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PROCESS FEASIBILITY STUDY IN SUPPORT OF SILICON MATERIAL TASK I

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ABSTRACT

Analyses of process system properties were continued for materials involved in the alternate processes under consideration for semiconductor silicon. Primary efforts centered on physical and thermodynamic property data for dichlorosilane. The following property data are reported for dichlorosilane which is involved in processing operations for solar cell grade silicon: critical temperature, critical pressure, critical volume, critical density, acentric factor, vapor pressure, heat of vaporization, gas heat capacity, liquid heat capacity and density.

Work was initiated on the assembly of a system to prepare binary gas mixtures of known proportions and to measure the thermal conductivity of these mixtures between 30° and 350°C. The binary gas mixtures will include silicon source material such as silanes and halogenated silanes which are used in the production of semiconductor silicon.

Chemical engineering analysis of the BCL process was continued with major efforts being concentrated to the preliminary process design. Primary activities in the preliminary design were devoted to determining production labor requirements for operating the major process equipment. The plant was divided into the following sections for determining labor: Purification (I), Deposition (II), Electrolysis (III), Waste Treatment (IV) and Product Handling (V). The results indicated the produciton labor requirements were 0.06309 man-hr/kg silicon production for the plant size of 1,000 metric tons/year.

TABLE OF CONTENTS

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 Garciá-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, °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:

$$\Delta H_v = \Delta H_{v_1} \left[\frac{T_c - T}{T_c - T_1}\right]^n \qquad \text{(IA-4)}$$

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 vlaues, 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:

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

where C_p^o is the ideal gas heat capacity, ω is the acentric factor, X is the Stiel polar factor and the funcions: $(\Delta C_\sigma)^{(0p)}$, 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:

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

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

TABLE IA-1

CRITICAL CONSTANTS AND PHYSICAL PROPERTIES OF DICHLOROSILANE

Identification	Dichlorosilane
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, cm^3/gr mol	228.3*
Critical Compressibility Factor, Z_c	.276*
Critical Density, ρ_c, gr/cm^3	.4424*
Acentric Factor (ω)	.1107

