

440.
2/29/80

DR. 823

DOE/JPL/954343-79/16

PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL TASK I

Quarterly Technical Progress Report (XVI), June—August, 1979

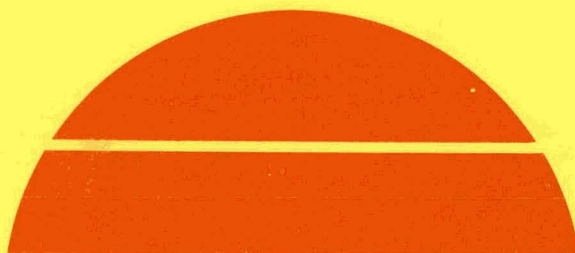
By
Ku-Yen Li
Keith C. Hansen
Carl L. Yaws

September 1979
Date Issued

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

Lamar University
Chemical Engineering Department
Beaumont, Texas

MASTER



U.S. Department of Energy

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED



Solar Energy

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

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.

DOE/JPL/954343-79/16
Distribution Category UC-63b

PROCESS FEASIBILITY STUDY IN SUPPORT OF
SILICON MATERIAL TASK I

QUARTERLY TECHNICAL PROGRESS REPORT (XVI)

Issue Date: September, 1979

Reporting Period: June-August, 1979

Ku-Yen Li, Keith C. Hansen,
and Carl L. Yaws

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

MASTER

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 a 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

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED

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
L. WAYNE SANDERS
FRED H. PITTS
C.S. FANG

Graduate-Student Assistants

JOHN HERA, JR.
PRABODH M. FATEL
PRAFUL N. SHAH
STEVEN FORTENBERRY
MILTON L. HOOPER
LEE-HSIN TSAO
STEVE HAO CHANG

ABSTRACT

During this reporting period, primary efforts were expended on process system properties, chemical engineering and economic analysis.

Analysis of process system properties was continued for silicon source materials under consideration for producing silicon. The following property data are reported for dichlorosilane which is involved in processing operations for silicon: critical constants, vapor pressure, heat of vaporization, heat capacity, density, surface tension, thermal conductivity, heat of formation and Gibb's free energy of formation. The properties are reported as a function of temperature to permit rapid engineering usage.

Major efforts were expended on completion of the preliminary economic analysis of the BCL Process (Battelle Columbus Laboratories). Cost analysis results for the process (Case A-two deposition reactors and six electrolysis cells) are presented based on a preliminary process design of a plant to produce 1,000 metric tons/year of silicon. Fixed capital investment estimate for the plant is \$12.47 million (1975 dollars) (\$17.47 million, 1980 dollars). Product cost without profit is 8.63 \$/kg of silicon (1975 dollars) (12.1 \$/kg, 1980 dollars).

TABLE OF CONTENTS

	<u>Page</u>
I. PROCESS SYSTEM PROPERTIES ANALYSES (TASK 1).....	1
A. DICHLORISILANE PROPERTIES.....	1
B. THERMAL CONDUCTIVITY INVESTIGATION.....	20
II. CHEMICAL ENGINEERING ANALYSES (TASK 2).....	21
A. BCL PROCESS (BATTELLE COLUMBUS LABORATORIES).....	21
B. OTHER PROCESSES.....	24
III. ECONOMIC ANALYSES (TASK 3).....	25
A. BCL PROCESS (BATTELLE COLUMBUS LABORATORIES).....	25
B. OTHER PROCESSES.....	38
IV. SUMMARY - CONCLUSIONS.....	39
V. PLANS.....	40
MILESTONE CHART	

I. PROCESS SYSTEM PROPERTIES ANALYSES (TASK 1)

A. DICHLOROSILANE PROPERTIES

Process system properties analysis was continued for silicon source materials under consideration for semiconductor silicon production. Major efforts centered on property data of dichlorosilane which is involved in the processing operations for producing silicon.

Physical Properties and Critical Constants (Table IA-1)

Physical properties and critical constants are listed in Table IA-1 for dichlorosilane. Values of critical temperature, T_C , critical pressure, P_C , and critical volume, V_C , for dichlorosilane were estimated by using Lydersen's structural contribution method with derived critical property increments for silicon (H16). This method produced only 2.3% error for T_C and 3.4% error for V_C when compared with the experimental values of trichlorosilane and it produced 0% error for T_C , V_C , and P_C when compared with the known values of silicon tetrachloride. The estimated values for the known values for the critical properties are also within reasonable agreement (4% for T_C , 0.2% for P_C , and 14% for V_C) of calculated Russian values (H10).

The critical compressibility factor, Z_C , was determined from its definition:

$$Z_C = \frac{V_C R T_C}{P_C} \quad (\text{IA-1})$$

The result from Eq. (IA-1) was the same as that derived by the Garcia-Barcena' boiling point method (H16):

$$Z_C = f(T_b) - g(T_b/M) \quad (\text{IA-2})$$

Vapor Pressure (Figure IA-1)

The vapor pressure of dichlorosilane has been determined from -80°C to 30°C (H23, H35). The experimental data was extended over the entire liquid range using the YSSP vapor pressure correlation (H30):

$$\log P_V = A + \frac{B}{T} + C \log T + DT + ET^2 \quad (\text{IA-3})$$

where P_V is the vapor pressure of saturated liquid, mm Hg; T is temperature, $^\circ\text{K}$; and A , B , C , D , E are correlation constants derived using a generalized least squares computer program. Average absolute deviation was about 1% for the 13 experimental data points.

Heat of Vaporization (Figure IA-2)

Heat of vaporization data for dichlorosilane are available only at the boiling point (H1, H0, H10, H19, H31). Using the known value at the boiling point, Watson's correlation was used to extend the heat of vaporization over the entire liquid phase:

$$\Delta H_V = \Delta H_{V_1} \left[\frac{T_C - T}{T_C - T_1} \right]^n \quad (\text{IA-4})$$

where $n = .38$ and ΔH_{V_1} applies at the boiling point (T_1).

Heat Capacity (Figures IA-3 and IA-4)

Ideal gas heat capacity data for dichlorosilane are available from various American (H5, H13, H25, H26), Russian (H6, H7, H10, H12, H32) and other (H9, H33) workers. The values, which are in close agreement, are based on bond additivities and spectral measurement. The JANAF values were selected.

Measured saturated-liquid heat capacity data for dichlorosilane are unavailable in the literature. Values were estimated from -60°C to 60°C using the Yuan and Stiel corresponding state method (H16). For polar liquids, the correlation takes the form:

$$C_{\sigma_1} - C_P^0 = \Delta C^{(0p)} + \omega(\Delta C_\sigma)^{(1p)} + X(\Delta C_\sigma)^{(2p)} + X^2(\Delta C_\sigma)^{(3p)} + \omega^2(\Delta C_\sigma)^{(4p)} + X\omega(\Delta C_\sigma)^{(5p)} \quad (\text{IA-4})$$

where C_P^0 is the ideal gas heat capacity, ω is the acentric factor, X is the Stiel polar factor and the functions: $(\Delta C_\sigma)^{(0p)}$, etc. are tabulated as functions of the reduced temperature. The relationship that heat capacity times density is constant was used to extend the values over the entire liquid range. Application of the Yuan and Stiel correlations to silicon tetrachloride, trichlorosilane, and silicon tetrafluoride gave average absolute percentage errors of 3.1, 6.7, and 4.3 respectively. Due to the limited experimental data points, the calculated liquid heat capacities should be considered as order-of-magnitude estimates.

Density (Figure IA-5)

Liquid density data are available at the melting point (H8, H9, H10, H18, H27) and at 7°C (H35). The limited data were extended over the entire liquid range using a modification of the Rackett equation:

$$\rho = \rho_C Z^{-(1-T_r)^{2/7}} \quad (\text{IA-5})$$

where ρ_C is critical density, T_r is reduced temperature and Z is a parameter defined by the experimental data.

Surface Tension (Figure IA-6)

The Brock and Bird corresponding states method (H16) was used to estimate the surface tension of dichlorosilane since no experimental data is available. The equation is:

$$\sigma = P_c^{2/3} T_c^{1/3} (0.133 \alpha_c - 0.281) (1 - T_r)^{11/9} \quad (\text{IA-7})$$

where σ is surface tension, dynes/cm; α_c is the Riedel parameter, P_c is critical pressure, atm.; T_c is critical temperature, °K; and T_r is the reduced temperature. Application of this method to silicon tetrachloride and trichlorosilane gave results within 4% and 0.8% absolute deviation with experimental data, respectively.

Viscosity (Figures IA-7 and IA-8)

Gas viscosity calculations at low pressure were made using the methods of (1) Yoon and Thodos for non-hydrogen-bonding polar gases, (2) Golubev, and (3) Reichenberg (H16). Since the calculated values were in close agreement, they were fitted to the series expansion:

$$\eta_G = A + BT + CT^2 \quad (\text{IA-8})$$

where η_G is in micropoise; T is temperature, °K; and A , B and C are computer derived parameters using a generalized least squares program. The average absolute percentage deviation was less than 1.8%.

Liquid viscosities at temperatures below the boiling point were calculated using the methods of Thomas, and of Morris (up to 60°C) (H16). Values from the boiling point to the critical point were calculated using the correlation methods of Letson and Stiel, and Stiel and Thodos (H16). Calculated values were extended over entire liquid range and fitted to the equation:

$$\log \eta_L = A + \frac{B}{T} + CT + DT^2 \quad (\text{IA-9})$$

where η_L is in centipoise; T is temperature, °K; and A , B , D and D are derived parameters using a generalized least squares computer program. This was done in order to fit together the calculated values which apply in the different temperature ranges. The average percentage deviation was 3.3% with the greater deviation being near the melting point; therefore, this should be considered to be an order-of-magnitude correlation.

Thermal Conductivity (Figures IA-9 and IA-10)

Gas-phase thermal conductivity data are available from 28°C to 350°C (H28). The data were correlated and extended to higher temperatures by a series expansion in temperature:

$$\lambda_G = A + BT + CT^2 + DT^3 \quad (\text{IA-10})$$

where λ_G is gas thermal conductivity, cal/cm x sec x °C; T is temperature, °K; and A, B, C and D are computer derived constants characteristic of the chemical compound. The absolute deviation between data and correlation values was less than 0.5%.

Thermal conductivity data of the liquid phase is unavailable. Modifications of the estimation methods of Sato and Reidel (H16):

$$\lambda_L = \frac{2.64 \times 10^{-3}}{M^{1/2}} \frac{3 + 20 (1 - T_r)^{2/3}}{3 + 20 (1 - T_{r_b})^{2/3}} \quad (\text{IA-11})$$

and of Robbins and Kingrea (H16):

$$\lambda_L = \frac{(88 - 4.94 H) \times 10^{-3}}{\Delta S^*} \frac{.55}{T_r} C_{p_L} \rho^{4/3} \quad (\text{IA-12})$$

where used to derive values at 32°C. These modified estimation methods produced error of less than 1% absolute deviation on the one published value of SiCl₄. The average of the estimate at 32°C was extended over the entire liquid range using a modification of the Stiel and Thodos method (H16):

$$\lambda_L = \frac{f(\rho_r)}{\Gamma Z_C^5} + \lambda_G \quad (\text{IA-13})$$

The modified Sato-Reidel equation produced a similar range of values. Since assumptions in these calculations include the accuracy of the one data point for silicon tetrachloride and the chemical similarities in a homologous series, these values should be considered only order-of-magnitude estimates.

