410
11-3-80
JPL

MASTER

DOE/JPL/954343-80/19

10. 1988

PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL
TASK I

Quarterly Technical Progress Report (XIX), March 1—May 31, 1980

By
Carl L. Yaws
Ku-Yen Li

June 1980
Date Issued

Work Performed Under Contract No. NAS-7-100-954343

Lamar University
Chemical Engineering Department
Beaumont, Texas

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$6.00
Microfiche \$3.50

PROCESS FEASIBILITY STUDY IN SUPPORT OF
SILICON MATERIAL TASK I

QUARTERLY TECHNICAL PROGRESS REPORT (XIX)

Issue Date: June 1980

Reporting Period: March 1 - May 31, 1980

Carl L. Yaws and Ku-Yen Li

LAMAR UNIVERSITY
Chemical Engineering Department
P.O. Box 10053
Beaumont, Texas 77710

JPL Contract No. 954343

Contractual Acknowledgement

The JPL Low-Cost Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

Approval Signature

Carl L. Yaws

ACKNOWLEDGEMENT

The authors wish to acknowledge the valuable help and contributions of the following in the performance of this work:

Faculty-Staff

LARRY L. DICKENS
C. S. FANG
FRED H. PITTS
KEITH C. HANSEN

Graduate-Student Assistants

PRABODH M. PATEL
PRAFUL N. SHAH
STEVE HAO CHANG
HARRY YU
LEE-HSIN TSAO
CHUAM-TIO CHU

ABSTRACT

Analyses of process system properties were continued for chemical materials important in the production of silicon. Major physical, thermodynamic and transport property data are reported for silicon including critical constants, vapor pressure, heat of vaporization, heat of sublimation, heat capacity, density, surface tension, viscosity and thermal conductivity. The property data covers both liquid and solid phases and are reported as a function of temperature for rapid engineering usage.

Major efforts in chemical engineering analysis centered on the HSC process (Hemlock Semiconductor Corporation). The approach for the process involves performing initial analysis for DCS production (dichlorosilane) and then performing analysis of polysilicon production from the DCS. For the DCS production, status and progress are reported for primary activities of base case conditions (65%), reaction chemistry (65%), process flowsheet (60%), material balance (50%) and energy balance (40%). Two key features - redistribution reactor relocation and final distillation - are introduced to increase yield of DCS by about 10-20%, help insure purity and reduce potential dust (fine particle nucleation) components in the polysilicon feed material.

The preliminary flowsheet for DCS production was forwarded to Hemlock Semiconductor Corporation for initial screening and review. Hemlock Semiconductor is in agreement in regards to relocation of the redistribution reactor to increase yield. Additional follow-up review is in progress including boron removal options identified by Hemlock Semiconductor.

TABLE OF CONTENTS

	<u>PAGE</u>
I. PROCESS SYSTEM PROPERTIES ANALYSES (TASK 1)....	1
II. CHEMICAL ENGINEERING ANALYSES (TASK 2).....	25
III. SUMMARY - CONCLUSIONS.....	30
IV. PLANS.....	31

MILESTONE CHART

I. PROCESS SYSTEM PROPERTIES ANALYSES (TASK 1)

During this reporting period, analyses were continued for process system properties of chemical materials important in the production of silicon. Primary progress and status are reported for physical, thermodynamic and transport properties of silicon.

PHYSICAL PROPERTIES (TABLE I-1)

Experimental values for the melting point have been reported (1, 32, 49, 67, 110); however, all other values have been calculated. Estimated values for the boiling point range from 2285°C to 3267°C (10, 31, 52, 55, 109, 124, 125, 137). Our value is estimated to give a reasonable computer fit to the available vapor pressure data. Estimated values of critical properties are reported by van Laar's calculation (5, 34, 43, 44, 101, 125), Baibus (4) and Gates and Thodos (31, reported in Table I-1). Solid properties listed in Table I-1 are at room temperature while liquid properties are at the melting point.

VAPOR PRESSURE (FIGURE I-1)

Recent vapor pressure data reported by American (1, 18) and British (6) workers was selected and extended using the YSSP vapor pressure correlation (157):

$$\log P_V = A + \frac{B}{T} + C \log T + DT + ET^2$$

where P_V is the vapor pressure of saturated liquid, mm Hg; T is temperature, °K; and A , B , C , D and E are correlation constants derived using a generalized least squares program. Other data (10, 125, 142) was not used because of high percentage error which is reported to be due to extensive reaction of the silicon (54, 165). For the 44 experimental data points used (which are all in the range below 0.2 mm Hg) the average absolute deviation was 17%.

HEAT OF VAPORIZATION (FIGURE I-2)

Heat of vaporization values of about 3850 cal/gm are available (1, 6, 18, 55) as well as older (10, 125a, 147) and Russian (142) values of about 3170 cal/gm. From the vapor pressure data near the melting point, the heat of vaporization was determined using the Clausius-Clapyrin equation. Using these values, Watson's correlation (165) was used to extend the heat of vaporization to the boiling point.

$$\Delta H_V = \Delta H_{V_1} \left[\frac{7500 - T}{7500 - T_1} \right]^n \quad (I-2)$$

where $n = 0.38$ and all other terms have their usual meanings. The calculated values give a 1.3% absolute percentage deviation with the five experimental references giving values near 3850 cal/gm near the melting point.

