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OFFICE OF ENGINEERING RESEARCH

OKLAHOMA STATE UNIVERSITY

INTERACTIONS OF LIKE AND UNLIKE MOLECULES

NASA GRANT NGL 37-002-011

REPORT

TO

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October 1 , 1969

PROGRESS REPORT

NASA GRANT NGL 37-002-011

OER PROJECT NO. 3

INTERACTIONS OF LIKE AND UNLIKE MOLECULES

REPORT PERIOD

April 1, 1969 to September 30, 1969

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ABSTRACT

The present project is concerned with molecular interactions in gaseous and liquid mixtures. The work on gaseous mixtures has as its goal development of improved methods for characterizing the interaction energy between unlike molecules. Such characterization is the key to prediction of gas mixture properties. The liquid phase study is devoted to development of models for prediction of thermodynamic mixture properties of polar liquid mixtures. Such models would find application in such areas as the screening of solvents for extractive distillation.

Specific items of progress in the gas phase studies during this report period include:

(1) Data on volumetric properties of helium-krypton mixtures have been analyzed to provide second and third virial coefficients for pure and mixed interactions in the region 225 to 325°K.

(2) An apparatus for measurement of solid-gas and vapor-liquid equilibrium from 90°K to room temperature has been designed and fabricated. Testing of the apparatus is in progress prior to beginning study of solid-gas equilibria in the helium-krypton system.

(3) Calculations have been made which elucidate the effect of experimental variables on the accuracy of pair-potential parameters determined from virial coefficient data.

For the liquid phase studies:

(1) Barker's quasi-lattice theory has been applied to mixing properties of alcohol-paraffin systems. Comparisons with experimental data reveal an accuracy comparable to the lattice-gas model recently developed in this work.

(2) A simplified vapor pressure apparatus has proved satisfactory for measurement of binary solution vapor pressures. Data have been obtained on binary mixtures of hexane, benzene, and ethanol, and excess free energies and entropies calculated therefrom.

SEMI-ANNUAL PROGRESS REPORT

September 1, 1969

A. Total Number of Faculty Involved

One faculty member, Dr. Robert L. Robinson, Jr., Project Director, has been principly involved in this project. Dr. K. C. Chao, Department of Chemical Engineering, Purdue University, has served extensively as consultant in the liquid-phase study during this project period.

B. Total Number of Students Involved

Six Chemical Engineering graduate students have been active in the project area; two are supported by this project. Mr. D. D. Dillard has worked on the gas phase studies and Mr. C. M. Kuo has worked on the liquid phase studies. Both these Ph.D. students, supported by this project, plan to complete their work in the near future. Mr. F. H. Kate and Mr. H.-M. Lin are Ph.D. candidates working in the project area but are supported by NSF funds. Both these students began in September, 1968, on this project and will continue and extend the work of Mr. Dillard and Mr. Kuo. In addition, two M. S. candidates, Mr. C. J. Mundis and Mr. V. C. Smith have worked in the project area but received no support from the project. Both these men recently completed their M. S. theses and finished their work on the project.

C. Any Industrial Involvement

There has been no industrial involvement during this reporting period.

D. Publications

No publications have appeared in this progress period. However, one manuscript has been submitted to Journal of Chemical Physics, and two other manuscripts are currently in preparation.

E. Multidisciplinary Efforts

No formal multidisciplinary efforts have been involved, but close contact and exchange of information with Dr. Lionel Raff, Chemistry, and Dr. Thomas Winter, Physics, have been maintained on projects of mutual interest.

F. Projects or Parts of Your Project Either Supported in Part by Other Sources or Forecast to be Supported

A National Science Foundation Grant for a two-year period in the amount of $54,800 was received, effective September 1, 1968, to provide continued support of this project. The NSF project title is "Unlike-Molecule Interactions and Properties of Simple Mixtures." The proposal on which the NSF grant was based was a direct outgrowth of knowledge obtained from the present NASA project.

G. Seminars

No seminars were held during this report period.

H. Curricula Changes as a Result of the Findings or Efforts in this Project

No curricula changes have been made.

PROGRESS

I. Gas Phase Study

In one part of this study, experimental data on the volumetric properties of helium-krypton mixtures have been obtained using a Burnett Apparatus. Data have been obtained from 100 to 2000 psia for five compositions (0, 25, 50, 75, and 100% krypton) at three temperatures, -50, 0, +50°C. These data were obtained by Mr. D. D. Dillard, Graduate Associate.

Work in this part of the project has centered on extraction of compressibilities and virial coefficients from the raw Burnett data. The Burnett technique has found favor in recent years due to its experimental simplicity. Unfortunately, extraction of information from the data is a sensitive problem in non-linear regression. Differences in opinion persist on proper treatment of the data, as emphasized by a recent conference at the National Bureau of Standards, Washington, devoted entirely to the Burnett method.

Second and third virial coefficients have been determined from the Burnett data and are presented in Figures 1 and 2. The data treatment method used was similar to that suggested by Canfield (1). Comparisons of the helium data with recent literature data are shown in Table 1; comparisons for krypton are shown in Figure 3.

Mr. H.-M. Lin, Graduate Assistant, has been working on this project, under NSF support, since September, 1968. This phase of the project has been concerned with methods for prediction of mixture properties by suitable "combination rules" and known pure component properties. Literature data on equilibrium and transport properties at low pressures have been collected. These data are currently being employed to test existing "combination rule" models for predicting unlike-molecule intermolecular pair-potential parameters from known pure component parameters.

As a prerequisite to the above tests, a study was performed to assess the uncertainties in pair-potential parameters determined from macroscopic property data. Results of this analysis are given in the attached paper manuscript and will not be discussed further here.

Mr. Fred Kate, Graduate Assistant, joined the project, under NSF support, in September, 1968. He has worked on the design and fabrication of an equilibrium apparatus capable of measuring solid-gas and vapor-liquid equilibria in binary systems at low temperatures and high pressures. During the past report period, he has assembled the apparatus and is currently testing the vacuum and temperature control systems. The equipment is shown in Figures 4 and 5. The apparatus is essentially a gas flow type where the dense phase (solid or liquid) saturates the gas as the gas passes through a series of trays. The effluent is sent to a chromatograph for analysis.

Solid-gas equilibria will be investigated in the helium-krypton system as soon as the apparatus is deemed ready. These data, in conjunction with the Burnett data, will determine the interaction virial coefficient for helium-krypton from 80 to 323°K. This wide temperature range should permit accurate evaluation of potential parameters.