Heat and Free Energy of Formation (Figures IA-11 and IA-12)

Heat of formation and Gibb's free energy of formation for the ideal gas have been estimated by Russian (H32, H36) and American (H25) workers up to at least 1500°K. Some estimated values differ significantly having about 35% deviation for ΔH_f and about 45% deviation for ΔG_f (H32, H36). The JANAF values (H25) were selected.

TABLE IA-1

CRITICAL CONSTANTS AND PHYSICAL PROPERTIES OF DICHLOROSILANE

<u>Identification</u>	<u>Dichlorosilane</u>
Formula	SiH_2Cl_2
State (std. cond.)	gas
Molecular weight, M	101.008
Boiling Point, T_b , °C	8.3
Melting Point, T_m , °C	-122.0
Critical Temperature, T_c , °C	178.9*
Critical Pressure, P_c , atm	44.0*
Critical Volume, V_c , $\text{cm}^3/\text{gr mol}$	228.3*
Critical Compressibility Factor, Z_c	.276*
Critical Density, ρ_c , gr/cm^3	.4424*
Acentric Factor (ω)	.1107

*Estimated

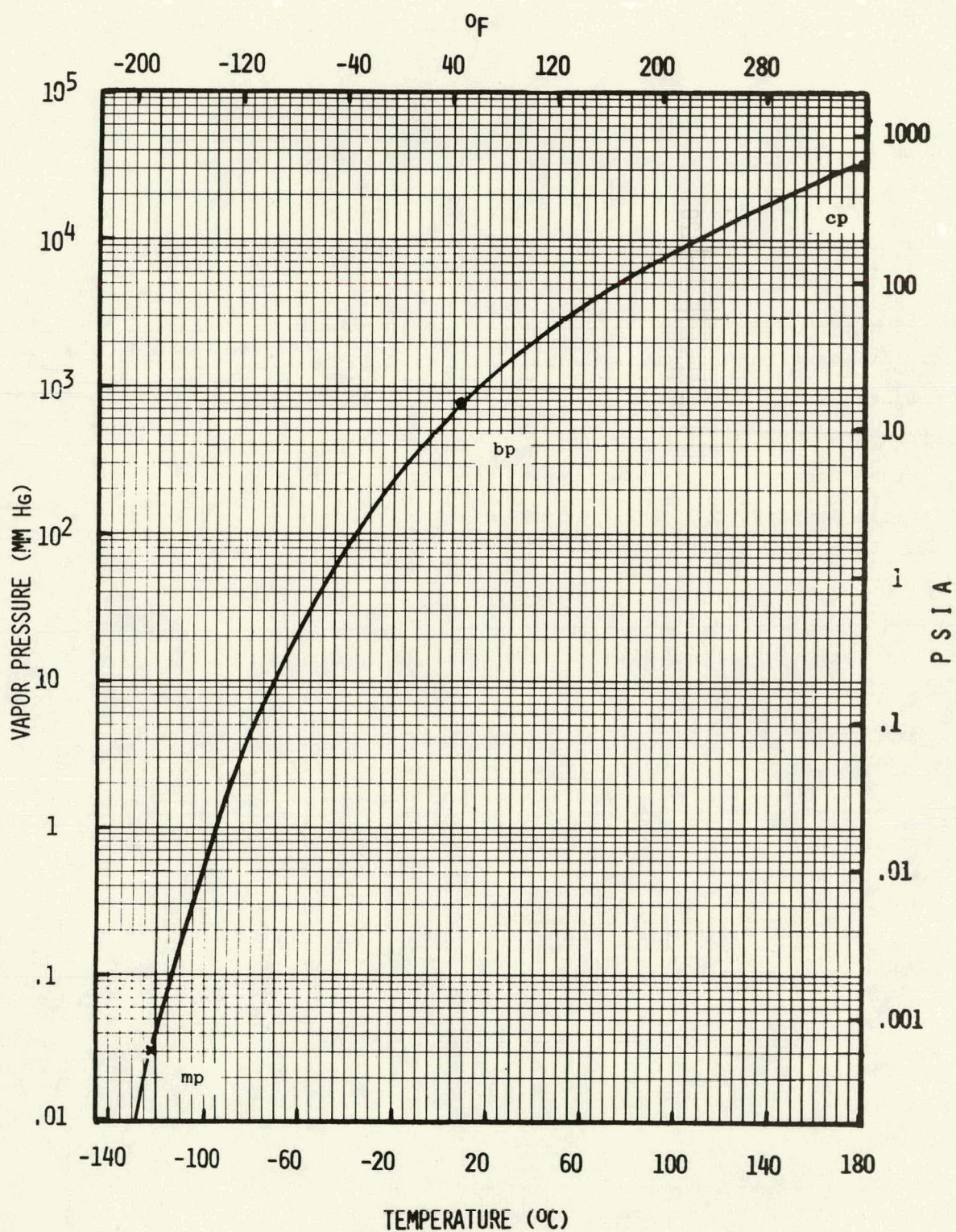


Figure IA-1. Vapor Pressure vs Temperature for Dichlorosilane

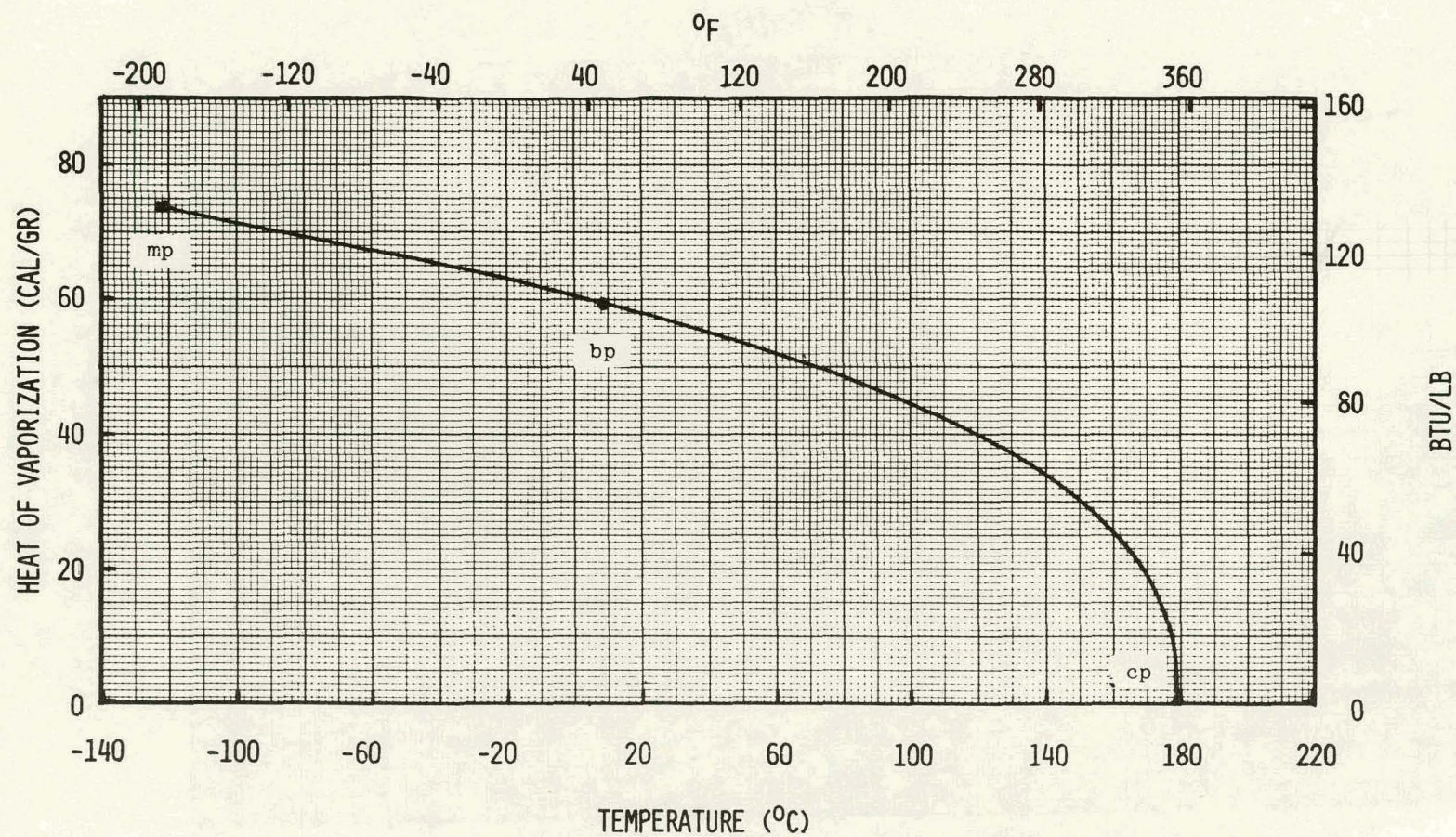


Figure IA-2. Heat of Vaporization vs Temperature for Dichlorosilane

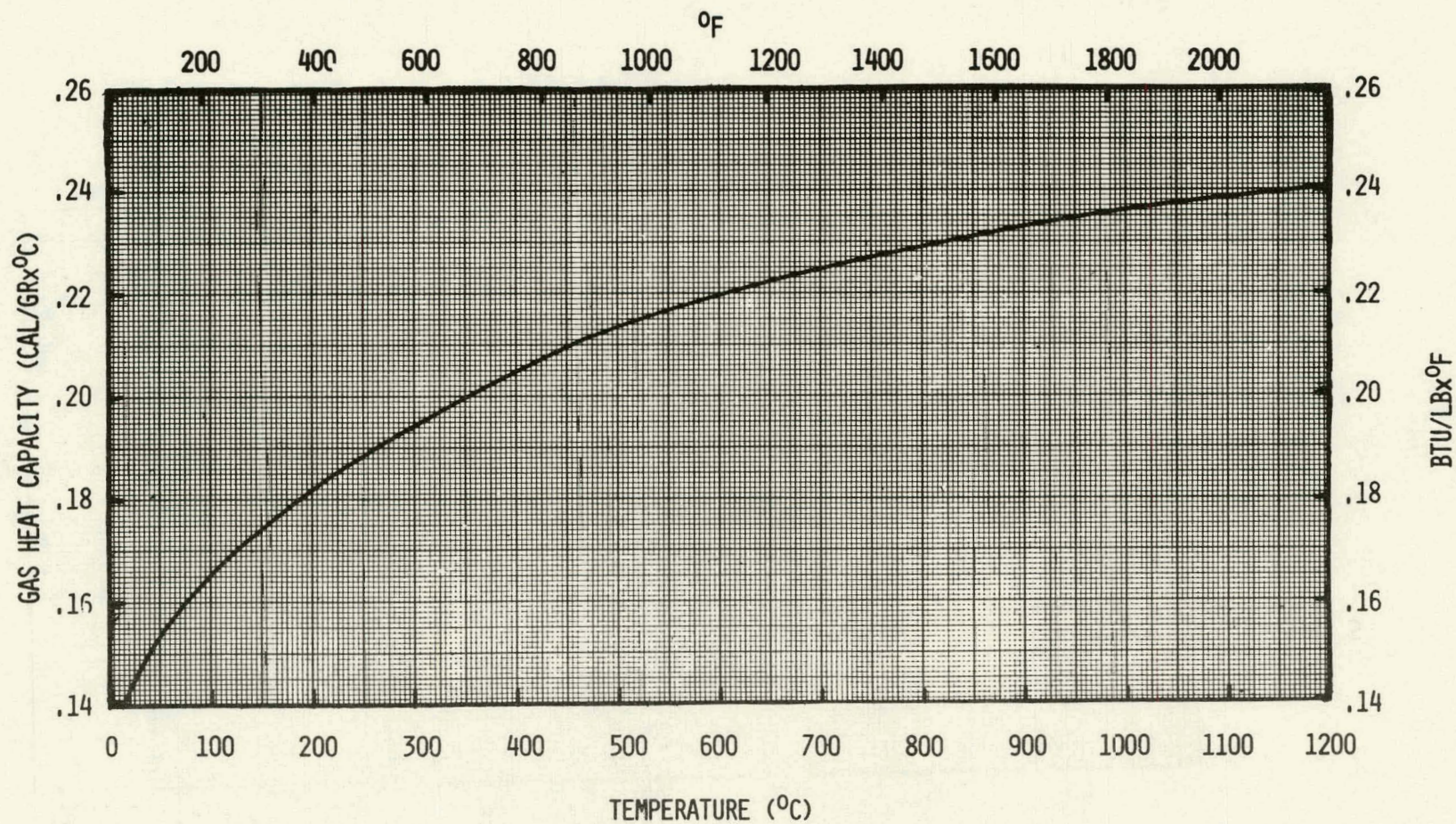


Figure IA-3. Gas Heat Capacity vs Temperature for Dichlorosilane

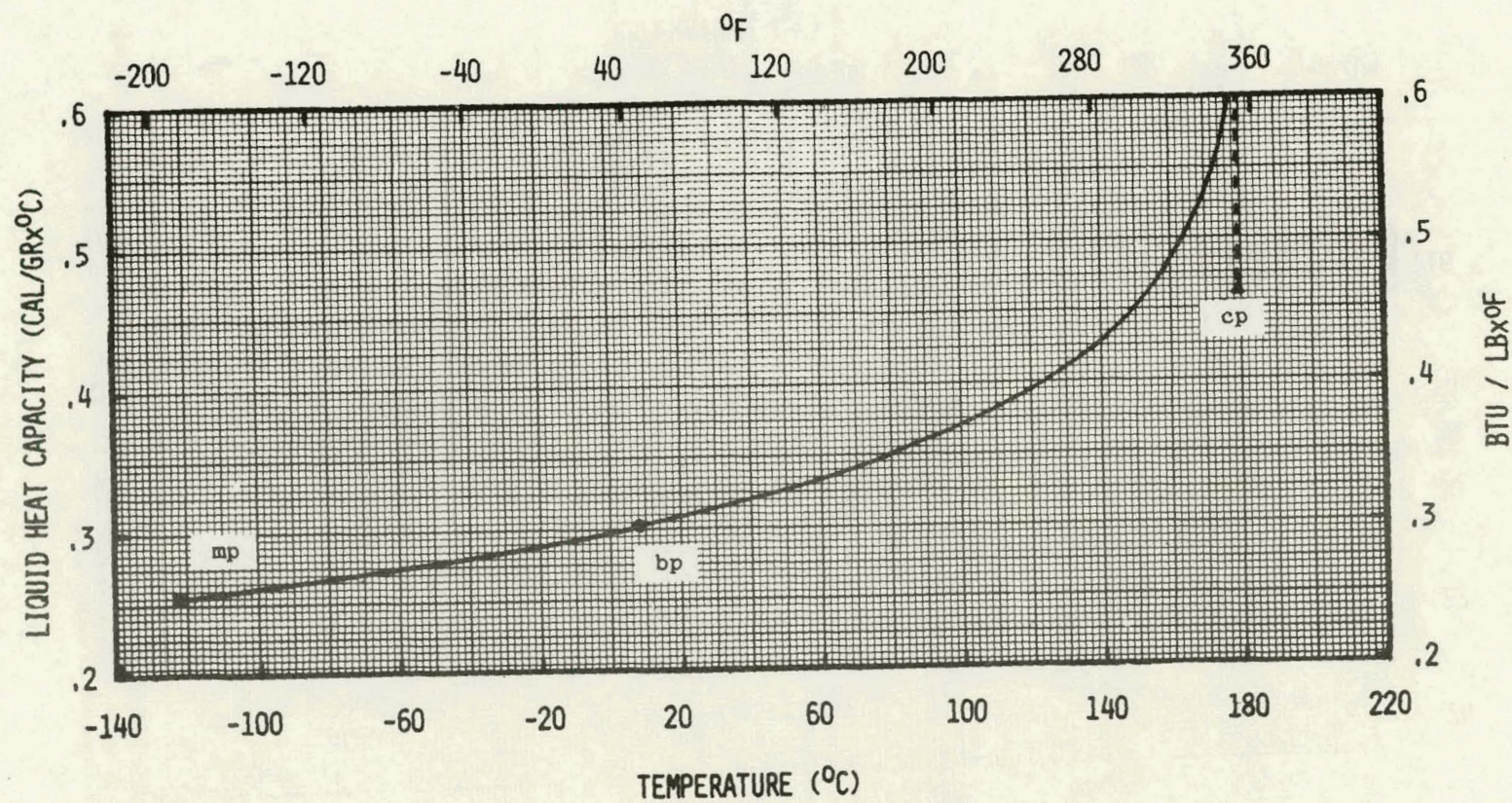


Figure IA-4. Liquid Heat Capacity vs Temperature for Dichlorosilane

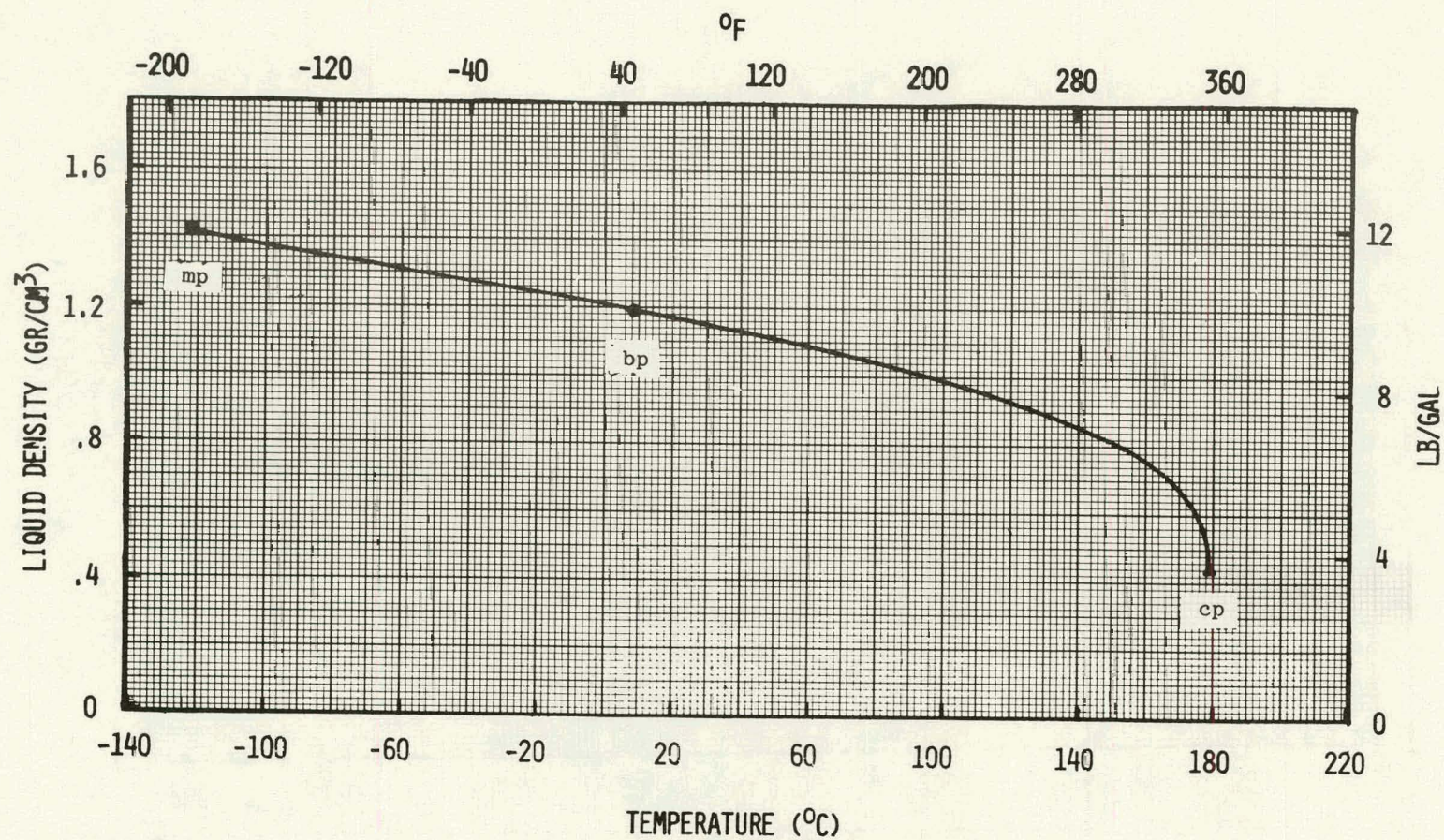


Figure IA-5. Liquid Density vs Temperature for Dichlorosilane