HEAT OF SUBLIMATION (FIGURE I-3)

Heat of sublimation based on limited data have been reported recently in the literature (18, 54, 106). Using the YSSP correlation of vapor pressure data (as described earlier), heats of sublimation were calculated using the Clausius-Clapeyron equation (123):

$$\Delta H_{\text{sub}} = P \Delta V_{\text{sub}} \frac{\delta P}{\delta T} \quad (I-3)$$

where ΔH_{sub} is the heat of sublimation, cal/gr-mol; P is the vapor pressure, atm; and $\Delta V_{\text{sub}} = V_{\text{gas}} - V_{\text{solid}}$. The derivative, $\delta P / \delta T$, was determined from differentiation of the YSSP vapor pressure equation. Considering the possible inaccuracy in the extrapolation of very low vapor pressures at low temperatures, these values should be considered only order-of-magnitude calculations below 600°C.

HEAT CAPACITY (FIGURES I-4 & I-5)

Liquid heat capacities have been reported from experiments done in the range from the melting point to about 200°C above the melting point (67, 100). The values of Kantur (67) were selected because the temperature range was significantly greater with the temperatures appearing to be more accurately determined. The average values of heat capacity and temperature was taken as a reference point and the values were extended over the liquid range using the relationship:

$$\text{Liquid Heat Capacity} \times \text{Liquid Density} = \text{constant} \quad (I-4)$$

Calculated values agree within two percent of the values published in the experimental work (67).

Solid heat capacities have been reported by many authors (144, 138, 55, 34, 96, 164, 62, 115, and others) which give similar values. The JANAF and Touloukian values (138, 144) were selected.

DENSITY (FIGURES I-6 & I-7)

Several authors (93, 37, 14, 25, 9) have reported measured liquid density values from the melting point to about 400°C above the melting point. The data was extended to the boiling point using a modification of the Rackett equation (166):

$$\rho = \rho_c z^{-(1 - T_r)^{2/7}} \quad (I-5)$$

where ρ_c is critical density; T_r is reduced temperature and z is a parameter defined by the experimental data. Calculated values give a 0.5% average absolute deviation from the thirty reported experimental values. The vertical line at the melting point indicates the change in density upon melting.

Solid density measurements of silicon are recorded near room temperature (133, 134) at the melting point (85) and many others give linear thermal expansion data which are summarized by Touloukian (144). Solid densities at various temperatures were calculated using the percentage linear expansions (144) according to the relation:

$$\rho = \rho_1 \times \{1 - [3x(\text{percent linear expansion})]\} \quad (I-6)$$

Calculated values gave less than one percent deviation with the measured values over the solid range.

SURFACE TENSION (FIGURE I-8)

Limited data for the surface tension of silicon show a wide range of values (79, 71, 130, 25, 40). From the experimental data in close agreement (79, 71, 130), values were extended to the boiling point using the Othmer relation (123):

$$\sigma = \sigma_1 \left[\frac{7500 - T}{7500 - T_1} \right]^n \quad (I-7)$$

where σ is surface tension at T , dynes/cm, and n is the correlation parameter, 1.2. The other parameters have their usual meaning. Calculated values agree with the limited data (5 values) with a 1.5% absolute error.

LIQUID VISCOSITY (FIGURE I-9)

Liquid viscosity data for silicon are available from the melting point to about 400°C above the melting point (9, 81, 127, 163). Values from the melting point to the boiling point were calculated using a $\log \eta_L$ vs $1/T$ linear relationship. Average absolute percentage error was 9.1% on 19 data points, due largely to the wide scatter of the experimental data.

THERMAL CONDUCTIVITY (FIGURES I-10 & I-11)

No liquid thermal conductivity measurements or calculations are available in the literature. An estimation of the thermal conductivity at the melting point was made using a modification of the Missenard relation (123):

$$\lambda_{L_O} = \frac{k (T_b \rho_o)^{1/2} C_{p_L}}{M^{1/2} N^{1/4}} \quad (I-8)$$

and the values were extended to the boiling point by combining this equation with the Reidel (123) equation:

$$\lambda_L = A \left[1 + \frac{20}{3} (1 - T_r)^{2/3} \right] \quad (I-9)$$

The calculated values are generally in agreement with the fact that liquid metals have larger thermal conductivities than normal organic liquids (123). The same calculations for λ_L for the metals: Tin, Antimony, Lead, Gallium, Potassium, Iron and Mercury at their melting points gave an average absolute deviation of 30%. Therefore, these values are given only as order-of-magnitude estimates.

Solid thermal conductivity data has been reported by several authors (104, 23, 83 and others). The recommended values of Touloukian (144) were selected.