II. Liquid Phase Study

Mr. C. M. Kuo, Graduate Assistant, has continued his work on group-contribution models for prediction of mixing properties in non-ideal liquid solutions.

Calculations have been made for mixing properties in n-alcohol-n-paraffin systems based on the quasi-lattice models presented by Guggenheim (2) and Barker (3). These calculations were made to furnish comparisons with the solution model developed and described in the previous progress report. The calculations show that the new model is comparable to the quasi-lattice model in prediction of excess enthalpies, but slightly superior in prediction of excess free energies and entropies.

Mr. V. C. Smith has completed work on the design and testing of a simplified mixture vapor pressure apparatus for measurement of total solution vapor pressures (4). The apparatus, shown in Figure 6, permits samples of known composition to be prepared prior to degassing. Degassing is accomplished by boiling under reflux and subsequently freezing the solution within the equilibrium cell. The cell has been used to measure vapor pressures at 25°C in the binary systems of benzene ethanol and hexane. Results are shown in Figures 7 through 9. This cell facilitates measurements which yield excess free energies. The free energies may be combined with literature data on excess enthalpies to yield excess entropies. Such properties are indispensible in testing models for behavior of non-ideal solutions. (Results are shown in Figures 10 through 12, along with entropies predicted by the Wilson (5) equation.)

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TABLE I

COMPARISON OF VALUES FOR THE SECOND VIRIAL OF HELIUM, cc/g-mol

Reference	T = 323.15°K	T = 273.15°K	T = 223.15°K
This Work	11.57	11.93	12.06
Holborn (6)	11.73	11.86	11.93
Michels (22)	11.57	11.87	
Blancett (7)	11.82	11.91	12.21
Hall (13)	11.76	11.94	12.16
Wiebe (8)	11.43	11.70	
Tanner (9)	11.39	11.70	
Keesom (10)	11.30	11.48	11.59
Canfield (1)		12.09	
White (11)		12.08	
Schneider (12)		11.77	
Barieau (14)		11.98	

