translation: *High Temp.* 10, 877–881.]
- Kuniya, Y., Fujii, T., and Yuizumi, M. (1976). Thermodynamic properties of phosphorus-, arsenic-, and antimony triiodides. *Denki Kagaku* 44, 124–130.
- LAZAREV, V. B., GREENBERG, J. H., SHEVCHENKO, V. J., MARENKIN, S. F., AND KOSLOV, S. E. (1976). Sublimation thermodynamics of Cd₃P₂. J. Chem. Thermo. 8, 61–65.
- Lichter, B. D., and Sommelet, P. (1969). Thermal properties of A^{III}B^V compounds. II. High temperature heat contents and heats of fusion of InAs and GaAs. *Trans. Metall. Soc. AIME* 245, 1021–1027.
- Lyon, W. G., Westrum, E. F., and Chavret, M. (1971). Heat capacity and thermodynamic properties of thallous fluoride from 5 to 445 K. J. Chem. Thermo. 3, 571-581.
- Mamedov, K. K., Kerimov, I. G., Mekhtiev, M. I. and Masimov, E. A. (1972). Specific heat, entroy, and enthalpy of Ga and In chalcogenides at low temperatures. *Inorg. Mater.* 8, 1843–1845.
- Manley, T. R., and Williams, D. A. (1965). Mean square amplitudes and thermodynamic functions of some group Vb pyramidal trihalides. *Spectrochim. Acta* 21, 1467–1470.
- Martosudirdjo, S., and Pratt, J. N. (1974). Calorimetric studies of the heats of formation of IIIB-VB adamantine phases. *Thermochim. Acta* 10, 23-31.
- Medzhidov, R. A., and Rasulov, S. M. (1976). Enthalpy and specific heat of germanium telluride at high temperatures. *High Temp* 14, 581–583.
- Melekh, B. T., Stepanova, N. B., Fomina, T. A., and Semenkovich, S. A. (1971). Thermodynamic

- properties of compounds in the tin-selenium system. Russ. J. Phys. Chem. 45, 1144-1145.
- Mikus, F. F., and Carlyon, S. J. (1950). The equilibrium between ammonia and hydrogen telluride. J. Amer. Chem. Soc. 72, 2295–2296.
- MIKUS, F. F., AND POSS, F. J. (1949). Equilibrium between ammonia and hydrogen selenide. J. Amer. Chem. Soc. 71, 429–431.
- Mills, K. C. (1972). The heat capacities of $Ga_2O_3(c)$, $Tl_2O_3(c)$, ZnO(c), and CdO(c). High Temp.—High Pressures 4, 371–377.
- MILLS, K. C. (1974). Thermodynamic Data for Inorganic Sulphides, Selenides, and Tellurides. Butterworths, London.
- MILLS, K. C. (1976). Molar heat capacities and enthalpies of transition for InSe(c), InSe_{1.2}(c) and In₂Se₃(c). *High Temp.—High Pressures* 8, 225–230.
- NORTHTROP, D. A. (1971). Thermogravimetric investigation of the vaporization of lead telluride, tin telluride, and germanium telluride. J. Phys. Chem. 75, 118–132.
- Nover, J. C., and Richardson, F. D. (1972). Stannous oxide and the solubility of oxygen in tin. Inst. Min. Metall. Trans. Sect. C 81, 63-68.
- O'Hare, P. A. G. (1968a), The thermodynamic properties of gaseous Ge₂, GeF₄, GeF₂, and GeF. *US AEC ANL*. Rept. No. 7523.
- O'Hare, P. A. G. (1968b). The thermodynamic properties of As₂, As₄, and some arsenic fluorides. US AEC ANL Rept. No. 7456.
- Pankratz, L. B. (1965). High-temperature heat contents and entropies of gallium phosphide, indium phosphide, and indium sulfide. U.S. Bur. Mines Rept. Invest. No. 6592, 7 pp.
- Pupp, C., Murray, J. J., and Pottie, R. F. (1974). Vapour pressures of arsenic over InAs(c) and GaAs(c). The enthalpies of formation of InAs(c) and GaAs(c). J. Chem. Thermo. 6, 123–134.
- RAI, B., AND SINGH, J. (1971). Dissociation energies of bismuth and beryllium monofluorides. Spectrosc. Lett. 4, 129–137.
- RAMAKRISHNAN, E. S., AND CHANDRASEKHARAIAH, M. S. (1975). Thermodynamic stability of amorphous germanium monoxide. *Trans. Indian Inst. Metals* 28, 58–63.
- RASULOV, S. M., AND MEDZHIDOV, R. A. (1977). Thermodynamic properties of glassy, crystalline, and liquid arsenic selenide. Russ. J. Phys. Chem. 51, 969–970.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978). Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10⁵ Pascals) Pressure and at Higher Temperatures. US Geol. Surv. Bull. No. 1452. U.S. Govt. Print. Off., Washington, D.C.