TABLE I-1

PHYSICAL PROPERTIES AND CRITICAL CONSTANTS OF SILICON

<u>No.</u>	<u>Identification</u>	<u>Silicon</u>
1.	Symbol	Si
2.	State (std. cond.)	Solid
3.	Atomic Weight	28.086
4.	Boiling Point, b.p., °C	2,878*
5.	Melting Point, m.p., °C	1,412 ± 2
6.	Critical Temperature, T_C , °C	4,886*
7.	Critical Pressure, P_C , atm	530*
8.	Critical Volume, V_C , cm ³ /gr mol	232.6*
9.	Critical Density, ρ_C , gr/cm ³	0.1207*
10.	Vapor Pressure, mm Hg	2.8×10^{-4} (at m.p.)
11.	Heat of Vaporization, cal/gr	3,812 (at m.p.)
12.	Heat of Sublimation, cal/gr	4,075 (at m.p.)
13.	Heat of Fusion, cal/gr	264* (at m.p.)
14.	Liquid Heat Capacity, cal/gr-mol °C	6.755 (at m.p.)
15.	Solid Heat Capacity, cal/gr-mol °C	4.78 (at 25°C)
16.	Liquid Density, gr/cm ³	2.533 (at m.p.)
17.	Solid Density, gr/cm ³	2.329 (at 25°C)
18.	Percent Expansion on Freezing	10% (at m.p.)
19.	Surface Tension, dynes/cm	736 (at m.p.)
20.	Liquid Viscosity, centipoise	0.88 (at m.p.)
21.	Liquid Thermal Conductivity, cal/secxcmx°C	1.025×10^{-3} (at m.p.)
22.	Solid Thermal Conductivity, cal/secxcmx°C	0.353 (at 25°C)

*estimated

Figure I-1--Vapor Pressure vs. Temp. for Silicon

Figure I-2--Heat of Vaporization vs. Temp. for Silicon

Figure I-3--Heat of Sublimation vs. Temp. for Silicon

Figure I-4--Liquid Heat Capacity vs. Temp. for Silicon

Figure 1-5--Solid Heat Capacity vs. Temp. for Silicon

Figure I-6 -- Liquid Density vs. Temp. for Silicon

Figure I-7 -- Solid Density vs. Temp. for Silicon

Figure I-8 -- Surface Tension vs. Temp. for Silicon

Figure I-9 -- Liquid Viscosity vs. Temp. for Silicon

Figure I-10 -- Liquid Thermal Conductivity vs. Temp. for Silicon

Figure I-11 -- Solid Thermal Conductivity vs. Temp. for Silicon

REFERENCES

1. Batdorf, R.L and Smits, F. M., Jour. Appl. Phys., 30, 259 (1959).
2. Akiyama, Kenji, Nat'l Tech, Dept. (Matsushita Elec. Ind. Co., Osaka), 8, 114-20 (1962).
3. Anderson, C. T., J. Am. Chem. Soc., 52, 2301-4 (1930).
4. Baibuz, V. F., Tr. Gos. Inst. Prikl Khim, 49, 113-19 (1962).
5. Bailar, J. C., Jr., Ed., "Comprehensive Inorganic Chemistry", 1, Pergamon Press, Oxford (1973).
6. Grieveson, P. and Alcock, C. B., Special Ceramics, P. Popper, ed., Heywood & Co., London (1960).
7. Barin, I. and Knacke, O., Thermochemical Properties of Morg. Substances, 686 (1973).
8. Baughan, E. C., Quant. Rev., 7, 116 (1953).
9. Baum, B. A., others, Izv. Akad Nauk SSSR, Metal, 1967 (1), 62-9, Russ.
10. Baur, E. and Brunner, R., Helv. Chim. Acta, 17, 958 (1934).
11. Beers, D. S., others, Proc. Intern. Conf. Phys. Semicond., Exeter, England, 1962, 41-8.
12. Belogurov, B. B., Zhur. Fiz Khim, 34, 440-3 (1960).
13. Bermann, R. and Foster, E. L., Proc. Roy. Soc. (London), A237, 344-54 (1957).
14. Bobkovski, V. N., others, Konstr. Mater Osn. Grafita, 1970, No. 5, 138-43 (Russ.).
15. Boublik, T., others, "The Vapor Pressure of Pure Substances", Elsevier, N. Y. (1973).
16. Burki, Friedrich, Helvetica Chim. Acta, 2, 27-38 (1919).
17. Carruthers, J. A., others, Proc. Roy. Soc. (London) A238, 502-14 (1957).
18. Davis, S. G., others, J. Chem. Phys., 34, 659-64 (1961).
19. Davydov, K. N., others, Fiz. Kim. Osnovy Proizvodstva Stali, Akad Nauk SSR., Trudy 3-ei Kerf, 1955, 350-69 (1957).
20. Dayal, B., The Sp. Heat's of Metallic Si, Proc. Indian Acad. Sci., 20A, 87-91 (1944).
21. Dean, J. A., Ed., "Lange's Handbook of Chemistry", 11th ed., McGraw-Hill, N. Y. (1973).