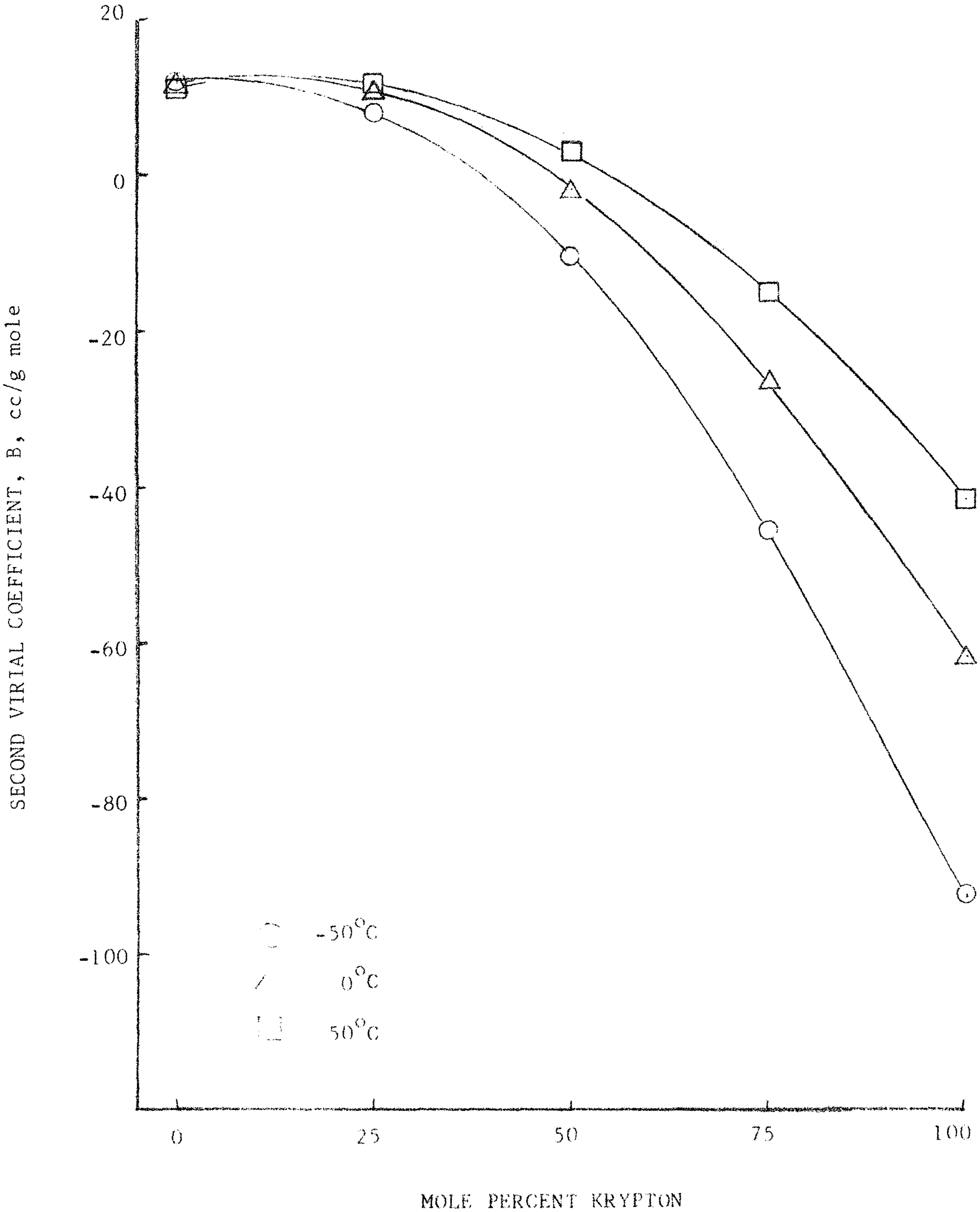


Figure 1

Second Virial Coefficients of Helium Krypton Mixtures

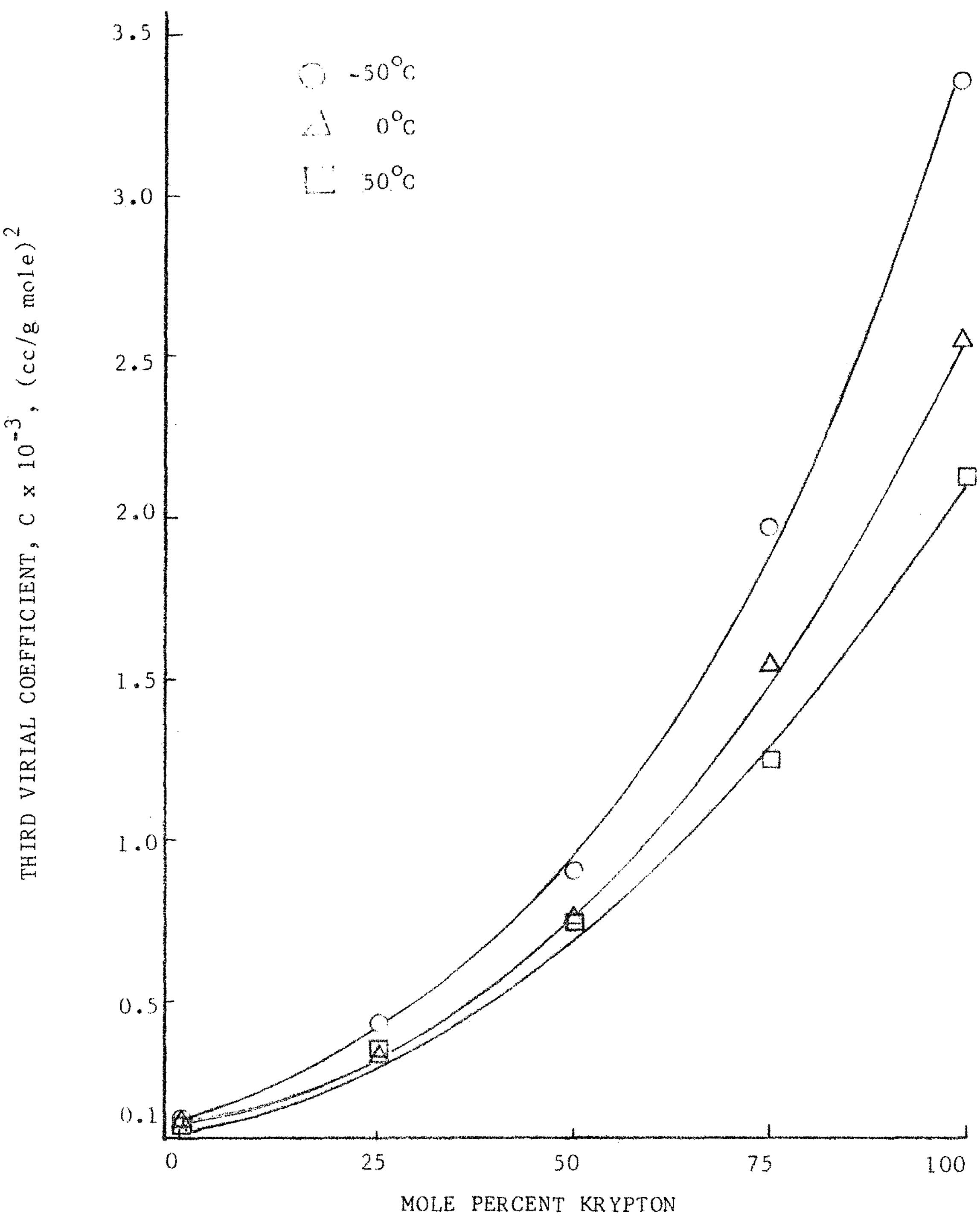


Figure 2

Third Virial Coefficients of Helium-Krypton Mixtures

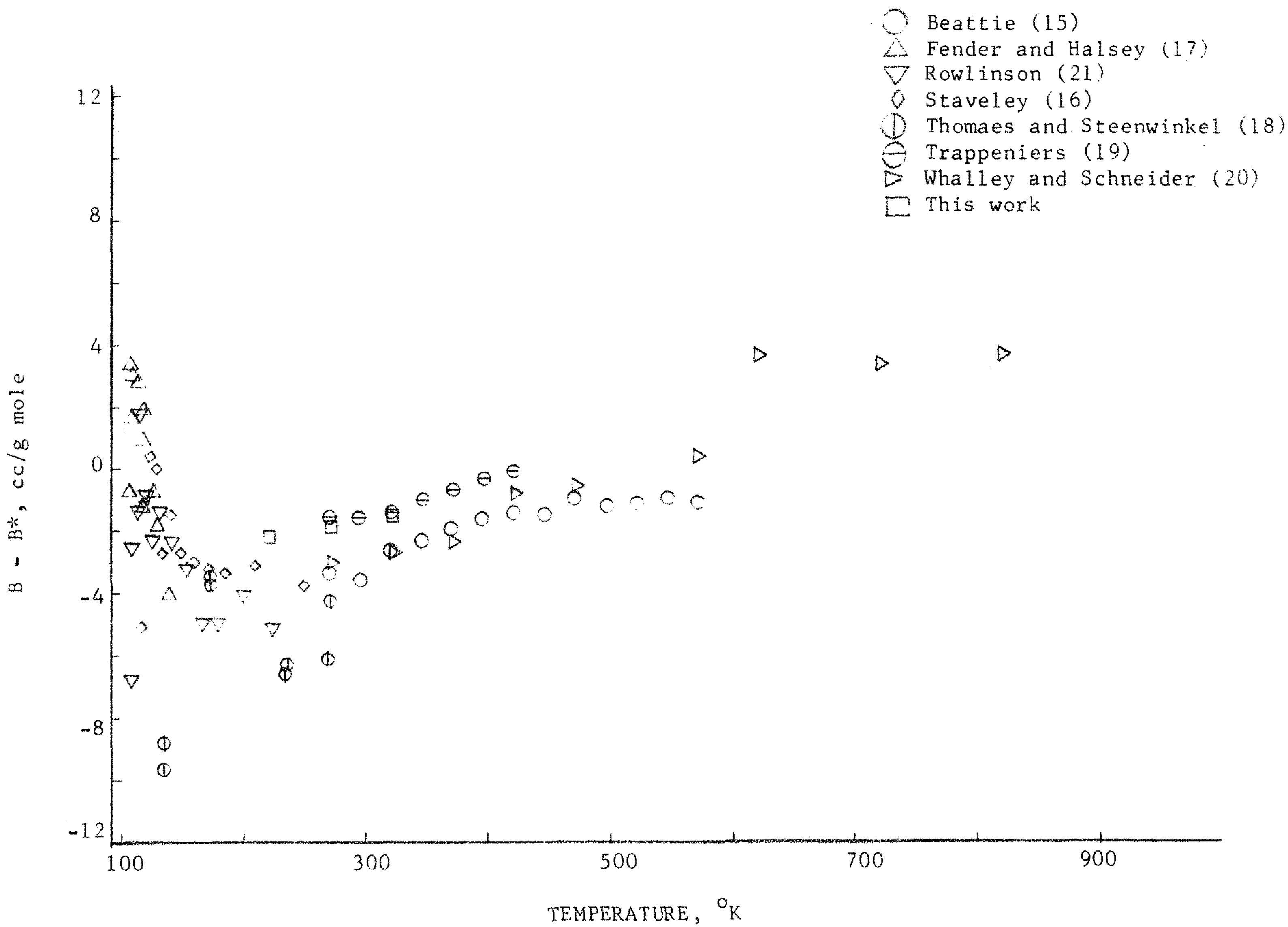


Figure 3

Deviation of Experimental Second Virial Coefficients, B, from the Empirical Square-Well Potential Virial, B*