- ROBIE, R. A., AND WALDBAUM, D. R. (1968).

 Thermodynamic Properties of Minerals and Related Substances at 298.15°K (25.0°C) and One Atmosphere (1.013 bars) Pressure and at Higher Temperatures. US Geol. Surv. Bull. No. 1259, U.S. Govt. Print. Off., Washington, D.C.
- Saalfeld, F. E., and Svec, H. J. (1963). The mass spectra of volatile hydrides. I. The monoelemental hydrides of the group IVB and VB elements. *Inorg. Chem.* 2, 46–50.
- SHAMSUDDIN, AND MISRA, S. (1973). Thermodynamic properties of lead selenide. Scr. Metall. 7, 547-554.
- SHAULOV, YU. KH., AND MOSIN, A. M. (1973a).
 Thermodynamic functions of gallium chlorides.
 Russ. J. Phys. Chem. 47, 642-643.
- SHAULOV, YU. KH., AND MOSIN, A. M. (1973b).
 Thermodynamic functions of arsenic chlorides.
 Russ. J. Phys. Chem. 47, 644-645.
- SHINKAIEV, A. N. (1973). Thermodynamic functions of gallium nitride in the solid state. *Izv. Vyssh. Ycheb. Zaved. Khim. Khim. Tekhnol.* 16, No. 9, 1451-1453.
- SHISHKIN, Yu. A., MARUSIN, V. V., AND KOLYSHEV, A. N. (1973a). Thermodynamic properties of stannane at high temperatures. Russ. J. Phys. Chem. 47, 404-405.
- Shiskin, Yu. A., Marusin, V. V., and Kolyshev, A. N. (1973b). Thermodynamics of lead (IV) hydride at high temperatures VINITI 6966-6973.
- Sokolov, V. V., Pashchinkin, A. S., Novoselova, A. V., Ryazantsev, A. A., Dolgikh, V. A., and Klinchikova, S. A. (1969). Saturated vapor pressures of tin and lead tellurides and lead selenide. *Inorg. Mater.* 5, 12–15.
- Stull, D. R., and Prophet, H. (1971). JANAF Thermochemical Tables, 2nd ed. Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. 37, Washington, D.C.
- SULLIVAN, C. L., ZEHE, M. J., AND CARLSON, K. D. (1974). Heats of reaction for gaseous species in the vaporization of solid Sb₂Te₃. *High Temp. Sci.* 6, 80-97.
- Trifonov, V. A., Dolgikh, V. A., Popovkin, B. A., Belousov, V. I., and Novoselova, A. V. (1975). Dissociation of antimony and bismuth triiodides in the gas phase. *Russ. J. Inorg. Chem.* 20, 825–828.
- UY, O. M., AND DROWART, J. (1969). Mass spectrometric determination of the dissociation energies of the molecules BiO, BiS, BiSe, and BiTe Trans. Faraday Soc. 65, 3221–3230.
- Vasil'ev, V. P., Nikoi'skaya, A. V., Chernyshov, V. V., and Gerasimov, Ya. I. (1973). Thermodynamic properties of thallium sulfides. *Inorg. Mater.* 9, 807–809.
- Vasil'ev, V. P., Nikol'skaya, A. V., and Gerasimov, Ya. I. (1971). Thermodynamic