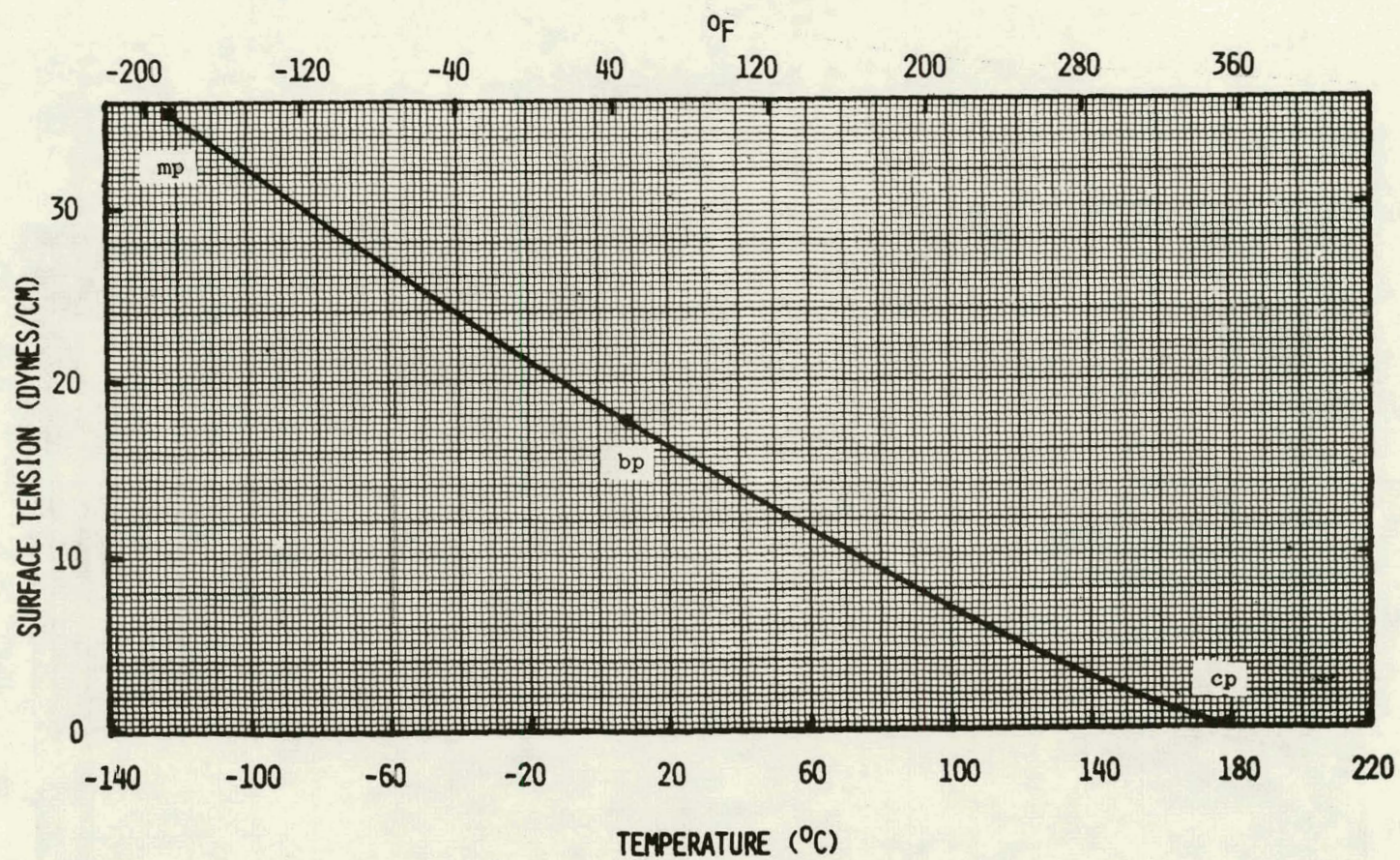


Figure IA-6. Surface Tension vs Temperature for Dichlorosilane

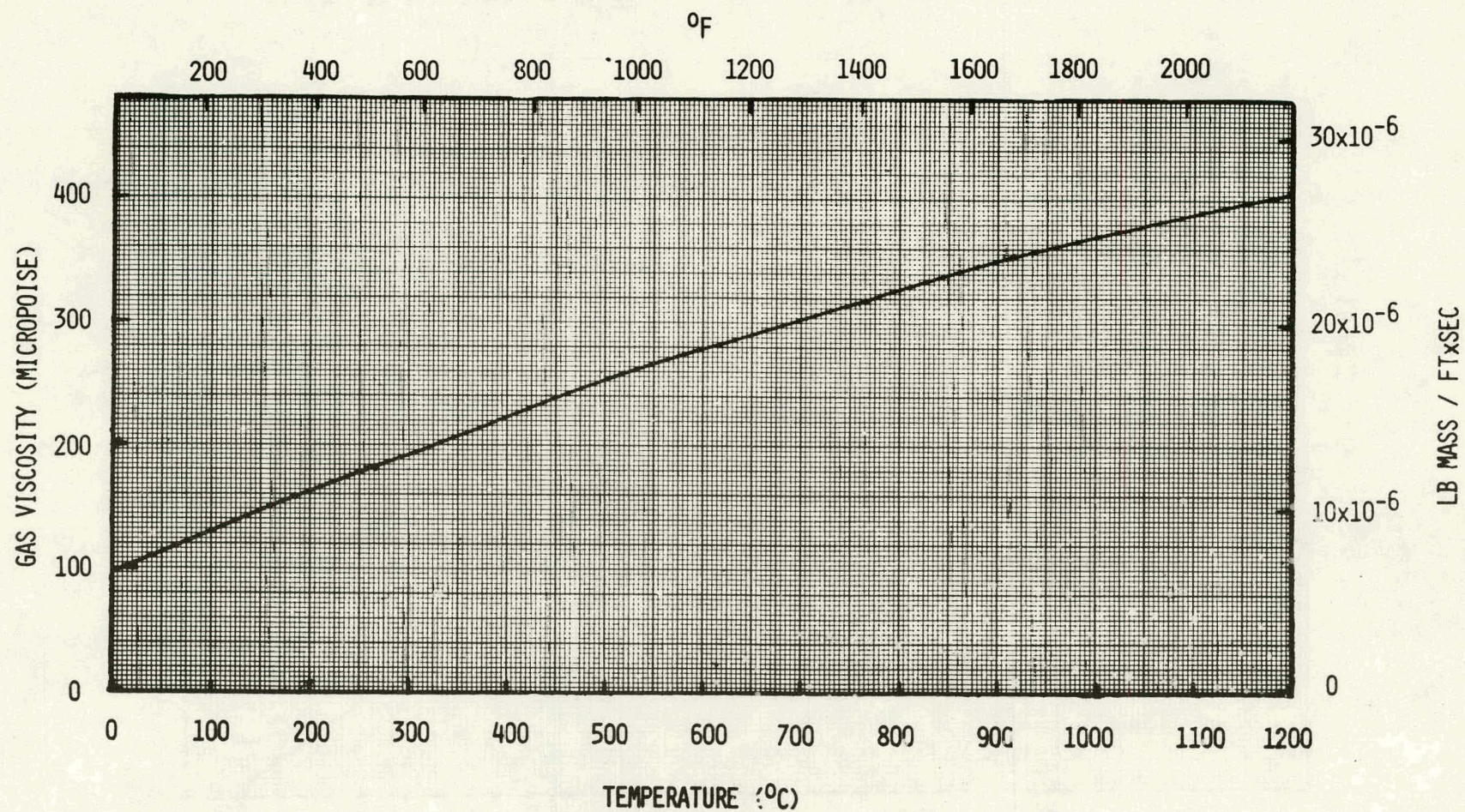


Figure 1A-7. Gas Viscosity vs Temperature for Dichlorosilane

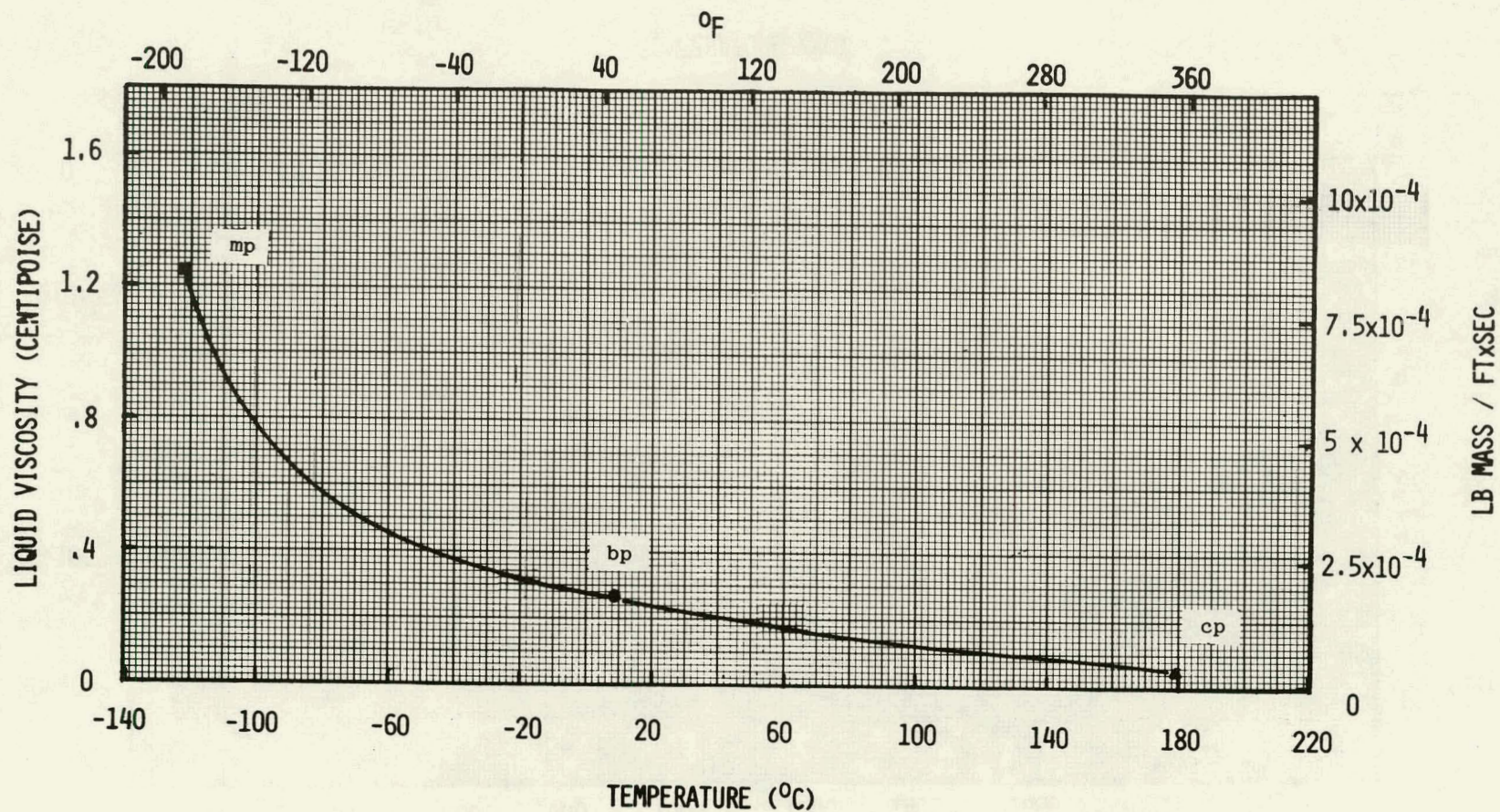


Figure IA-8. Liquid Viscosity vs Temperature for Dichlorosilane

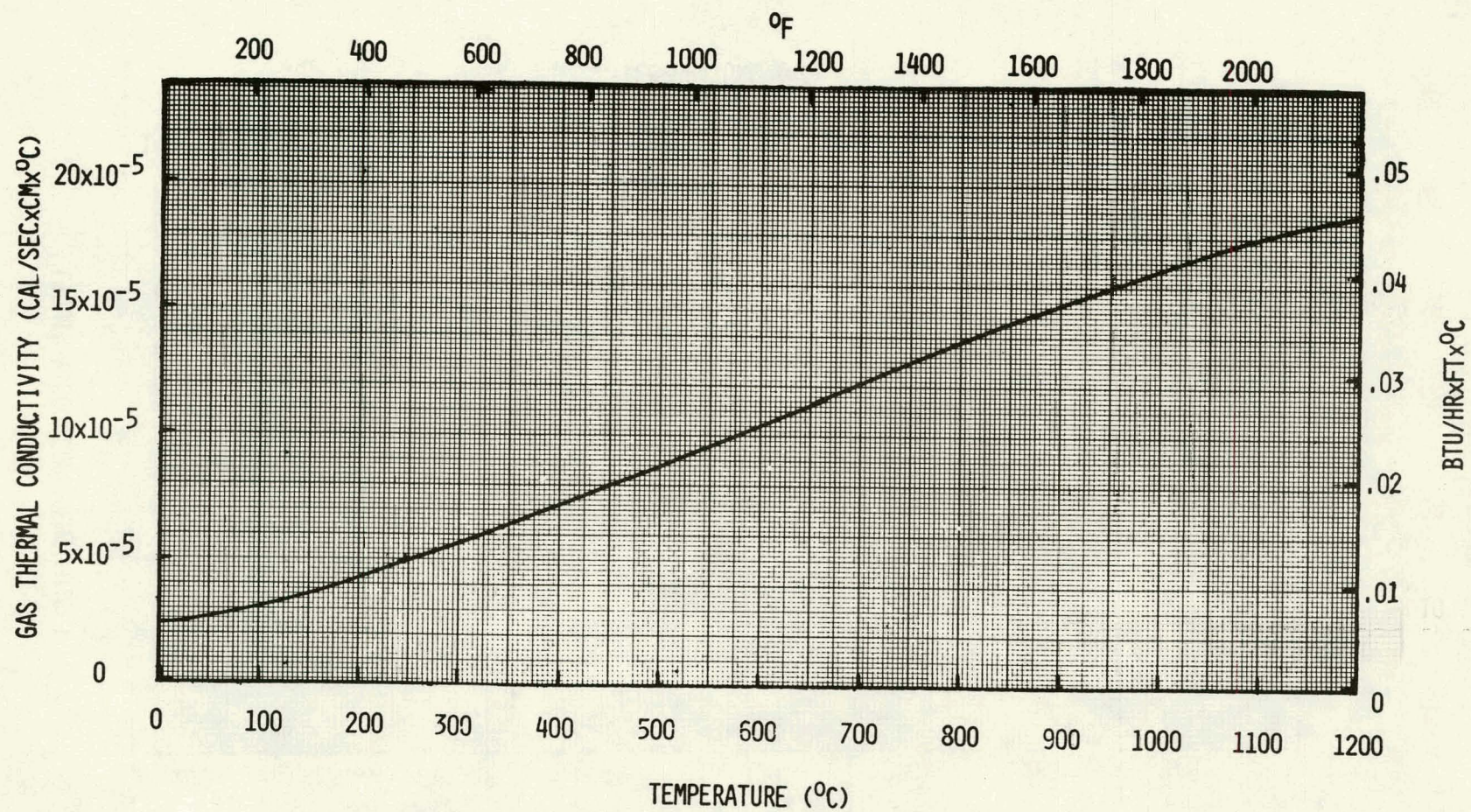


Figure IA-9--Gas Thermal Conductivity vs Temperature for Dichlorosilane

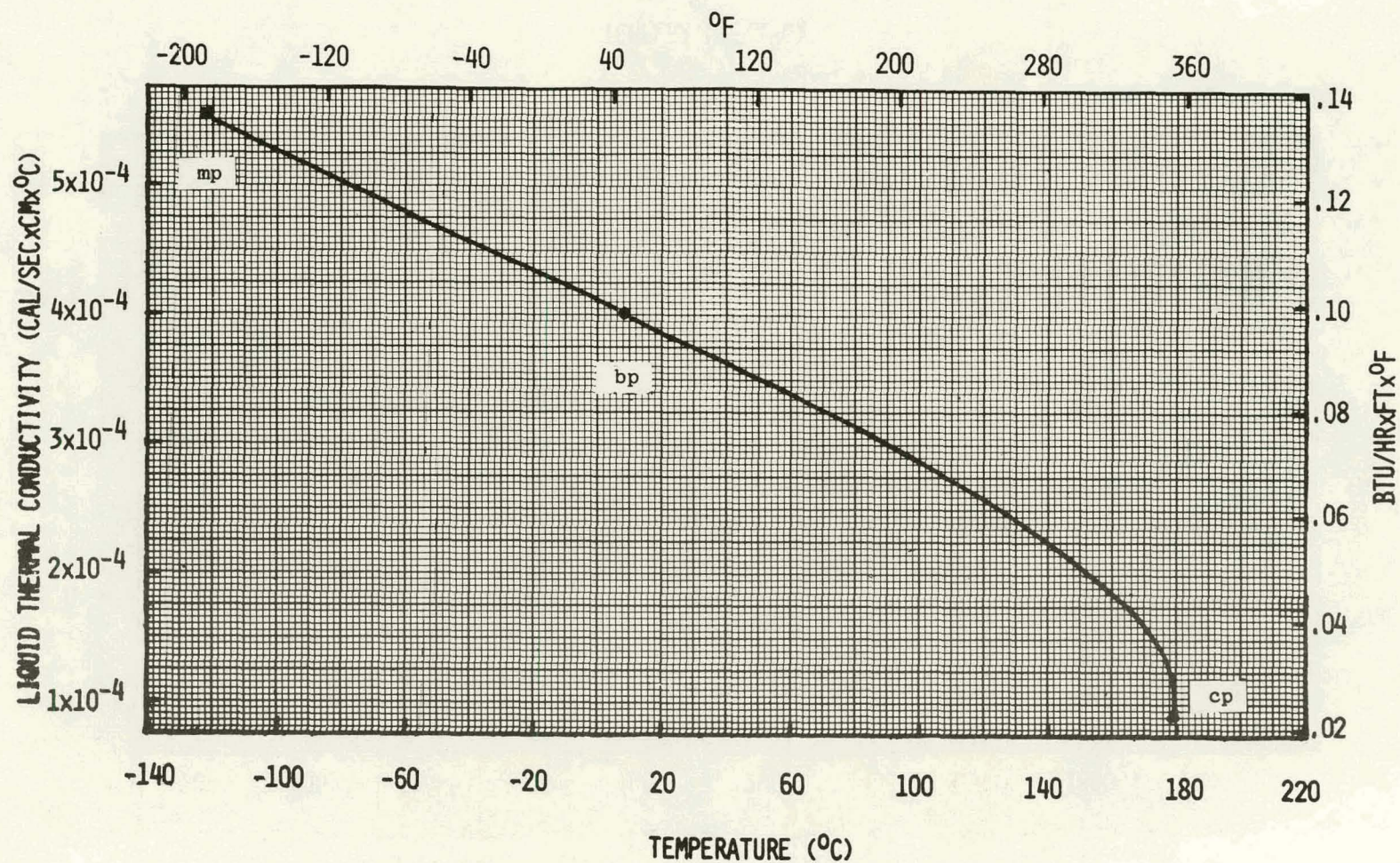


Figure IA-10--Liquid Thermal Conductivity vs Temperature for Dichlorosilane

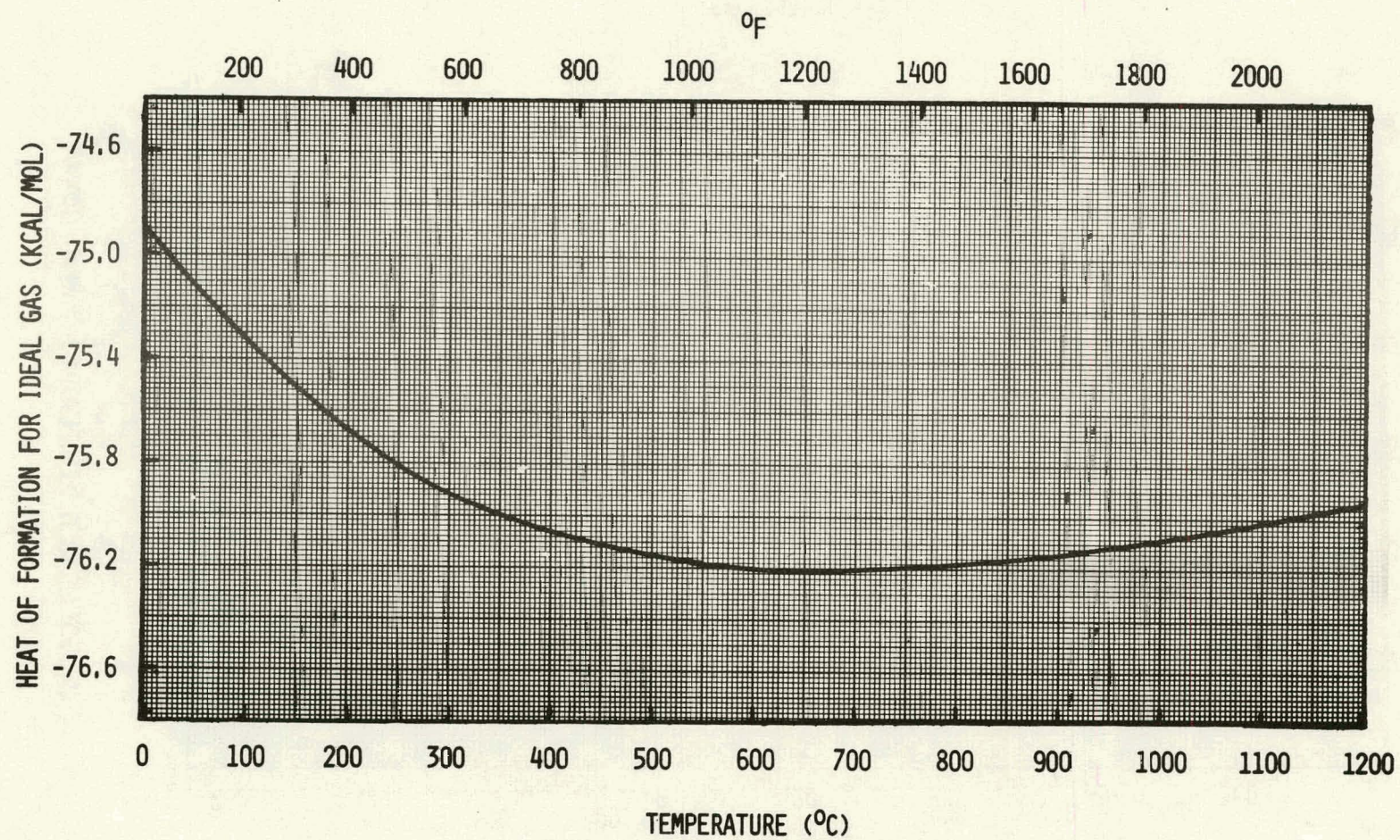


Figure IA-11--Heat of Formation vs Temperature for Dichlorosilane

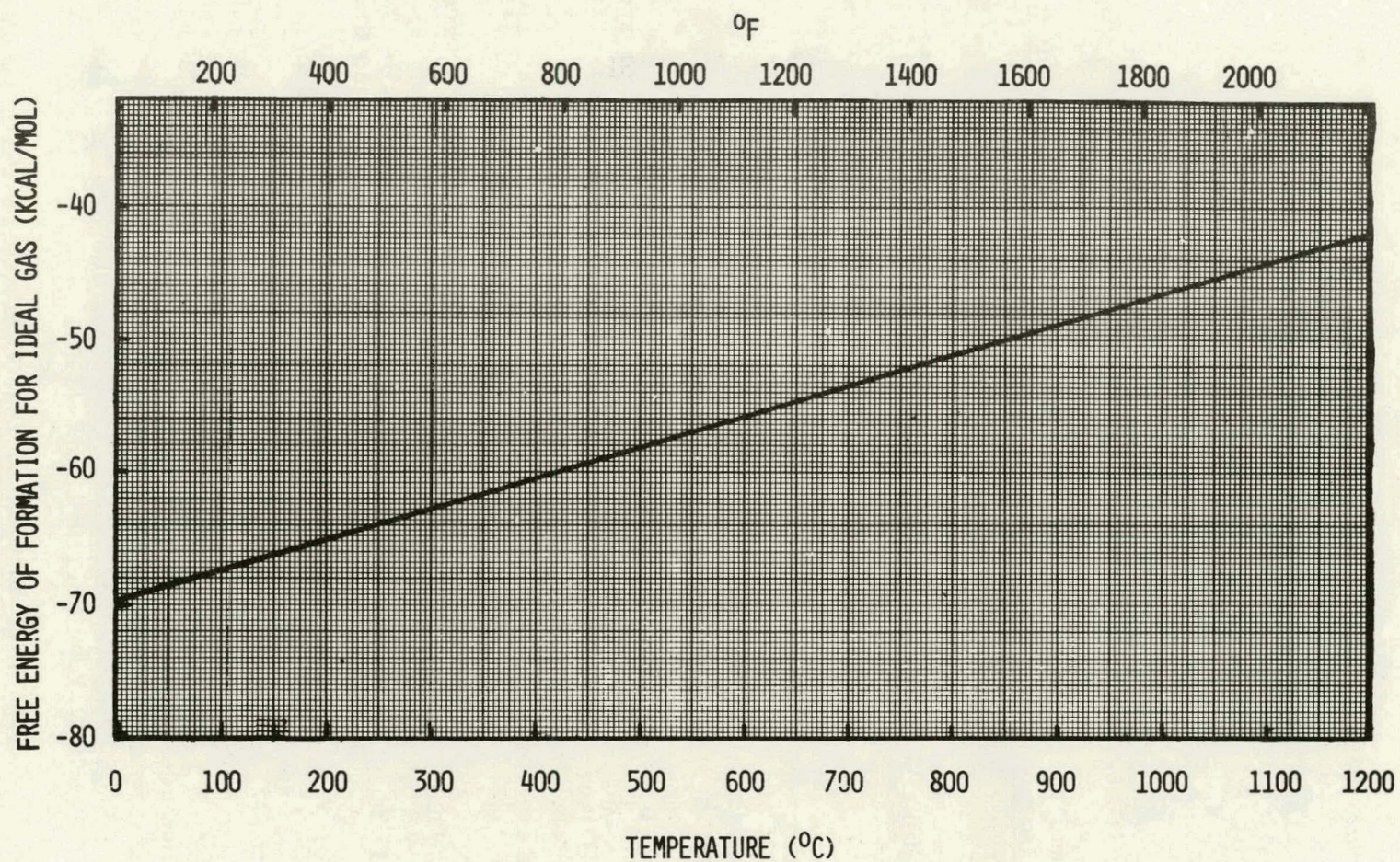


Figure IA-12--Free Energy of Formation vs Temperature for Dichlorosilane

REFERENCES FOR DICHLOROSILANE PROPERTIES

- H 1. Bailer, Jr., J. C., others, Comprehensive Inorganic Chemistry, Vol. 1, Pergamon Press, Elmsford, New Jersey (1973).
- H 2. Dean, J. A., ed., Lange's Handbook of Chemistry, 11th ed., McGraw-Hill, New York (1973).
- H 3. Ebsworth, E. A., Volatile Silicon Compounds, MacMillan Co., New York (1963).
- H 4., Gmelin, Gmelins Handbüch der Anorganischen Chemie, No. 15, Silicium Part B, Verlag Chemie, GMBH, Weinheim, Bergstrasse (1959).
- H 5. Hunt, L. P., others, J. Electrochem Soc., 119 (12), 1741-5 (1972).