REFERENCES (Continued)

22. Ditchburn, R.W. and Gilmour, J. C., *Revs. Modern Phys.*, 13, 310-27 (1941).
23. Dolling, F. and Cowley, R. A., *Proc. Phys. Soc. (London)*, 88, (2), 463-94 (1966) England.
24. Elyutin, V.P. and Pavlov, Y. A., *Silicon*, *Osn. Met*, 1968, 5, 375-84.
25. Elyutin, V. Pl, others, *Fiz. Khim. Poverkh. Yavlenii Rasplavakh*, 1971, 153-6.
26. Erdman, C. A., others, *J. Appl. Phys.*, 1973, 44 (7), 3127-9.
27. Fedoroff, M., *Monogr Met Haute Purete*, 1977, 3, 523-76 (Fr.)
28. Fine, M. E., *J. Chem. Phys*, 21, 1427 (1953).
29. Flubacher, P., others, *Phil. Mag*, (8), 4, 273-294 (1959).
30. Gashenko, S. I., others, *Kremnii Gernamii*, 1970, No. 2, 59-61.
31. Gates, D.S. and Thodos, G., *AIChE Journal*, 6, 50-4, (1960).
32. Gayler, M. L. V., *Nature*, 142, 478 (1938).
33. Gel'd, P. V., others, *Fiz. Metal. i Metallovel. Akad. Nauk, SSSR, Ural. Filial*, 2, 244-53 (1956).
34. Gmelin's Handbook of I. C., System 15, Silicon, Part C.
35. Gibbons, D. F., *Thermal Expansion of Some Crystals with the Diamond Structure*, *Phys. Rev.*, vol 112, pp. 136-140 (1958).
36. Gel'd, P.V. and Gertman, Y. A., *U. S. At. E. Com. AEC-tr-4879*, 181-5 (1960).
37. Gel'd, P.V. and Gertnam, Y. M., *Fiz Metal i Metalloved Akad. Nauk SSSR*, 12, No. 1, 47-50 (1951).
38. Gerlich, D., others, *J. Appl. Phys*, 36, (1), 76-9 (1965).
39. Glassbrenner, C. J., *Univer. Microfilms order No. 64-3533*, 208 pp.
40. Gogiberidze, Y. M., others, *Poverkh. Yavleniya Rasplavakh*, 1968, 114-17, (Russ), Eremko, V. D. (ed.).
41. Goldsmid, H. J., *Proc. Phys. Soc., (London)* 67B, 360-3 (1954).
42. Gul'yaev, P.V. and Petrov, A. V., *Soviet Phys. Solid State*, 1, 330-4 (1959).
- 42a. Guertler, W. and Pirani, M., *Z. Metllkunde II*, 1-7 (1919).
43. Hampel, C. A. (ed.), *Rare Metals Handbook*, Reinhold Pub. Co., N. Y. (1954).
44. Hampel, C. A., *The Encyclopedia of the Chemical Elements*, Reinhold Book Co., N. Y. (1968).

REFERENCES (Continued)

45. Hampel, C.A. and Hawley, G. G., The Encyclopedia of Chemistry, 3rd ed., Van Nostrand Reinhold Co., N.Y. (1973).
46. Hamilton, R.A.H. and Parrott, J. E., Phys.Lett. A, 1969, 29 (9), 556-8
47. Hart, M, and Morgan, I.G., At. Masses Fundam. Constants, Proc. Int. Conf. 4th, 1971 (pub. 1972), 505-15.
48. Ho, Cho. Yen and Powell, R.W., Nat. Bur. Stand. Spec. Pub., 1967, No. 302, 33-46 (Eng.).
49. Hoffman, F. and Schulze, A., Physik, Z., 38, 901-5 (1937); Metallwirtschaft, 17, No. 1, 3-6 (1938).
50. Hölbling, R., The Prep. and Some Prop. of Pure Metallic Si, Z. Angew Chem., 40, 655-9 (1927).
51. Holyer, J., AD 62 1152, Avail CFSTI, 44pp.
52. Honig, R. E., V. P. Data for the Solid & Liq. Elements, RCA Rev., vol. 23, pp. 567-586 (1962).
53. Honig, R. E., J. Chem. Phys., 21, 573 (1953).
54. Honig, R. E., J. Chem. Phys., 22, 1610 (1954).
55. Hultgren, Ralph, others, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio (1973).
56. Hsiao, S.N. and Liu, I. H., Wu Li Hsueh Pao, 20 (8) 699-704, 1964 (Ch).
57. Hsieh, Yu-Chang, J. Chem. Phys., 22, 306-11 (1954).
58. Hull, G.W. and Geballe, Tilt, Phys. Rev., 96, 845 (1954).
59. "International Critical Tables", Vol. I-VI, McGraw-Hill, N. Y. (1926-1929).
60. Ioffe, A. F., Doklady Akad. Nauk. SSSR, 87, 369-72 (1952).
61. Ioffe, A.V. and A.F., Zhur. Tekh. Fiz., 24, 1910-11 (1954).
62. Ivanova, L. I., Zhur. Obschchei. Khim., (J. Gen. Chem), 21, 444-52 (1951).
63. Jasper, J. J., J. Phys. Chem. Ref. Data, 1 (4), 841 (1972).
64. Jayaraman, A., others, Phys. Rev, 130, 540-7 (1963).
65. Kalishevich, G. I., others, Zh. Fiz. Khim., 39 (12), 2999-3001 (Russ.) (1965).
66. Kaplun, A.B. and Solov'ev, A. N., Zh. Prikl. Mekhan i. Tekhn. Fiz., 1966 (4), 139-41 (Russ).
67. Kantur, P. B., others, Ukrain, Fiz. Zhur., 5, 358-62 (1960).