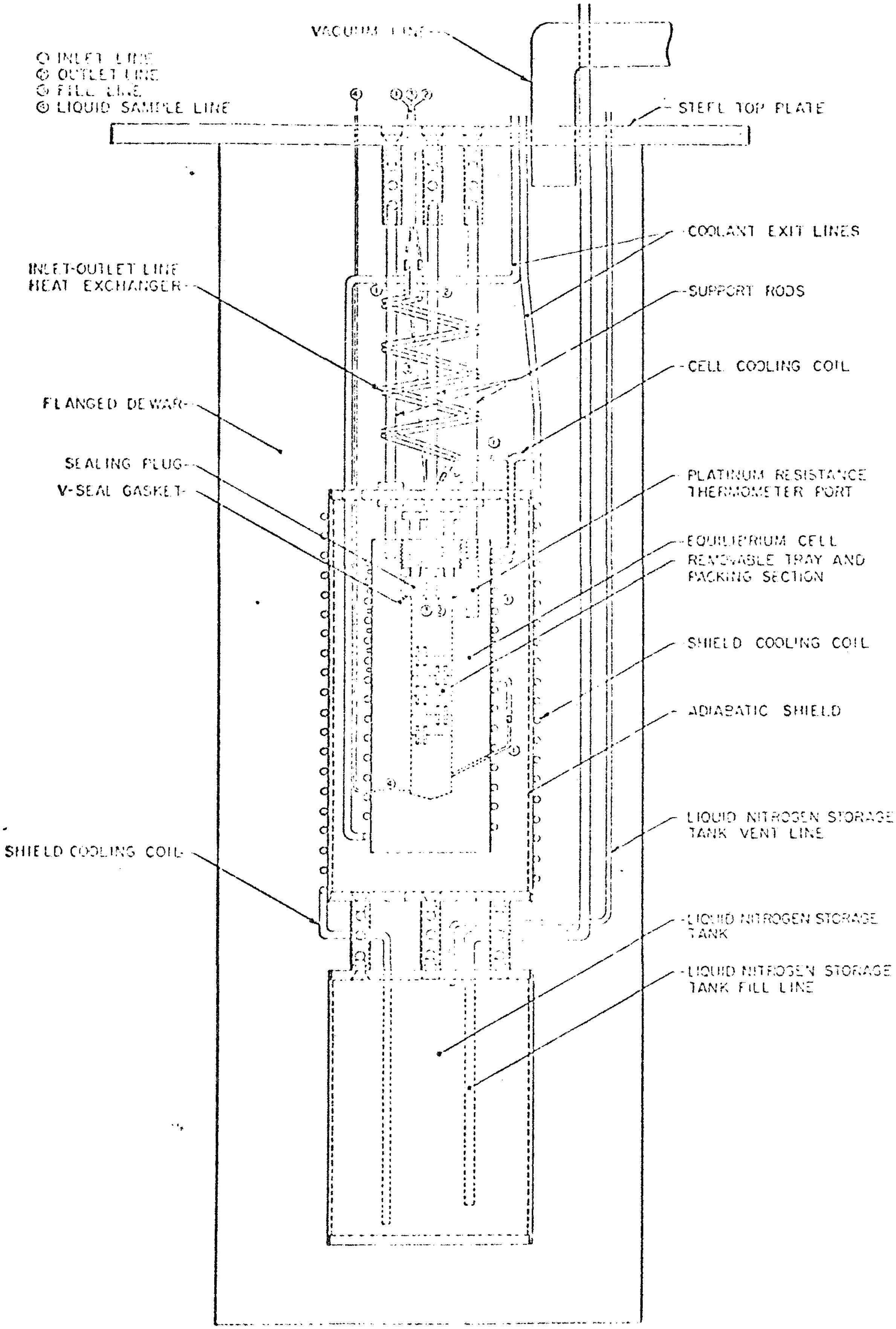


Figure 4. Detailed Schematic Diagram of Equilibrium Cell

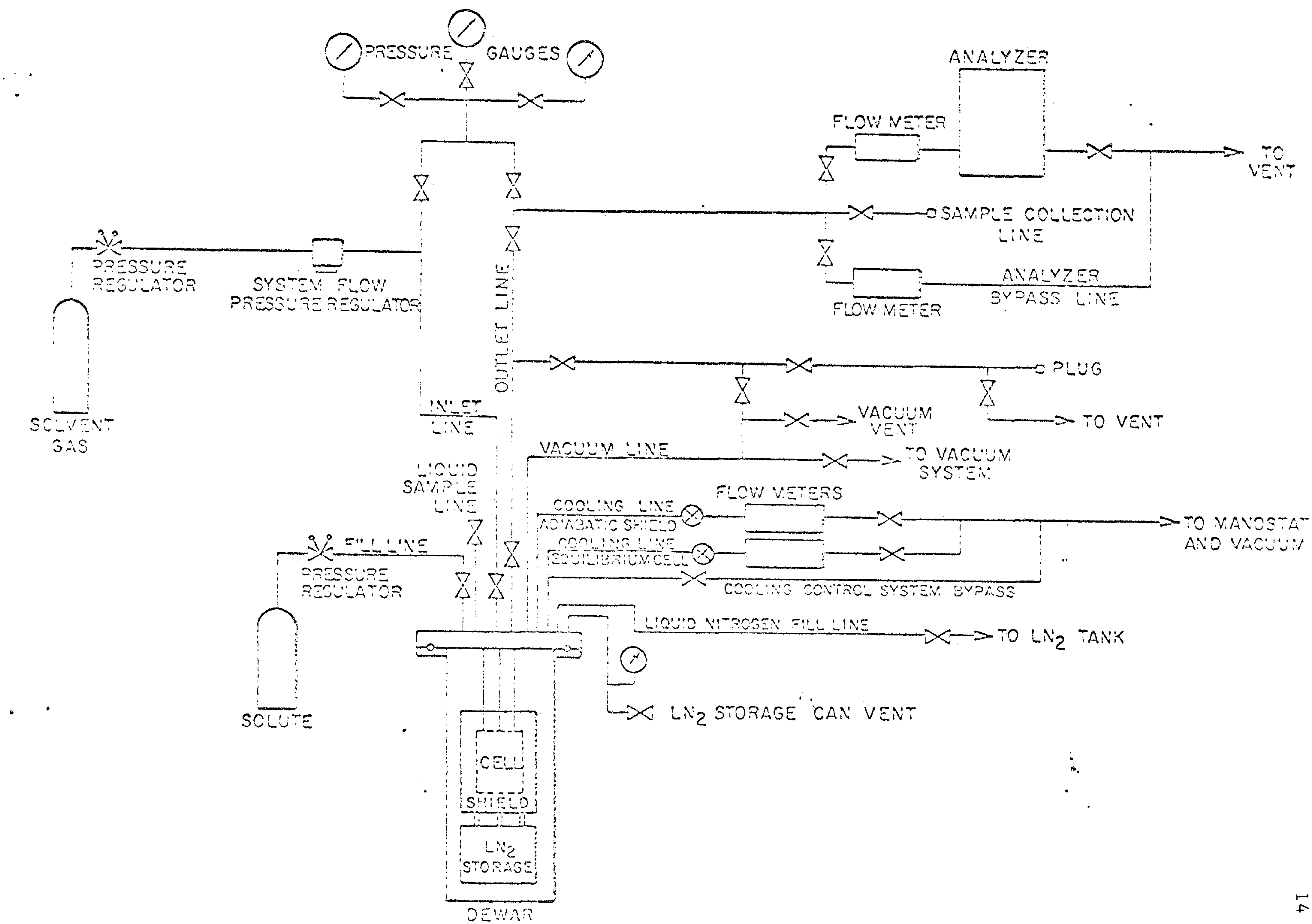
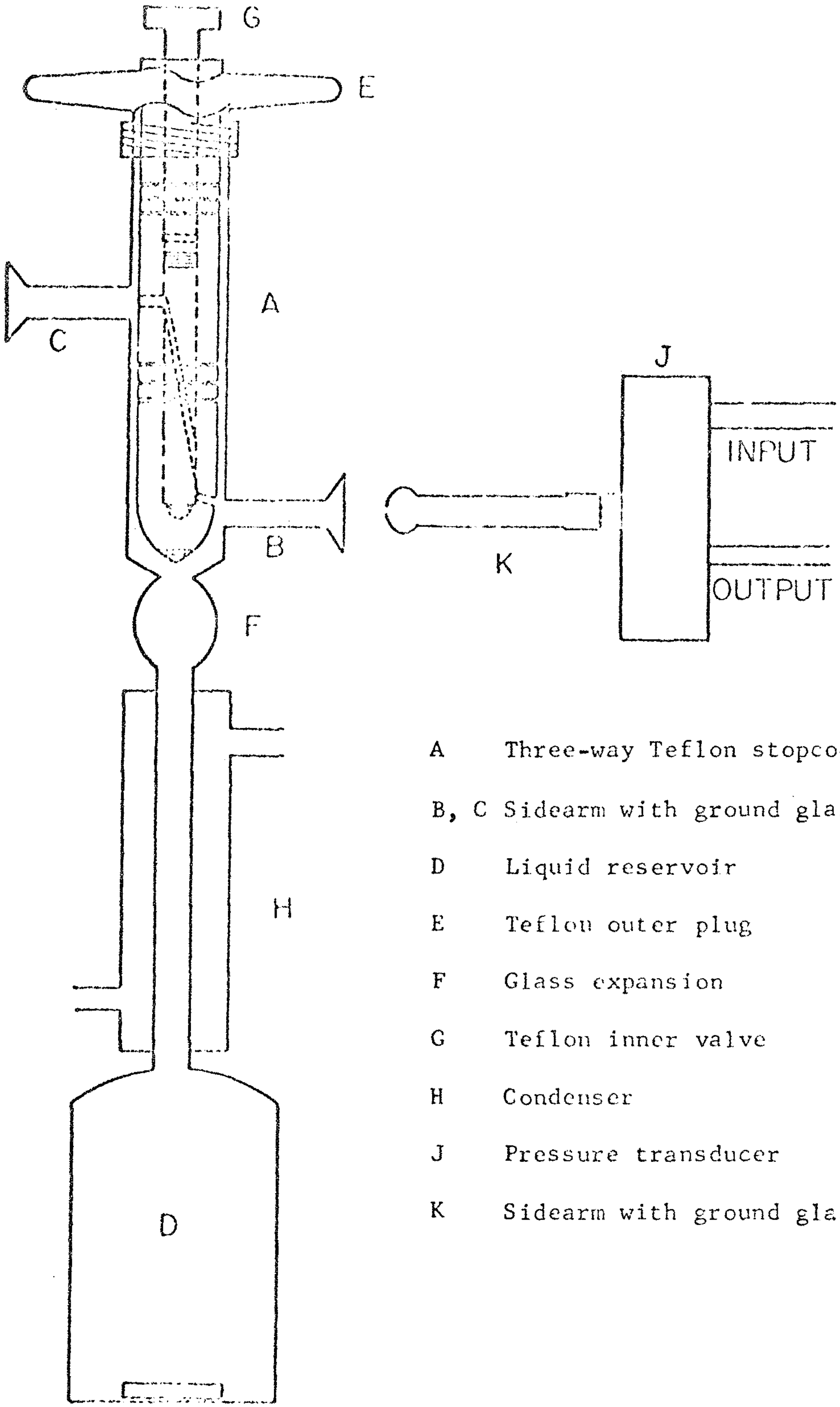


Figure 5. Schematic Diagram of Phase Equilibrium Equipment



A	Three-way Teflon stopcock
B, C	Sidearm with ground glass joints
D	Liquid reservoir
E	Teflon outer plug
F	Glass expansion
G	Teflon inner valve
H	Condenser
J	Pressure transducer
K	Sidearm with ground glass joint