*Estimated

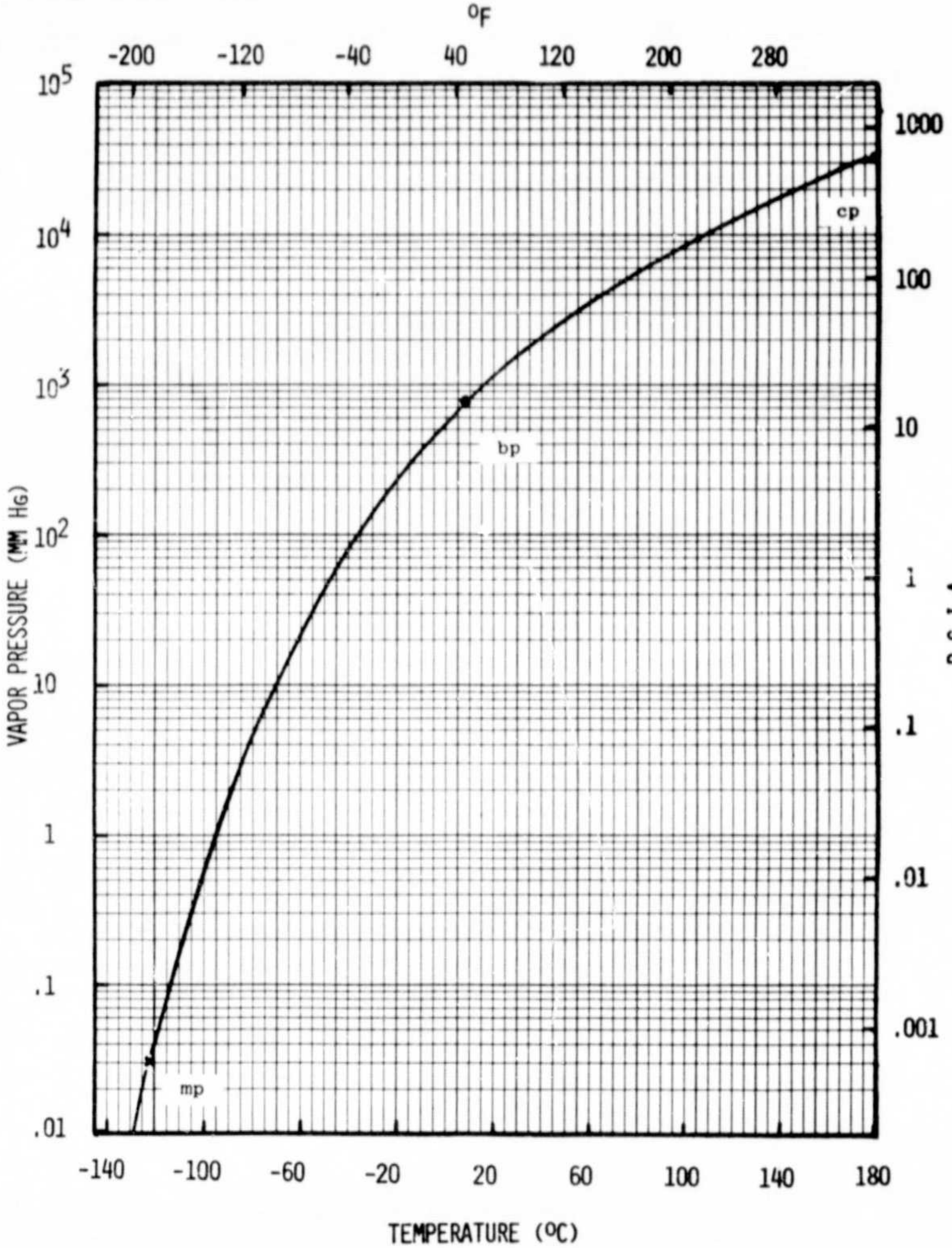


Figure IA-1. Vapor Pressure vs Temperature for Dichlorosilane

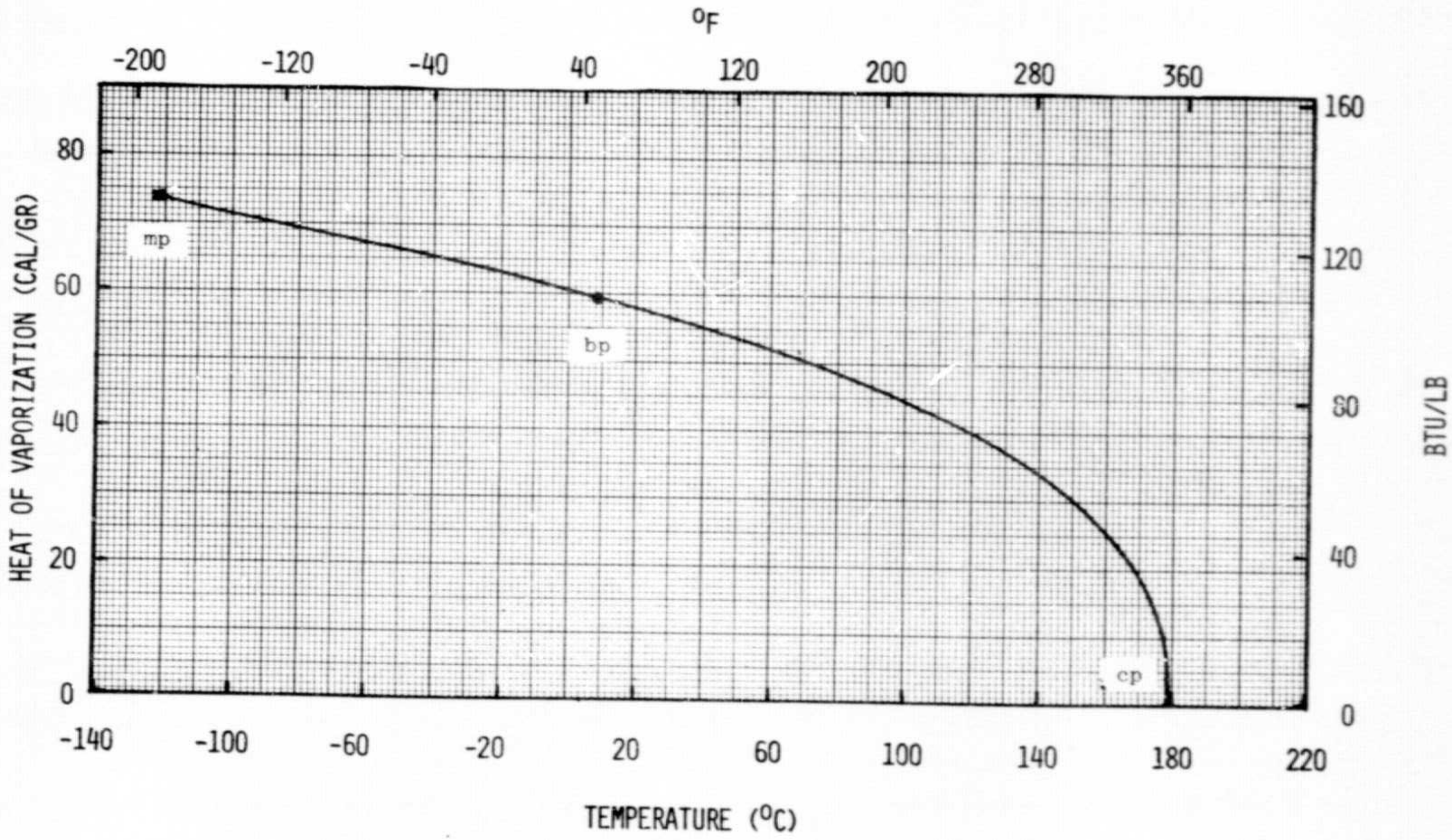


Figure IA-2. Heat of Vaporization vs Temperature for Dichlorosilane

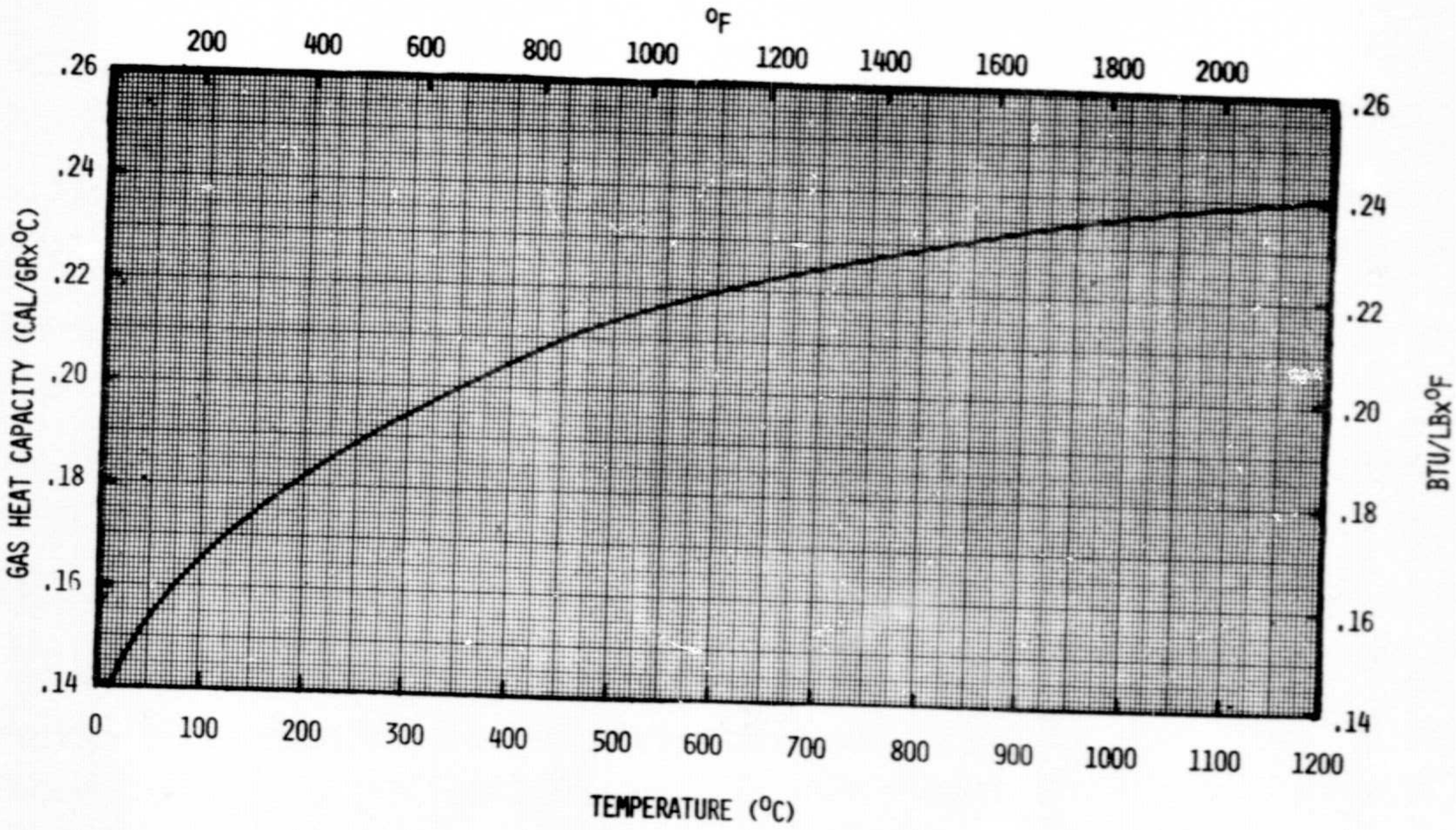


Figure IA-3. Gas Heat Capacity vs Temperature for Dichlorosilane

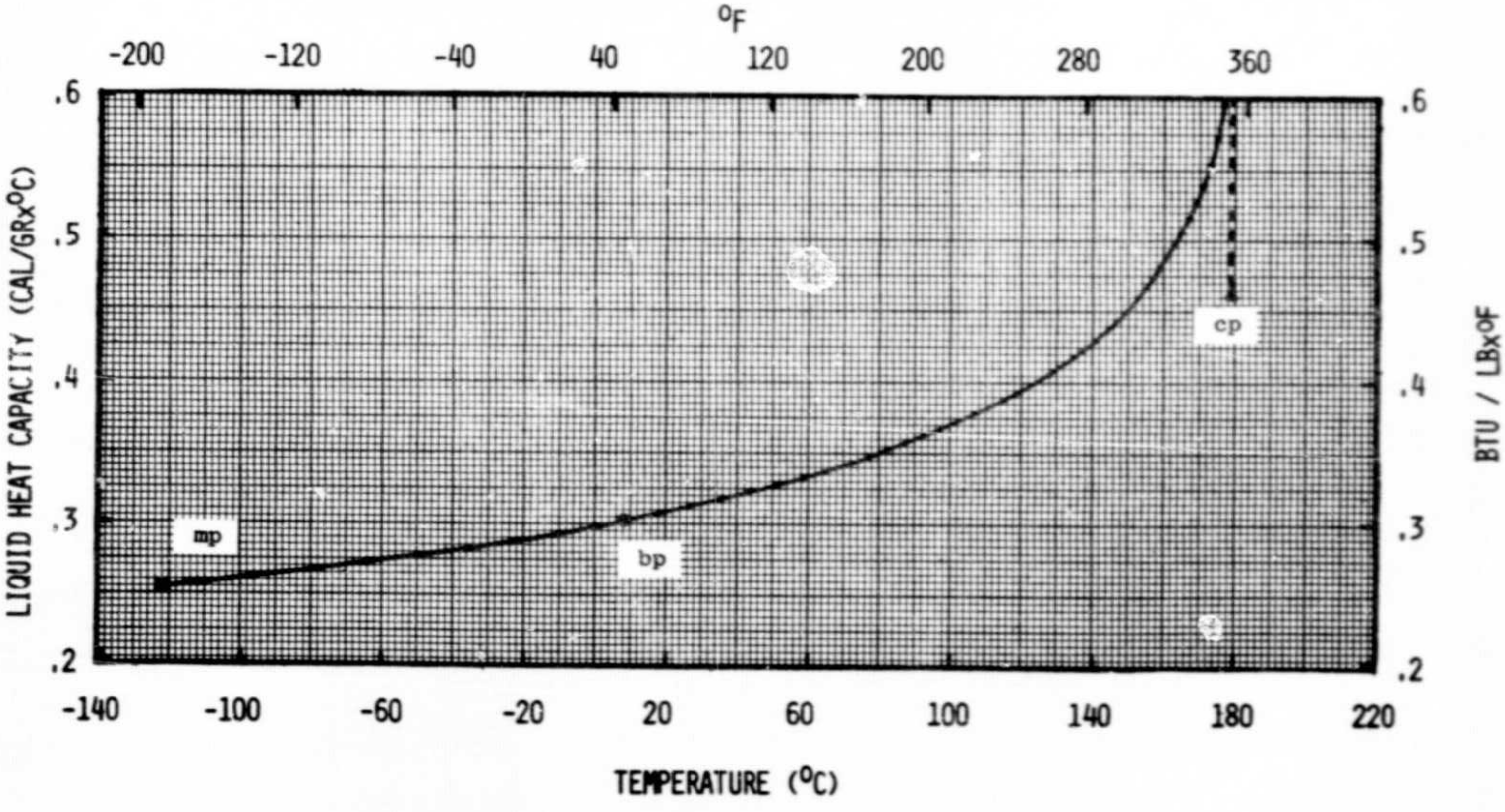


Figure IA-4. Liquid Heat Capacity vs Temperature for Dichlorosilane

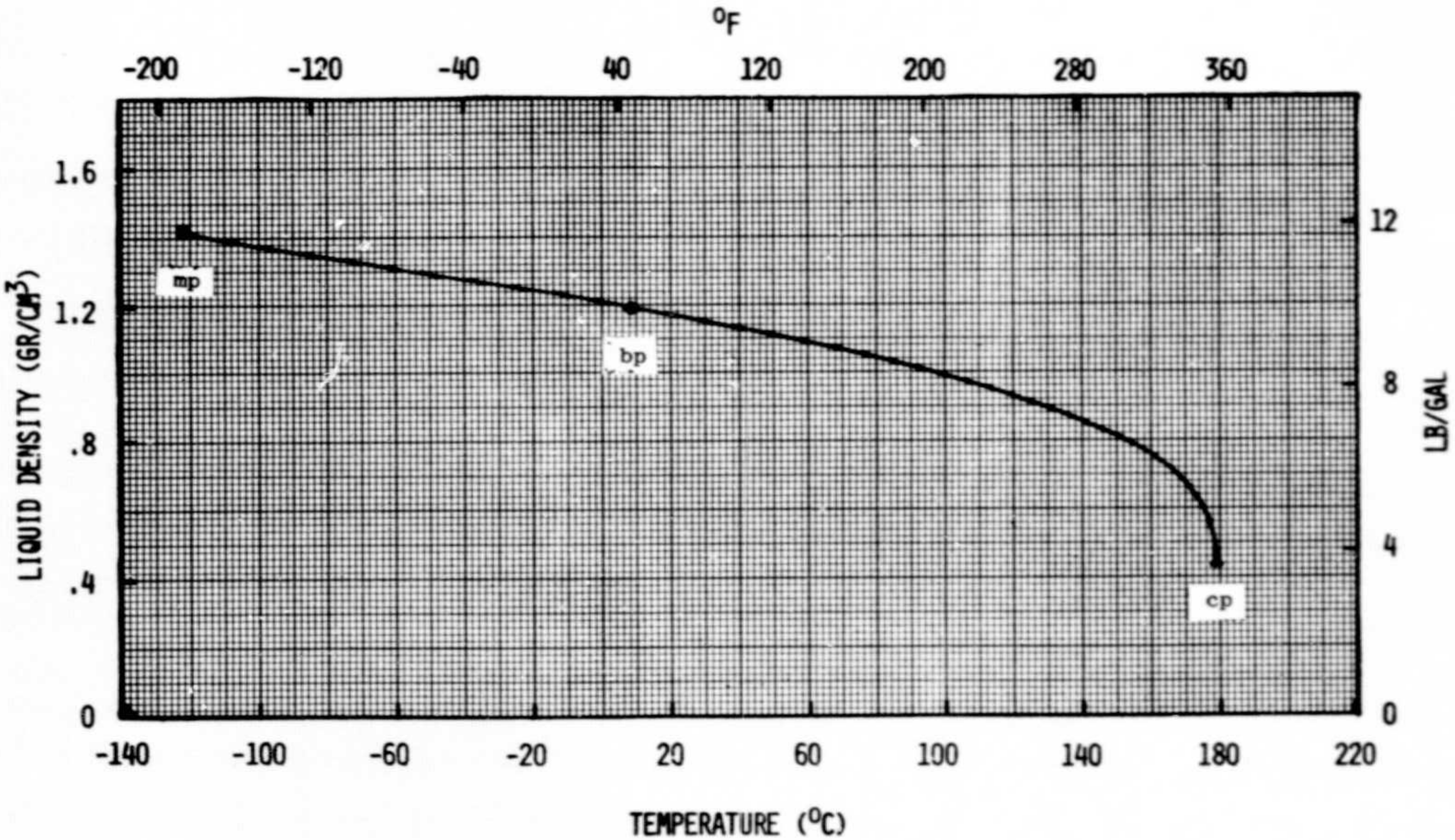


Figure IA-5. Liquid Density vs Temperature for Dichlorosilane

B. THERMAL CONDUCTIVITY INVESTIGATION

During this reporting period work has been directed toward the assembly of a system to measure thermal conductivity values of binary gas mixtures from 30°C to 