REFERENCES (Continued)

68. Karapet'yants, M. Kh. & M. L., Thermodynamic Constants of Inorganic & Organic Compounds, Ann Arbor Humprey Science Pub., Ann Arbor, Mich. (1970).
69. Karapet'yants, M. L., "Tables of Some Thermodynamic Properties of Different Substances", Trudy MKh TI in Mendeleeva, No. 3, Moscow (1961) (Russ.).
70. Karpov, Yu. S., Sprav. Elektrotekh Mater., Vtoroe, Pererab Izd., 1976, 3, 544-67, 669-70, (Russ.).
71. Keck, P.H. and Van Horn, W., The Surface Tension of Liq. Si & Ge., Phys. Rev., Vol. 91, pp. 512-513 (1953).
72. Keesom, P.H. and Pearlman, N., Natl. Bur. Standards Circ., 519, 279-83 (1952).
73. Keesom, P.H. and Seidel, G., Phys. Rev., 113, 33-9 (1959).
74. Kelley, K. K., Bull. Bur. Mines, No. 383 (1935).
75. Kelley, K. K., Contributions to Data on Theoretical Metallurgy, Bur. Mines Bull., No. 477 (1950).
76. Kelley, K. K., Bull. Bur. Mines, No. 584, 159 (1960).
77. Kelley, K. K., Bull. Bur. Mines, No. 592, 113 (1961).
78. Khusanova, B. N., Vestn. Mosk. Univ. Fiz. Astron., 1968, 23 (4), 117-18 (Russ.).
79. Kingery, W.D. and Humenik, M., Jr., J. Phys. Chem., 57, 359-63 (1953).
80. Kirk, R. E. and Othmer, D. F., "Encyclopedia of Chemical Technology", 1st and 2nd ed., Interscience Encyclopedia Inc., N. Y., (1948-1970).
81. Klein, A. H., others, U.S.A. E. C., I. S. 835, 17pp.
82. Kocherov, P. V., others, Tr. Ural'sk Politekhn Inst., No. 144, 139-41 (1965) Russ.
83. Kokkas, A. G., RCA Rev., 1974, 35 (4), 579-81.
84. Korsunskii, A.M. and Bondareva, A. G., Zh. Fiz. Khim., 1973, 47 (11) 2762-4.
85. Krestovnikov, A. N., others, Dokl. Akad. Nauk SSSR, 174 (3) 634-7 (1967) Russ.
86. Krikorian, O. H., U.S.A. E. Comm., UCRL-6132, 7 pp. (1960).
87. Kulin, S., others, U.S. Clearinghouse Fed. Sci. Tech. Infor., A. D. 1970, No. 703275, 43 pp., Avil. CFSTI.
88. Kuprovskii, B. B. & Gel'd, P. V., Fiz. Metal. i. Metalloved, 3, 182-3 (1956).
89. van Laar, J. J., Proc. Acad. Sci. Amsterdam, 20, 492-504.

REFERENCES (Continued)

90. Landolt - Bornstein, Spriner-Verlag, Berlin.
91. Lange, N. A., ed., "Handbook of Chemistry", 10th ed., McGraw-Hill, N. Y. (1961).
92. Lees, J. and Williamson, B. H. J., Nature, 208, 50007, 278-9 (1965).
93. Logan, R.A. and Bond, W. L., Density Change in Silicon on Melting, J. Appl. Physics, vol. 30, 322 (1959).
94. Lucas, L. D., Mem. Sci. Rev. Met, 61, 1-24, 97-116 (1964).
95. Lucas, L.D. and Urbain, G., Compt Rend, 255, 2414-16 (1962).
96. Magnus, A., The Specific Heast of C, Si & SiC, Ann. Physik, 70, 303-31 (1923).
97. Manuilov, L. A. & Klyukuvskii, G. I., Fizicheskaya Khimiya i Khimiya Kremniya (Phys. Chem. & Chem. of Si) 3rd ed., Muscow; "Vysshaya Shkola", 311 p. (1962).
98. Maissel, L., Thermal Expansion of Silicon, J. Appl. Physics, vol. 31, p. 211 (L) (1960).
99. Mauer, F.A. and Bolz, L. H., P. B. Rept, 136066.
100. McSkimin, H. J., others, Measurement of Elastic Constants of Si Single Crystals & Their Thermal Constants, Phys. Rev., vol. 83, p. 1080 (L), (1951).
101. Mellor, J. W., "Inorganic and Theoretical Chemistry", (original volumes and supplements), Longmans, Green and Co., London (1956).
102. Mette, H., others, Phys. Rev., 117, 1491-3 (1960).
103. Meyer, F. and Sparnaay, M. J., Surface Phys Phosphors Semicond., 321-410 (1975).
104. Morris, R.G. and Martin, J. J., J. Appl. Phys., 34 (8), 2388-9 (1963).
105. Nakamura, Tetsuro, Nippon Kagaku Zasshi, 86 (5), 491-7 (1965).
106. Nesmeyanov, A. N., Vapor Pressure of the Elements, Academic Press, N. Y. (1963).
107. Nordmeyer, P. and Bernulli, Ber. Physik. Ges., 5, 175-78.
108. Novikova, S.I. and Strelkov, P. G., Fiz. Tverdugo Tela, 1, 1841-3 (1959).
109. Ohe, S., "Computer Aided Data Book of Vapor Pressure", , Data Book Publising Company, Tokyo, Japan (1976).
110. Olette, M., Phys. Chem. Steelmaking Proc., Dedham, Mass. 1956, 18-26 (1958).
111. Ormont, B. F., Doklady Akad Nauk SSSR, 106, 687-90 (1957).
112. Padnos, B. N., Internations Si Device Technology, V. Chem/ Metallurgical Prop. of Si, NASA Acc. No. N66 19917.