Figure 6. Equilibrium Cell

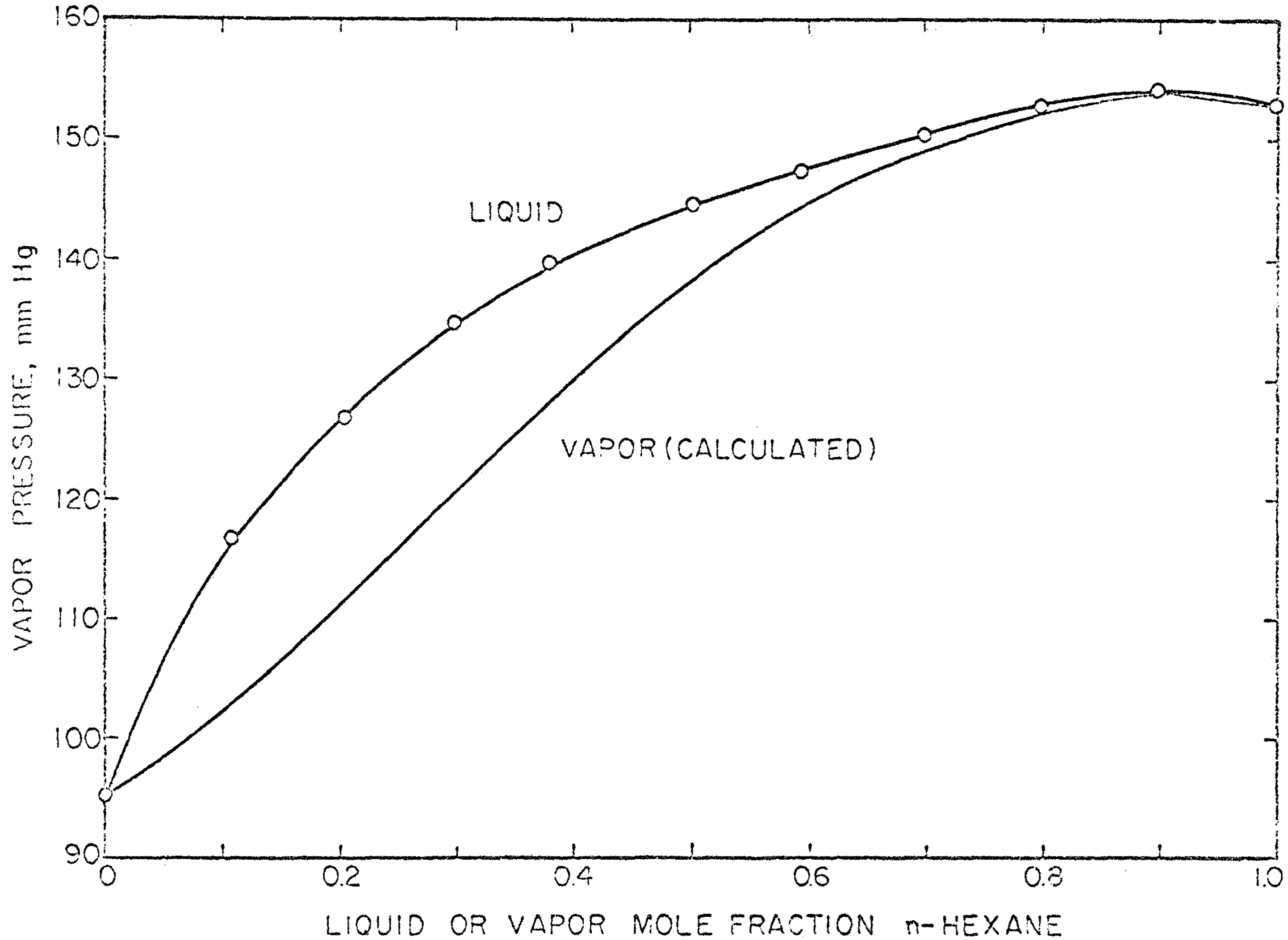


Figure 7. Vapor Pressure at 25° C for the System n-Hexane-Benzene

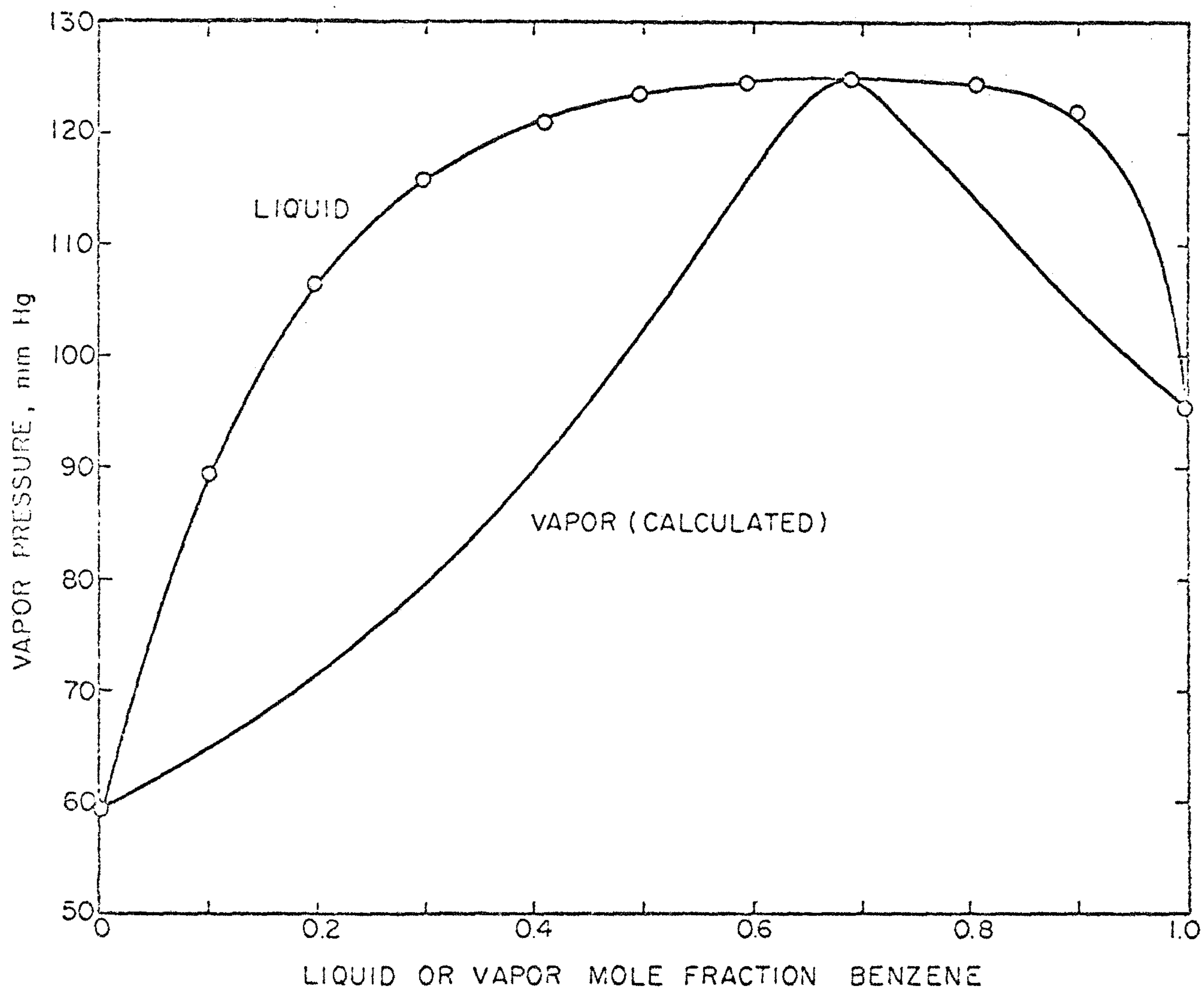