- H 6. Karapet'yants, M. Kh. and M. I., Thermodynamic Constants of Inorganic and Organic Compounds, Ann-Arbor-Humphrey Science Pub., Ann Arbor, Mich. (1970).
- H 7. Karapet'yants, M. L., Tables of Some Thermodynamic Properties of Different Substances, Trudy MKh TI in Mendeleeva, No. 34, Moscow (1961) Russ.
- H 8. Kirk, R. E., Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 18, Interscience Publishers, New York (1969).
- H 9. Landolt-Bornstein Tables, Original volumes to present, Springer-Verlag, Berlin, Germany (1956-present).
- H10. Lapidus, I. I., others, Thermophysical Properties of Gases and Liquids, No. 1, Rabinovich, V. A., ed., 102, Israel Program for Scientific Translation (1970).
- H11. Lapidus, I. I., others, Tepolfiz Vys. Temp. (High Temp.), 6 (1), 60 (1968).
- H12. Lapidus, I. I., others, Izv. Vysshikh. Uchebn., Zavedenii, Tsvetn. Met., 9 (2), 92-96 (1966) Russ.
- H13. O'Neal, H. E. and Ring, M. A., Inorg. Chem., 5 (3), 435 (1966).
- H14. Pedley, J. B., others, Comput. Anal. Thermochem. Data (1972).
- H15. Prostov, V. N. and Popova, O. G., Zh. Fiz. Khim., 49 (3), 631-3 (1975) Russ.
- H16. Reed, R. C., others, The Properties of Gases and Liquids, 3rd ed., McGraw-Hill Publishing Co., New York (1977).
- H17. Reed, R. C. and Sherwood, T. K., The Properties of Gases and Liquids, 2nd ed., McGraw-Hill Book Co., New York (1966).
- H18. Rochow, E. G., An Introduction to the Chemistry of the Silicones, John Wiley and Sons, New York (1946).