REFERENCES (Continued)

113. Pawlek, F., Metall, 19, (12), 1249-52 (1965) Ger.
114. Pearson, G.L. and Treuting, R. G., Surface Melt Patterns on Silicon, Acta Cryst., Vol. 2, 397-399 (1958).
115. Pehlke, R.P. and Elliot, J. F., Trans AIME, 215, 781-5 (1959).
- 115a. Perry, R. H., others, "Chemical Engineers' Handbook", 45th ed., McGraw-Hill, N. Y. (1973).
116. Perry, R.H. and Chilton, C. H., "Chemical Engineers' Handbook", 5th ed., McGraw-Hill, N. Y. (1973).
117. Petrov, B.K. and Kochetkov, A. I., Radiotekh. Elektron, 1974, 19, (1), 214-16 (Russ).
118. Phillips, J. C., Phys. Rev., 113, 147-55 (1959).
119. Popel', S. I., others Zh. Fiz. Khim., 1970, 44, (1), 260-1.
120. Redin, R. D., U. S. Clearinghouse Fed. Sci. Tech. Inform., AD 1969, AD 698154, 13 pp. Avail. CFSTI.
121. Reeber, R. R., Phys. Status Solidi A., 1975, 32, (1), 321-31.
122. Reid, R.C. and Sherwood, R. K., "The Properties of Gases and Liquids", 2nd ed., McGraw-Hill, N. Y. (1966).
123. Reid, R. C., others, "The Properties of Gases and Liquids", 3rd ed., McGraw-Hill, N. Y. (1977).
124. Raznjevic', Kuzman, Handbook of Thermodynamic Tables and Charts, McGraw-Hill, N. Y. (1976).
125. Runyan, W. R., Silicon Semiconductor Technology, McGraw-Hill Book Co., N. Y., (1965).
- 125a. Ruff, O. and Konschak, M., Z. Elektrochem. 32, 515-25 (1926).
126. Russell. A. S., Physik Z., 13, 59-65, Measurements of Sp. Ht. at Low Temps.
127. Samsonov, G. V., Handbook of the Physicochemical Properties of the Elements, (translated from Russian) IFI/PLENUM, N. Y. (1968).
128. Serebrennikor, N.N. and Gel'd, P. V., Doklady Akad Nauk. SSSR, 87, 1021-4 (1952).
129. Shanks, H. R., Phys. Rev., 130, 1743-8 (1963).
130. Shashkov, Yu.M. and Kolesnikova, T. P., Zh. Fiz. Khim., 37 (6) 1397-9 (1963).
131. Stuckes, A.D. and Chasmar, R. P., Rept. Meeting on Semiconductors, Rugby, 1956, 119-25.

REFERENCES (Continued)