Figure 3. Vapor Pressure at 25° C for the System Benzene-Ethanol

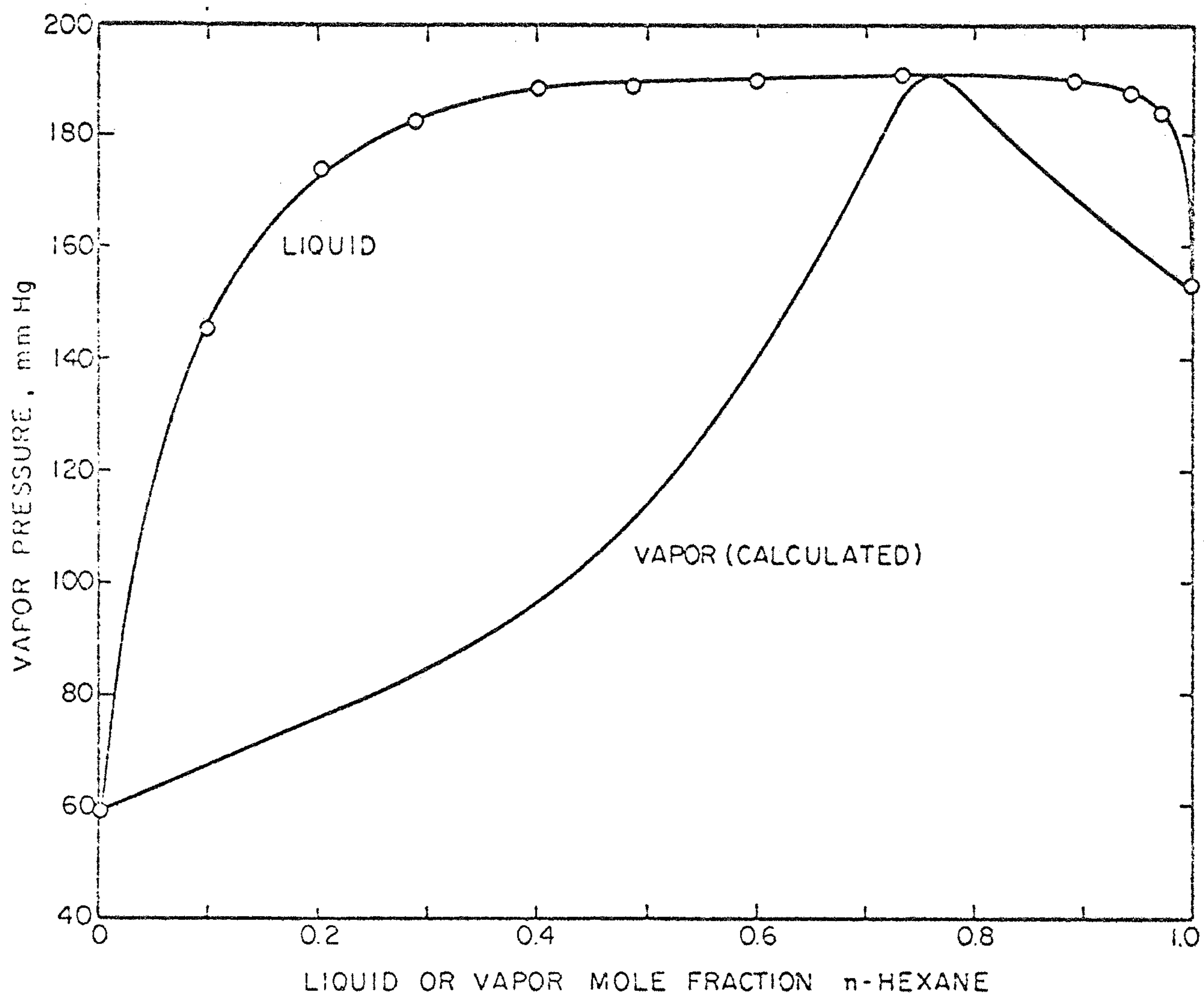


Figure 9. Vapor Pressure at 25° C for the System n-Hexane-Ethanol

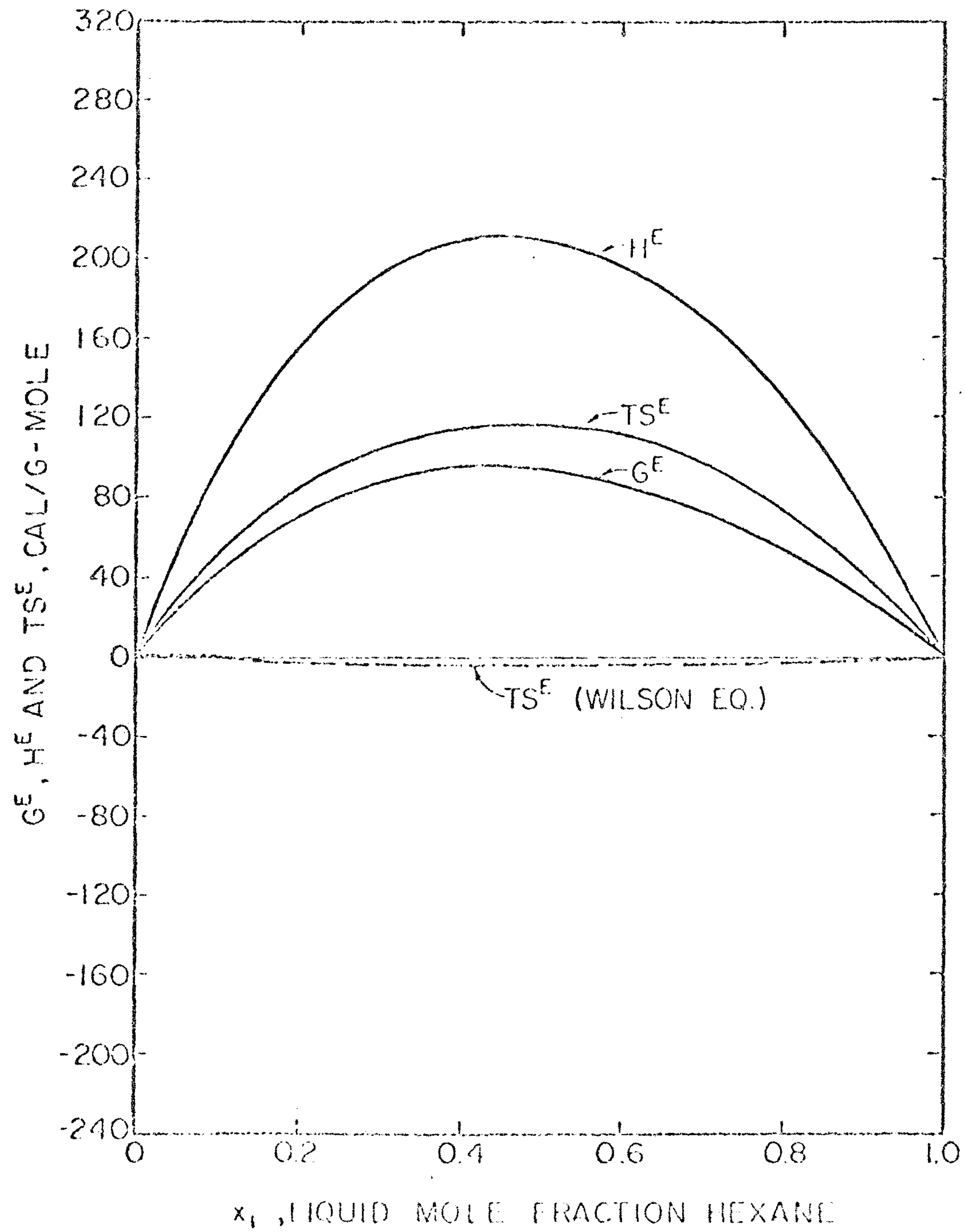