- H19. Seifer, A. L., others, *Izv. Vysshikh. Uchebn., Zavedonij. Tsvetn. Met.*, 9 (3), 85 (1966) Russ.
- H20. Shakhparonov, M. I., others, *Zhur. Priklad. Khim.*, 33, 2699-2703 (1960).
- H21. Sneed, M. C. and Brasted, R. C., *Comprehensive Inorganic Chemistry*, Vol. 7 D. Van Nostrand Co., New York (1958).
- H22. Stock, A., *Hydrides of Boron and Silicon*, Cornell Univ. Press, New York, (1933) (reissued 1957).
- H23. Stock, A. and Smieski, C., *Siliciumwasserstoffe: VI, Chlorierung and Metylierung der Manosilans*, 52, 695 (1919).
- H24. Stone, F. G. A., *Hydrogen Compounds of Group IV Elements*, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1962).
- H25. Stull, D. R., and Prophet, H., *JANAF Thermochemical Tables*, NSRDS-NBS 37, Nat. Bur. Stds., Washington, D. C. (1971).
- H26. Wagman, D. D., others, "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 270-3, Natl. Bur. Stds., Washington, D. C. (1968).
- H27. Weast, R. C., ed., *CRC Handbook of Chemistry and Physics*, 49th ed., C. R. C. Inc., Cleveland, Ohio (1968-1969).
- H28. Yaws, C. L., Fang, C. S., Hansen, K. C. and Miller, J. W., Jr., Quarterly Technical Progress Report (XI), ERDA/JPL 954343-78/11, Distribution Catagory UC-63 (June, 1978).
- H29. Yaws, C. L., others, *Solid State Technology*, 16, (1), 39 (1973).
- H30. Yaws, Carl L., *Physical Properties*, Chemical Engineering, McGraw-Hill Publishing Co., New York (1977).