350°C. Once the system is operational, thermal conductivity values of mixtures of silicon source materials (silanes and halogenated silanes) and other gases (such as hydrogen) used in the manufacture of silicon will be measured.

The components of the system will include the following:

1. A flowmeter - mixing tube assembly that will allow delivery of the two gases at metered rates and thoroughly mix the gases before any measurements are made.

2. A manifold system to allow handling of reactive gases and to route the mixtures to either the thermal conductivity cell or to a gas chromatograph for analysis.

3. A gas chromatograph fitted with a multiport sampling valve to allow analysis of the gas mixture at any desired time.

4. A hot-wire thermal conductivity cell to make vapor phase thermal conductivity measurements on the gas mixtures between 30°C and 350°C.

5. A disposal system to safely dispose of the reactive and pyrophoric materials after use.

II. CHEMICAL ENGINEERING ANALYSIS (TASK 2)

A. BCL PROCESS (BATTELLE COLUMBUS LABORATORIES)

Major activities were continued during this reporting period on the preliminary process design for BCL process. Primary efforts in the preliminary design were devoted to manpower estimates for production labor requirement.

In initial manpower estimate activities, the plant was separated into several different sections for subsequent determination of production labor required in each section.

The Purification Section (I) includes light ends distillation column; heavy ends distillation column; feed storage tank; purified storage tank; emergency storage tank and feed and in-process material circulation pumps. The purification section provides purified silicon tetrachloride as the raw material for the deposition of silicon.

The deposition of silicon is achieved in the Deposition Section (II). The Deposition Section (II) includes the fluid bed deposition reactor; reactor condensers; feed material vaporizer; silicon product cooler and initial silicon collection.

The zinc for producing the silicon is provided by the Electrolysis Section (III). This section includes electroysis cells where the zinc dichloride feed undergoes electrolysis to provide the zinc for subsequent reaction. The following equipment is also in the section: feed and storage tank; zinc chloride strippers and condensers and zinc vaporizer.

Waste Treatment (IV) and Product Handling (V) Sections comprise the remaining production labor items. Product handling involves general product collecting such as final collection of solid silicon product produced in the process. The waste treatment involves treatment of waste streams, such as neutralization, to meet environmental standards.

Results for the production labor requirement for the 1,000 metric tons/year silicon plant are shown on Table IIA-1.6. The tabulation gives manpower requirements for the Purification (I), Deposition (II), Electrolysis (III), Waste Treatment (IV), and Product Handling (V) sections of the plant.