132. Slack, G. A., Phys. Rev., 105, 829-31 (1957).
133. Straumanis, M.E. and Aka, E. Z., J. Applied Phys., 23, 330-4 (1952).
134. Smakula, A. and Kalnajs, J., Nuovo Cimento [10], 6, Suppl. 214-20 (1957).
135. Stuckes, A. D., Phil. Mag., 8, 5, 84-99 (1960).
136. Stull, D. R., Ind. Eng. Chem., 39 540 (1947).
137. Stull, D. R. and Prophet, H., Project Directors, "JANAF Thermochemical Tables", 2nd ed., NSRDS-NBS37, Natl. Bur. Stds., Washington, D. C., (1971).
138. Stull, D.R. and Sinke, G. C., "Thermodynamic Properties of the Elements", Adv. in Chem. Series, No. 18, A.C.S., Washington, D. C.
139. Suzuki, K. and Mikoshiba, N., Phys. Rev., B, 1971, [3] 3 (8), 2550-6 (Eng.).
140. Svehla, R. A., Tech. Report R-132 NASA, "Est. Visc. & Thermal Cond. of Gases at High Temps.", NASA, Washington, D. C. (1962).
141. Tavadze, F. N., others, Poverkh Yavleniya Rasplavakh, 1968, 159-62 (Russ).
142. Tsepilyawva, A. V., others, Vestnik Moskov Univ. Ser 11, 15, No. 5, 36-8 (1960)
143. Thompson, J.C. and Younglove, B. A., Phys. & Chem. Solids, 20, 146-9 (1961).
144. Touloukian, Y. S. and Makita, T., "Thermophysical Prop. of Matter", Supplement to Vol. 6, 83, IFI/Plenum, New York (1976).
145. Turovskii, B. M., Nauch. Tr. Nauch-Issled Proekt. Inst. Redkometal. Prom., 1971, 33, 41-4 (Russ).
146. Turovskii, B.M. and Ivanova, I.I., Izv. Akad. Nauk. SSSR. Neorg. Mater., 1974, 10 (12) 2108-11.
147. V. Wartenberg, H., Thermochemistry of Si, Nernst's Festschrift (Halle, 1912), 459-63.
148. V. Wartenberg, H., Z. Elektrochem, 19, 482 (1913).
149. V. Wartenberg, H., Z. Anorg. Allgem. Chem., 79, 71-87 (1913).
150. Wagman, D. D., others, "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 270-3, Nat., Bur. Stds., Washington, D. C. (1968).
151. Wawra, Hans, Z. Metallkd, 1975, 66 (7), 395-401 (Ger.)
152. Weast, R. C., ed., "CRC Handbook of Chemistry and Physics", 55th ed., CRC Press, Cleveland (1974).
153. White, G.K. and Woods, S. B., Phys. Rev., 103, 569-71 (1956).
154. White, G. K., others, Bull. Inst. Intern. Froid, Annexe, 1956-2, 91-5.

REFERENCES (Continued)

155. White G. K., J. Phys. D., 1973, 6 (17), 2070-8.
156. Wicks, C. E. and Block, F. E., "Thermodynamic Properties of 65 Elements", Bull. 605 Bur. of Mines, U. S. Govt. Printing Off., Washington, D. C. (1963).
157. Yaws, C. L., "Physical Properties", McGraw-Hill, N. Y. (1977).
158. Yaws, C. L., Miller, J. W., Jr., Lutwack, R., & Hsu, George, "Electricity from sunlight: Low Cost Silicon For Solar Cells", Fifth National Conference on Energy and the Environment, A.I.Ch.E.-A.P.A.C., Cincinnati (Oct. 31-Nov.3, 1977).
159. Younglove, B. A., University Microfilm, Mic 61-1381.
160. Zadukin, S. N., Soviet Phys. Solid State, 1, 516-17 (1959).
161. Zhdanova, V. V., others, Izv. Akad Nauk SSSR Neorg. Mater., 3 (7), 1263-4, (1967).
162. Tables Annuelles Internationales De Constantes et Donnees Numeriques, Herman and Co., Paris, Vol. 12 (1939).
163. Rea, Samuel N., Texas Instruments Report No. 03-78-30, July 1978, DOE/JPL 954887-78/3 Distribution Category UC-63, Dallas, TX.
164. Gel'd, P.V. and Serebrennikov, N. N., Doklady Akademii Nauk SSSR, 87, 1021, (1952) Russ.
165. Reynes, E. G. and G. Thodos, AIChE J., 8, 357 (1962).
166. Rackett, H. G., J. Chem. Eng. Data, 15, 514 (1970).

II. CHEMICAL ENGINEERING ANALYSIS

A. HSC PROCESS

During this reporting period, chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) was continued. The approach for the HSC process is based on performing initial analysis of the dichlorosilane (DCS) production. Upon completion of the chemical engineering analysis of the DCS production, then analysis of polysilicon production from the DCS will be performed. Experimental data and results from the Hemlock Semiconductor Corporation program using DCS as the feedstock will be used in the polysilicon production analysis.

For chemical engineering analysis of the DCS production, progress and status are summarized below for primary activities:

	<u>Prior</u>	<u>Current</u>
1. Base Case Conditions	30%	65%
2. Reaction Chemistry	25%	65%
3. Process Flow Diagram	20%	60%
4. Material Balance	0%	50%
5. Energy Balance	0%	40%
6. Property Data	0%	30%
7. Equipment Design	0%	10%
8. List of Major Equipment	0%	5%

The detailed status is shown in Table II-1.0 for the major items comprising the preliminary process design for the chemical engineering analysis.

In the course of performing the chemical engineering analysis for DCS production, the following features were suggested from an earlier scheme:

1. Redistribution Reactor

Relocate the Redistribution Reactor from D-2 distillate to D-3 bottoms. This relocation will increase the yield of DCS by about 10-20%. The relocation will also reduce the amount of Silane and Monochlorosilane (MCS) production.