- characteristics of higher sulfides of thallium and some regularities in the IIIb subgroup monochalcogenide series. *Dokl. Akad. Nauk SSSR* 199, 1094–1097.
- Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H. (1968). Selected Values of Chemical Thermodynamic Properties. Natl. Bur. Stand. (U.S.) Tech. Note 270-3, Washington, D.C.
- Yushin, A. S., and Devyatykh, G. G. (1969). Equilibrium constant for and heat of formation of hydrogen selenide from the elements. Russ. J. Phys. Chem. 43, 550-552.
- ZHDANOV, V. M. (1971). Low-temperature heat capacity, enthalpy, and entropy of germanium telluride. Russ. J. Phys. Chem. 45, 1356.

ACKNOWLEDGMENTS

We wish to acknowledge stimulating discussions with Professors S. G. Kuhn and C. C. Stephenson, and Mr. S. S. Barshay. This work was supported by NASA Planetary Atmospheres Program Grant NGL-22-009-521.

REFERENCES

- Barshay, S. S., and Lewis, J. S. (1978). Chemical structure of the deep atmosphere of Jupiter. *Icarus* 33, 593-611.
- BEER, R. (1975). Detection of carbon monoxide in Jupiter. Astrophys. J. 200, L167-L169.
- BEER, R., AND TAYLOR, F. W. (1978). The abundance of carbon monoxide in Jupiter. *Astrophys. J.* 221, 1100–1109.
- CAMERON, A. G. W. (1973). Abundances of the elements in the solar system. Space Sci. Rev. 15, 121–146.
- Dean, J. A. (1973). Lange's *Handbook of Chemistry*, 11th ed. McGraw-Hill, New York.
- FINK, U., LARSON, H. P., AND TREFFERS, R. R. (1978). Germane in the atmosphere of Jupiter. *Icarus* 34, 344-354.
- GOODEVE, C. F., AND STEIN, N. O. (1931). The absorption spectra and the optical dissociation of the hydrides of the oxygen group. *Trans. Faraday* Soc. 27, 393-404.
- LARSON, H. P., TREFFERS, R. R., AND FINK, U. (1977). Phosphine in Jupiter's atmosphere: The evidence from high-altitude observations at 5 micrometers. Astrophys. J. 211, 972-979.
- LARSON, H. P., FINK, U., AND TREFFERS, R. R. (1978). Evidence for CO in Jupiter's atmosphere from airborne spectroscopic observations at 5 microns. Astrophys. J. 219, 1084-1092.
- Lewis, J. S. (1969). Observability of spectroscopically active compounds in the atmosphere of Jupiter. *Icarus* 10, 393–409.

- Prather, M. J., Logan, J. A., and McElroy, M. B. (1978). Carbon monoxide in Jupiter's upper atmosphere: An extra-planetary source. *Astrophys. J.* 223, 1072–1081.
- PRINN, R. G. (1970). UV radiative transfer and photolysis in Jupiter's atmosphere. *Icarus* 13, 424-436.
- PRINN, R. G., and Barshay, S. S. (1977). Carbon monoxide on Jupiter and implications for atmospheric convection. Science 198, 1031–1034.
- PRINN, R. G., AND LEWIS, J. S. (1975). Phosphine on Jupiter and implications for the Great Red Spot. Science 190, 274–276.
- RIDGWAY, S. T. (1974). The infrared spectrum of

- Jupiter, 750 to 1200 cm⁻¹, Bull, Amer. Astron. Soc. **6**, 376.
- RIDGWAY, S. T., LARSON, H. P., AND FINK, U. (1976). The infrared spectrum of Jupiter, In Jupiter (T. Gehrels, Ed.), pp. 348–417, Univ. of Arizona Press, Tucson.
- ROSSINI, F. D., WAGMAN, D. D., EVANS, W. H., LEVINE, S., AND JAFFE, I. (1952). Selected Values of Chemical Thermodynamic Properties. U.S. Natl. Bur. Stand. Circular No. 500, Washington, D.C.
- Schulz, E. D., and Holland, A. C. (1963). The solar flux incident at the top of the atmospheres of Earth and neighboring planets for the spectral region 50 Å to 3000 Å, NASA CR-11