TABLE IIA-1.6

PRODUCTION LABOR REQUIREMENTS FOR
BCL PROCESS (BATTELLE COLUMBUS LABORATORIES)

Section		Labor man-hr/KG Si (oper/shift)
1. Purification	(I)	0.01402 (2)
2. Deposition	(II)	0.01402 (2)
3. Electrolysis	(III)	0.02103 (3)
4. Waste Treatment	(IV)	0.00701 (1)
5. Product Handling	(V)	0.00701 (1)
	TOTAL	0.06309 (9)

Note

Manpower estimate for production labor requirements based on:

1. Dividing plant into sections
   -type of unit operation
   -mark off working area

2. Specify work duties required in each section

3. Estimate operators required to perform work duties in each section
   -type of unit operation
   -size of working area
   -degree of automation (batch, semi-continuous, continuous, etc.)

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 activities were initiated on preliminary economic analysis for BCL process. The status of these economic analysis activities are given below for key items:

	Prior	Current
.Process Design Inputs	0%	90%
.Base Case Conditions	0%	60%
.Raw Material Cost	0%	60%
.Utility Cost	0%	60%
.Major Process Equipment Cost	0%	30%
.Production Labor Cost	0%	20%
.Plant Investment Cost	0%	10%
.Total Product Ccst	0%	10%

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 process design inputs forwarding for economic analysis are summarized in Table IIIA-1.1.

TABLE IIIA-1.0

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

Prel. Process Economic Activity	Status
1. Process Design Inputs	◒
1. Raw Material Requirements	◒
2. Utility Requirements	◒
3. Equipment List	◒
4. Labor Requirements	◒
2. Specify Base Case Conditions	◒
1. Base Year for Costs	◒
2. Appropriate Indices for Costs	◒
3. Additional	◒
3. Raw Material Costs	◒
1. Base Cost/Lb. of Material	◒
2. Material Cost/Kg of Silicon	◒
3. Total Cost/Kg of Silicon	◒
4. Utility Costs	◒
1. Base Cost for Each Utility	◒
2. Utility Cost/Kg of Silicon	◒
3. Total Cost/Kg of Silicon	◒
5. Major Process Equipment Costs	◒
1. Individual Equipment Cost	◒
2. Cost Index Adjustment	◒

Prel. Process Economic Activity	Status
6. Production Labor Costs	◒
1. Base Cost Per Man Hour	◒
2. Cost/Kg Silicon Per Area	◒
3. Total Cost/Kg Silicon	◒
7. Estimation of Plant Investment	◒
1. Battery Limits Direct Costs	◒
2. Other Direct Costs	◒
3. Indirect Costs	◒
4. Contingency	◒
5. Total Plant Investment (Fixed Capital)	◒
8. Estimation of Total Product Cost	◒
1. Direct Manufacturing Cost	◒
2. Indirect Manufacturing Cost	◒
3. Plant Overhead	◒
4. By-Product Credit	◒
5. General Expenses	◒
6. Total Cost of Product	◒

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
   -80 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"

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 ($Na/SiCl_4$)
2. SRI Process (Na/SiF_4, other)
3. Dow Process (C/SiO_2, other)
4. Aeorchem (Na/SiF_4, $Na/SiCl_4$, Na/Graphite, etc.)
5. UCC Silane Process (SiH_4/Si)

IV. SUMMARY - CONCLUSIONS

The following summary-conclusions are made based on major activities accomplished during this reporting period.

1. Task 1

Analyses of process system properties was continued for materials involved in the alternate processes under consideration for semiconductor grade silicon. Primary efforts centered on physical and thermodynamic property data for dichlorosilane. The following property data are reported for dichlorosilane which is involved in processing operations for solar cell grade silicon: critical temperature, critical pressure, critical volume, critical density, acentric factor, vapor pressure, heat of vaporization, gas heat capacity, liquid heat capacity and density.

Work was begun on the assembly of a system to measure thermal conductivity values of binary gas mixtures such as silanes and halogenated silanes used in the production of semiconductor silicon.

2. Task 2

Chemical engineering analysis of the BCL process was continued with major efforts being concentrated to the preliminary process design. Primary activities in the preliminary design were devoted to determining production labor requirements for operating the major process equipment. Production labor requirements are reported for the following sections of the plant: Purification (I), Deposition (II), Electrolysis (III), Waste Treatment (IV) and Product Handling (V).