- H31. Wintgen, R., *Ber.*, 52B, 724-31 (1919).
- H32. Golosova, R. M., others, *Russ. J. Phys. Chem.*, 45 (5), 598 (1971).
- H33. Mikawa, Y., *Nippon Kagaku Zasshi*, 81, 1512 (1960).
- H34. Delong, D. J. *Solid State Tech.*, 15 (10) 29-34 (1972).
- H35. Yaws, C. L., Miller, J. W., Jr., Lutwack, R., and Hsu, G., "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).
- H36. Shaulov, Y. K., others, *Zh. Fiz. Khim.*, 40 (8), 893 (1966).

B. THERMAL CONDUCTIVITY INVESTIGATION

During this reporting period work has been directed toward the calibration of the apparatus previously assembled to measure thermal conductivity values of binary gas mixtures. Initial calibration studies have been concentrated on the portion of the apparatus designed to prepare and analyze the mixtures. For this purpose, mixtures of varying proportions of the gases nitrogen and hydrogen were prepared and analyzed by gas chromatography. Once these gases can be handled satisfactorily, analyzed, and accurate thermal conductivity values can be obtained; then work will be initiated on mixtures of various silicon source materials such as silane and the halogenated silanes.

II. CHEMICAL ENGINEERING ANALYSIS (TASK 2)

A. BCL PROCESS (BATTELLE COLUMBUS LABORATORIES)

Major efforts were completed during this reporting period on the preliminary process design for the BCL Process (Case A-two deposition reactors and six electrolysis cells).