2. Final Distillation

An additional distillation column is added at the end of the process to separate potential light components (Silane, MCS, B_2H_6 , etc.) from the desired DCS product. This distillation column is being added to help insure the purity of DCS and to help reduce potential dust formation chlorosilanes (SiH_4 , MCS) in the CVD reactor feed.

The preliminary process flowsheet, shown in Figure IIA-1.0, for DCS production was forwarded to Hemlock Semiconductor Corporation for initial screening and review. The transmitted flowsheet incorporates relocation of the redistribution reactor to improve yield and final distillation to help insure purity of DCS and to help reduce potential dust formation chlorosilanes (SiH_4 , MCS) in the CVD reactor feed.

Initial screening response for the preliminary process flowsheet have been recently received from Hemlock Semiconductor Corporation. The response comments indicated agreement in regards to relocation of the redistribution reactor to increase yield by taking advantage of the DCS generated in the hydrogenation-hydrochlorination reactor as per Jeff Mui's data.

The response comments additionally focused attention on the issue of boron removal in the process and discussed several potential schemes for removal of the boron impurity.

Follow-up review of response comments is in progress with Hemlock Semiconductor Corporation including boron removal options.

TABLE IIA-1.0 CHEMICAL ENGINEERING ANALYSES:
PRELIMINARY PROCESS DESIGN ACTIVITIES FOR DCS PRODUCTION

27

<u>Prel. Process Design Activity</u>	<u>Status</u>	<u>Prel. Process Design Activity</u>	<u>Status</u>
1. Specify Base Case Conditions	0	7. Equipment Design Calculations	0
1. Plant Size	0	1. Storage Vessels	0
2. Product Specifics	0	2. Unit Operations Equipment	0
3. Additional Conditions	0	3. Process Data (P, T, rate, etc.)	0
		4. Additional	0
2. Define Reaction Chemistry	0	8. List of Major Process Equipment	0
1. Reactants; Products	0	1. Size	0
2. Equilibrium	0	2. Type	0
3. Process Flow Diagram	0	3. Materials of Construction	0
1. Flow Sequence, Unit Operations	0	8a. Major Technical Factors	0
2. Process Conditions (T, P, etc.)	0	(Potential Problem Areas)	0
3. Environmental	0	1. Materials Compatibility	0
4. Company Interaction	0	2. Process Conditions Limitations	0
(Technology Exchange)		3. Additional	0
4. Material Balance Calculations	0	9. Production Labor Requirements	0
1. Raw Materials	0	1. Process Technology	0
2. Products	0	2. Production Volume	0
3. By-Products	0	10. Forward for Economic Analysis	0
5. Energy Balance Calculations	0		
1. Heating	0	0 Plan	
2. Cooling	0	0 In Progress	
3. Additional	0	0 Complete	
6. Property Data	0		
1. Physical	0		
2. Thermodynamic	0		
3. Additional	0

Figure IIA-1.0 Process Flowsheet for DCS Production

B. OTHER PROCESSES

Other processes (such as Union Carbide process, Battelle process, Aerochem process, Energy Materials process, etc.) under consideration for solar cell grade silicon production are being monitored with respect to data relative to chemical engineering analysis.

III. SUMMARY - CONCLUSIONS

The following summary-conclusions are made as a result of progress during this reporting period.

1. Task 1

Analyses of process system properties were continued for chemical materials important in the production of silicon. Major physical, thermodynamic and transport property data are reported for silicon including critical constants, vapor pressure, heat of vaporization, heat of sublimation, heat capacity, density, surface tension, viscosity and thermal conductivity. The property data covers both liquid and solid phases and are reported as a function of temperature for rapid engineering usage.

2. Task 2

Major efforts in chemical engineering analysis centered on the HSC process (Hemlock Semiconductor Corporation). The approach for the process involves performing initial analysis for DCS production (dichlorosilane) and then performing analysis of polysilicon production from the DCS. For the DCS production, status and progress are reported for primary activities of base case conditions (65%), reaction chemistry (65%), process flowsheet (60%), material balance (50%) and energy balance (40%). Two key features - redistribution reactor relocation and final distillation - are introduced to increase yield of DCS by about 10-20%, help insure purity and reduce potential dust (fine particle nucleation) components in the polysilicon feed material.

The preliminary flowsheet for DCS production was forwarded to Hemlock Semiconductor Corporation for initial screening and review. Hemlock Semiconductor is in agreement in regards to relocation of the redistribution reactor to increase yield. Additional follow-up review is in progress including boron removal options identified by Hemlock Semiconductor.

IV. PLANS

Plans for the next reporting period are summarized below:

1. Task 1

Continue analysis of process system properties for chemical materials important to the production of silicon.

2. Task 2

Continue chemical engineering analysis of processes under consideration for producing silicon.

3. Task 3

Perform economic analysis of processes as results issue from chemical engineering analysis.

MILESTONE CHART

PROCESS FEASIBILITY STUDY IN
SUPPORT OF SILICON MATERIAL TASK I

JPL Contract No. 954343