3. Task 3

Preliminary economic analysis was initiated for the plant to produce 1000 metric tons/years of silicon.

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.

Complete assembly of the equipment and initiate calibration studies for preparing, analyzing and determining thermal conductivity of gas mixtures.

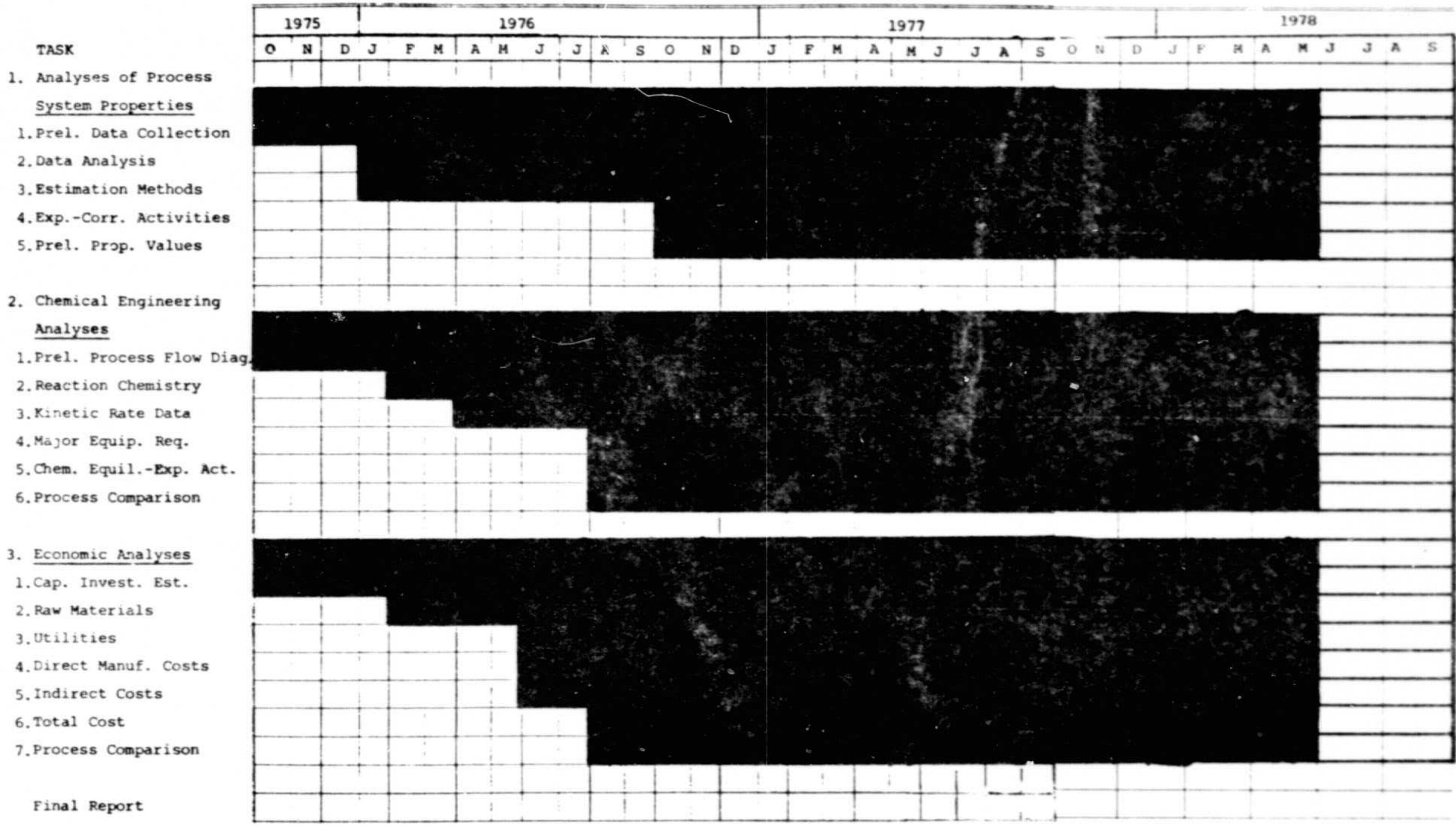
2. Task 2

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



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