The status, including progress since the last reporting period, for the process design is given below for key guideline items:

	<u>Prior</u>	<u>Current</u>
.Base Case Conditions	97%	100%
.Reaction Chemistry	97%	100%
.Process Flow Diagram	97%	100%
.Material Balance	95%	100%
.Energy Balance	95%	100%
.Property Data	90%	100%
.Equipment Design	90%	100%
.Production Labor	90%	100%

The results from the review of raw material requirement are shown in Table IIA-1.3. For major process equipment, two more heat exchangers, chlorination gas cooler (H-17) and cell gas cooler (H-18) were added in order to cool down the hot gases which come out from reactor and electrolysis cell. Based on the above changes, the utility requirements were revised and shown on Table IIA-1.4. The utility requirements include (1) electricity for electrolysis cell, heater and pumps; (2) steam for reboilers and preheater; (3) cooling water for cooler; (4) process water and (5) refrigerant. These utilities are required for the production of silicon in the process.

The results were forwarded for economic analysis.

Table IIA-1.3

Raw Material Requirements for
BCL Process (Battelle Columbus Laboratories)

<u>Raw Material</u>	<u>Requirements lb/KG of Silicon</u>
1. Silicon Tetrachloride, SiCl_4	15.68 ¹
2. Zinc, Zn	0.54
3. Caustic (50%), NaOH(aq)	5.23
or	
Lime (99%), Ca(OH)_2	2.85 ²
4. Argon	3.1 SCF^3
5. Nitrogen	7.6 SCF^3
6. Chlorine, Cl_2 (by-product)	11.12

1. Includes light wastes (4%), heavy wastes (4%) and additional losses (7%).
2. Includes neutralization of distillation section, deposition section, electrolysis section and chlorination losses.
3. Estimate from BCL

Table IIA-1.4 UTILITY REQUIREMENTS FOR BCL
PROCESS (BATTELLE COLUMBUS LABORATORIES)

<u>Utility/Function</u>		<u>Requirements/Kg of Silicon Product</u>
1. Electricity		30.92 kw-hr
1. Low Volatage D.C. for Electro-lysis	(20.51)	
2. Zinc Vaporizer Induction Heated	(5.62)	
3. Preheat Section of Deposition Unit Induction Heated	(1.39)	
4. Electrolysis Feed Tank Heater	(0.24)	
5. Molten Zinc Storage Heater	(0.10)	
6. SiCl ₄ Vaporizer	(0.53)	
7. Pumps, Blowers	(2.53)	
2. Steam (50 PSIA)		9.67 pounds
1. #1 Purification Column Reboiler	(4.59)	
2. #2 Purification Column Reboiler	(4.30)	
3. Caustic Storage Heating	(0.29)	
4. #1 Purification Column Preheater	(0.49)	
3. Cooling Water		37.88 Gallons
1. #1 Purification Column Condenser	(16.94)	
2. #2 Purification Column Condenser	(15.88)	
3. Purified Tet Cooler	(1.67)	
4. Chlorination Cooler (H-17)	(0.53)	
5. Cell Gas Cooler (H-18)	(2.86)	
4. Process Water		24.20 Gallons
1. Diluent for Waste Treatment	(24.20)	
5. Refrigeration		2.38 k \dot{B} tu
1. Reactor SiCl ₄ Condenser (H-11)	(1.28)	
2. SiCl ₄ Vent Condenser (H-07)	(1.10)	

Note: k = kilo = 10³

B. OTHER PROCESSES

The following other processes under consideration for solar cell grade silicon production are being monitored with respect to data relative to chemical engineering analyses:

1. Westinghouse Process
2. SRI Process
3. Dow Process
4. Aerochem
5. UCC Silane Process

III. ECONOMIC ANALYSIS (TASK 3)

A. BCL PROCESS (BATTELLE COLUMBUS LABORATORIES)

Major efforts were completed during this reporting period on the preliminary economic analysis for BCL process (Case A-two deposition reactors and six electrolysis cells). The status of these economic analysis activities are given below for key items:

	<u>Prior</u>	<u>Current</u>
.Process Design Inputs	95%	100%
.Base Case Conditions	60%	100%
.Raw Material Cost	60%	100%
.Utility Cost	60%	100%
.Major Process Equipment Cost	30%	100%
.Production Labor Cost	20%	100%
.Plant Investment Cost	10%	100%
.Total Product Cost	10%	100%

A summation of the key results for the BCL process is presented in the following table:

1. Process.....	BCL process
2. Plant Size.....	1,000 Metric Tons/year
3. Plant Product.....	Silicon
4. Product Form.....	Silicon Granules
5. Plant Investment.....	\$14,340,000/\$20,070,000 (1975 dollars) (1980 dollars)
	Fixed Capital \$12.47 Mega \$17.45 Mega
	Working Capital 1.87 Mega 2.62 Mega
	(15%) Total \$14.34 Mega \$20.07 Mega (1975 dollars) (1980 dollars)
6. Product Cost (No Profit).....	8.63 \$/kg/12.1 \$/kg (1975 dollars) (1980 dollars)
7. Inflation Factor (1975 to 1980).....	1.4

The detailed status sheet is shown in Table IIIA-1.0, and is representative of various subitems that make up the preliminary economic analysis activities. The detailed results from the preliminary economic analysis are presented in a tabular format. The guide for the tabular format is given below:

.Preliminary Economic Analysis Activities.....	Table IIIA-1.0
.Process Design Inputs.....	Table IIIA-1.1
.Base Case Conditions.....	Table IIIA-1.2
.Raw Material Cost.....	Table IIIA-1.3
.Utility Cost.....	Table IIIA-1.4
.Major Process Equipment Cost.....	Table IIIA-1.5
.Production Labor Cost.....	Table IIIA-1.6
.Plant Investment.....	Table IIIA-1.7
.Total Product Cost.....	Table IIIA-1.8

ECONOMIC ANALYSES:
PRELIMINARY ECONOMIC ANALYSIS ACTIVITIES FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

Prel. Process Economic Activity		Status	Prel. Process Economic Activity		Status
1.	Process Design Inputs	●	6.	Production Labor Costs	●
1.	Raw Material Requirements	●	1.	Base Cost Per Man Hour	●
2.	Utility Requirements	●	2.	Cgst/Kg Silicon Per Area	●
3.	Equipment List	●	3.	Total Cost/Kg Silicon	●
4.	Labor Requirements	●	7.	Estimation of Plant Investment	●
2.	Specify Base Case Conditions	●	1.	Battery Limits Direct Costs	●
1.	Base Year for Costs	●	2.	Other Direct Costs	●
2.	Appropriate Indices for Costs	●	3.	Indirect Costs	●
3.	Additional	●	4.	Contingency	●
3.	Raw Material Costs	●	5.	Total Plant Investment (Fixed Capital)	●
1.	Base Cost/Lb. of Material	●	8.	Estimation of Total Product Cost	●
2.	Material Cost/Kg of Silicon	●	1.	Direct Manufacturing Cost	●
3.	Total Cost/Kg of Silicon	●	2.	Indirect Manufacturing Cost	●
4.	Utility Costs	●	3.	Plant Overhead	●
1.	Base Cost for Each Utility	●	4.	By-Product Credit	●
2.	Utility Cost/Kg of Silicon	●	5.	General Expenses	●
3.	Total Cost/Kg of Silicon	●	6.	Total Cost of Product	●
5.	Major Process Equipment Costs	●			
1.	Individual Equipment Cost	●			
2.	Cost Index Adjustment	●			

0 Plan

● In Progress

● Complete

TABLE IIIA-1.1

PROCESS DESIGN INPUTS FOR
BCL PROCESS (BATTELLE COLUMBUS LABORATORIES)

1. Raw Material Requirements
 - Silicon tetrachloride, zinc, lime, argon and nitrogen
 - see table for "Raw Material Cost"
2. Utility
 - electricity, steam, cooling water and process water
 - see table for "Utility Cost"
3. Equipment List
 - 82 plus pieces of major process equipment
 - process vessels, heat exchangers, reactor, etc.
4. Labor Requirements
 - production labor for purification, deposition, electrolysis, etc.
 - see table for "Production Labor Cost"

TABLE IIIA-1.2
BASE CASE CONDITION FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

1. Capital Equipment

- January 1975 Cost Index for Capital Equipment Cost
- January 1975 Cost Index Value = 430

2. Utilities

- Electrical, Steam, Cooling Water, Nitrogen
- January 1975 Cost Index (U. S. Dept. Labor)
- Values determined by literature search and summarized in cost standardization work

3. Raw Material Cost

- Chemical Marketing Reporter
- January 1975 Value
- Raw Material Cost Index for Industrial Chemicals
- 1975 Cost Index Value = 206.9 (Wholesale Price Index, Producer Price Index)

4. Labor Cost

- Average for Chemical Petroleum, Coal and Allied Industries (1975)
- Skilled \$6.90/hr

5. Update to 1980

- historically cited 1975 dollars (LSA project)
- DOE decision to change to 1980 dollars (JPL, 6/22/79)
- reports to reflect both 1975 and 1980 dollars (JPL, 6/22/79)
- inflation factor of 1.4 to be used (JPL, 6/22/79)

Table IIIA-1.3

RAW MATERIAL COST FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

<u>Raw Material</u>	<u>Requirement lb/KG of Si</u>	<u>\$/lb of Material</u>	<u>Cost \$/KG of Si</u>
1. Silicon Tetrachloride (SiCl ₄)	15.68	0.135	2.117
2. Zinc (Zn)	0.54	0.38	0.205
3. Hydrate Lime (Ca(OH) ₂)	2.85	0.015	0.043
4. Argon (Ar)	3.1 SCF	0.016/SCF	0.050
5. Nitrogen (N ₂)	7.6 SCF	0.003/SCF	<u>0.023</u>
		Sub Total	2.438
6. Chlorine (Cl ₂)	-10.46 ¹	0.0332	<u>-0.347</u>
		TOTAL	2.091 (1975 dollars)
			x 1.4 inflation
			<u>2.927 (1980 dollars)</u>

Note:

1. This number is the result of by-product rate minus reactor chlorination rate, i.e., 11.12 - 0.66 lb. of Cl₂/KG Si.

Table IIIA-1.4
UTILITY COST FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

<u>Utility</u>	<u>Requirement/KG of Silicon</u>	<u>Cost of Utility</u>	<u>Cost \$/KG of Silicon</u>
1. Electricity	30.92 kw-hr	0.0324 \$/kw-hr	1.0018
2. Steam	9.67 pounds	1.35 \$/klb	0.0131
3. Cooling Water	37.88 Gallons	0.09 \$/kgal	0.0034
4. Process Water	24.20 Gallons	0.405 \$/kgal	0.0098
5. Refrigerant	2.38 MBtu	10.50 \$/MBtu	0.0250
TOTAL			1.0531 (1975 dollars) x 1.4 inflation 1.4743 (1980 dollars)

Note:

k = kilo = 10^3
M = mega = 10^6

TABLE IIIA-1.5

ESTIMATED COST OF MAJOR PROCESS EQUIPMENT FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

<u>Equipment</u>	<u>Purchased Cost, \$1,000</u>
1. (D-01) Light End Distillation Column	55.6
2. (D-02) Heavy End Distillation Column	55.6
3. (A-01) Primary SiCl_4 Vent Scrubber	0.8
4. (A-02) Final SiCl_4 Vent Scrubber	11.1
5. (H-01) L. E. Column Feed Heater	7.8
6. (H-02) L. E. Column Reboiler	2.2
7. (H-03) L. E. Column Condenser	2.3
8. (H-04) H. E. Column Feed Heater	7.8
9. (H-05) H. E. Column Reboiler	2.4
10. (H-06) H. E. Column Condenser	2.3
11. (H-07) SiCl_4 Vent Condenser	11.8
12. (H-08) SiCl_4 Vaporizer	6.7
13. (H-09) Reactor Condensers (2)	190.3
14. (H-10) Reactor ZnCl_2 Strippers (2)	27.9
15. (H-11) SiCl_4 Condenser	20.5
16. (H-12) Cell ZnCl_2 Stripper	10.9
17. (H-13) Therminol Cooler (Cold Circuit)	3.8
18. (H-14) Therminol Cooler (Hot Circuit)	9.1
19. (H-15) Start-up Heater	9.6
20. (H-16) Silicon Product Coolers (2)	7.7
20a. (H-17) Chlorination Cooler	15.9
20b. (H-18) Cell Gas Cooler	18.7
21. (T-01) SiCl_4 Storage Tank	33.6
22. (T-02) SiCl_4 Emergency Storage Tank	33.6
23. (T-03) L. E. Column Reflux Drum	6.7

TABLE IIIA-1.5 (Continued)

24.	(T-04) Surge Tank	19.0
25.	(T-05) Sump Tank	19.0
26.	(T-06) H. E. Column Reflux Drum	6.7
27.	(T-07) Pure SiCl_4 Storage Tank	28.8
28.	(T-08) Electrolysis Feed Tank	46.0
29.	(T-09) Molten Zinc Storage Tank	86.9
30.	(T-10) Therminol Head Tank	3.8
31.	(T-11) Therminol Drain Down Tank	5.3
32.	(T-12) Chlorine Supply Tank	2.4
33.	(T-13) Lime Solution Storage Tank	6.8
34.	(P-01) Purification Feed Pump	3.7
35.	(P-02) L. E. Column Feed Pump	3.4
36.	(P-03) L. E. Column Reflux Pump	8.4
37.	(P-04) Surge Tank Pump	9.8
38.	(P-05) Sump Pump	3.7
39.	(P-06) L. E. Column Bottom Pump	12.0
40.	(P-07) H. E. Column Reflux Pump	8.4
41.	(P-08) H. E. Column Bottom Pump	10.9
42.	(P-09) SiCl_4 Vaporizer Feed Pump	4.8
43.	(P-10) Reactor Condenser Circulation Pumps (2)	14.4
44.	(P-11) Cold Circuit Pump	6.7
45.	(P-12) Hot Circuit Pump	13.9
46.	(P-13) Primary Scrubber Recirculation Pump	0.9
47.	(P-14) Primary Scrubber Lower-loop Recirculation Pump	1.4
48.	(P-15) Primary Scrubber Upper-loop Recirculation Pump	1.5
49.	(P-16) Lime Solution Metering Pump	1.4

TABLE IIIA-1.5 (Continued)

50.	(F-01) L. E. Column Feed Filter	0.9
51.	(F-02) L. E. Column Reflux Filter	0.9
52.	(F-03) H. E. Column Feed Filter	0.9
53.	(F-04) H. E. Column Reflux Filter	0.9
54.	(F-05) Therminol Cooler Blower Filter	0.7
55.	(R-01) Fluidized Bed Reactors (2)	197.1
56.	(FN-01) Furnaces (2)	354.2
57.	(B-01) Seed Addition Hoppers (2)	9.6
58.	(B-02) Si Product Hoppers (4)	14.4
59.	(B-03) Zinc Hopper	2.4
60.	(C-01) Therminol Cooler Blower	4.8
61.	(C-02) Scrubber Vent Blower	5.4
62.	(E-01) Eductors (2)	1.3
63.	(EC-01) Electrolysis Cells (6)	444.6
64.	(PW-01) Power Supply and Bus	105.9
65.	(VP-01) Zinc Vaporizers (2)	<u>144.0</u>
TOTAL		2,177.7 (1975 dollars)
		x 1.4 inflation
		<u>3,048.8 (1980 dollars)</u>

TABLE IIIA-1.6

PRODUCTION LABOR COST FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

<u>Section</u>	<u>Labor Man-Hr/Kg Si</u>	<u>Labor Cost \$/Man-Hr</u>	<u>Cost \$/Kg Si</u>
1. Purification	0.01402	6.90	0.0968
2. Deposition	0.01402	6.90	0.0968
3. Electrolysis	0.02103	6.90	0.1451
4. Waste Treatment	0.00701	6.90	0.0484
5. Product Handling	0.00701	6.90	<u>0.0484</u>
		TOTAL	0.4355 (1975 dollars) <u>x 1.4 inflation</u> 0.6097 (1980 dollars)

Note: Costs are 1975 Dollars

TABLE IIIA-1.7

ESTIMATION OF PLANT INVESTMENT FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

	Investment \$1000
1. DIRECT PLANT INVESTMENT COSTS	
1. Major Process Equipment Cost	2,177.7
2. Installation of Major Process Equipment	936.4
3. Process Piping, Installed	1,611.5
4. Instrumentation, Installed	413.8
5. Electrical, Installed	217.8
6. Process Buildings, Installed	217.8
1a. SUBTOTAL FOR DIRECT PLANT INVESTMENT COSTS (PRIMARILY BATTERY LIMIT FACILITIES)	5,574.9
2. OTHER DIRECT PLANT INVESTMENT COSTS	
1. Utilities, Installed	1,045.3
2. General Service, Site Development, Fire Protection, etc.	261.3
3. General Buildings, Offices, Shops, etc.	304.9
4. Receiving, Shipping Facilities	457.3
2a. SUBTOTAL FOR OTHER DIRECT PLANT INVESTMENT COSTS (PRIMARILY OFFSITE FACILITIES OUTSIDE BATTERY LIMITS)	2,068.8
3. TOTAL DIRECT PLANT INVESTMENT COST, 1a + 2a	7,643.7
4. INDIRECT PLANT INVESTMENT COSTS	
1. Engineering, Overhead, etc.	1,197.7
2. Normal Cont. for Floods, Strikes, etc.	1,546.2
4a. TOTAL INDIRECT PLANT INVESTMENT COST	2,743.9
5. TOTAL DIRECT AND INDIRECT PLANT INVESTMENT COST, 3 + 4a	10,387.6
6. OVERALL CONTINGENCY, % of 5	2,077.5
7. FIXED CAPITAL INVESTMENT FOR PLANT, 5 + 6	<div style="border-top: 1px solid black;">12,465.2 (1975 dollars)</div> <div style="text-align: center;">x 1.4 inflation</div> <div style="border-top: 1px solid black;">17,451.2 (1980 dollars)</div>

TABLE IIIA-1.8

ESTIMATION OF TOTAL PRODUCT COST FOR BCL PROCESS
(BATTELLE COLUMBUS LABORATORIES)

	<u>\$/KG of Si</u>
1. Direct Manufacturing Cost (Direct Charges)	
1. Raw Materials	2.091
2. Direct Operating Labor	0.436
3. Utilities	1.053
4. Supervision and Clerical	0.065
5. Maintenance and Repairs	1.247
6. Operating Supplies	0.249
7. Laboratory Charge	0.065
2. Indirect Manufacturing Cost (Fixed Charges)	
1. Depreciation	1.247
2. Local Taxes	0.249
3. Insurance	0.125
3. Plant Overhead	0.675
4. By-Product Credit	-----
4a. Total Manufacturing Cost, 1 + 2 + 3 + 4	7.501
5. General Expenses	
1. Administration	0.450
2. Distribution and Sales	0.450
3. Research and Development	<u>0.225</u>
6. Total Cost of Product, 4a + 5	8.626 (1975 dollars)
	<u>x 1.4</u> inflation
	12.076 (1980 dollars)

B. OTHER PROCESSES

Technical reports for other processes under consideration for solar cell grade silicon production are being received and screened with respect to data relative to economic analysis:

1. Westinghouse Process (Na/SiCl₄)
2. SRI Process (Na/SiF₄, other)
3. Dow Process (C/SiO₂, other)
4. Aeorchem (Na/SiF₄, Na/SiCl₄, Na/Graphite, etc.)
5. UCC Silane Process (SiH₄/Si)

IV. SUMMARY - CONCLUSIONS

The following summary-conclusions are made as a result of accomplishments during this reporting period:

1. Task 1

Analysis of process system properties was continued for silicon source materials under consideration for producing silicon. The following property data are reported for dichlorosilane which is involved in processing operations for silicon: critical constants, vapor pressure, heat of vaporization, heat capacity, density, surface tension, thermal conductivity, heat of formation and Gibb's free energy of formation. The properties are reported as a function of temperature to permit rapid engineering usage.

Mixtures of nitrogen and hydrogen are being used to calibrate the apparatus previously assembled to determine thermal conductivity values of binary gas mixtures.

2. Task 2

Major efforts were continued on chemical engineering analysis of the BCL process including raw material, utility, major process equipment and labor requirements for the 1,000 MT/yr plant to produce silicon.

3. Task 3

Major efforts were expended on completion of the preliminary economic analysis of the BCL process (Battelle Columbus Laboratories). Cost analysis results are presented based on a preliminary process design of a plant to produce 1,000 metric tons/ year of silicon. Fixed capital investment estimate for the plant is \$12.47 million (1975 dollars) (\$17.47 million, 1980 dollars). Product cost without profit is 8.63 \$/kg of silicon (1975 dollars) (12.1 \$/kg, 1980 dollars).

V. PLANS

Plans for the next reporting period are summarized below:

1. Task 1

Continue analysis of process system properties for silicon source materials under consideration for producing silicon.

Studies will be initiated to measure thermal conductivity values on mixtures of silane and hydrogenated silanes.

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

TASK	1975				1976								1977								1978							
	Q	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S				
1. Analyses of Process																												
<u>System Properties</u>																												
1. Prel. Data Collection																												
2. Data Analysis																												
3. Estimation Methods																												
4. Exp.-Corr. Activities																												
5. Prel. Prop. Values																												
2. Chemical Engineering																												
<u>Analyses</u>																												
1. Prel. Process Flow Diag.																												
2. Reaction. Chemistry																												
3. Kinetic Rate Data																												
4. Major Equip. Req.																												
5. Chem. Equil.-Exp. Act.																												
6. Process Comparison																												
3. <u>Economic Analyses</u>																												
1. Cap. Invest. Est.																												
2. Raw Materials																												
3. Utilities																												
4. Direct Manuf. Costs																												
5. Indirect Costs																												
6. Total Cost																												
7. Process Comparison																												
Final Report																												

PROCESS FEASIBILITY STUDY IN
SUPPORT OF SILICON MATERIAL TASK I

JPL Contract No. 954343