Figure 10 Excess Thermodynamic Properties at 25° C for the System n-Hexane–Benzene

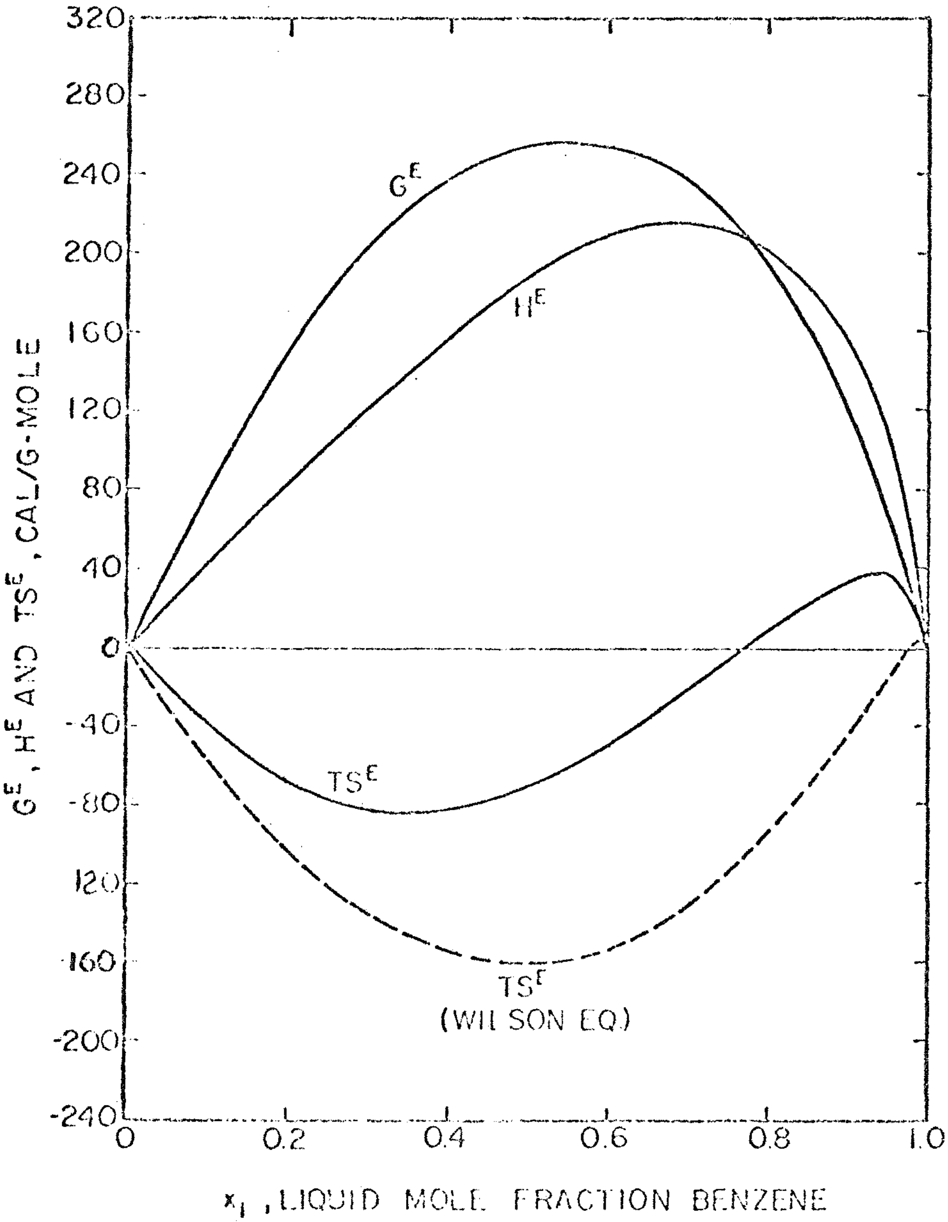


Figure 11. Excess Thermodynamic Properties at 25° C for the System Benzene--Ethanol

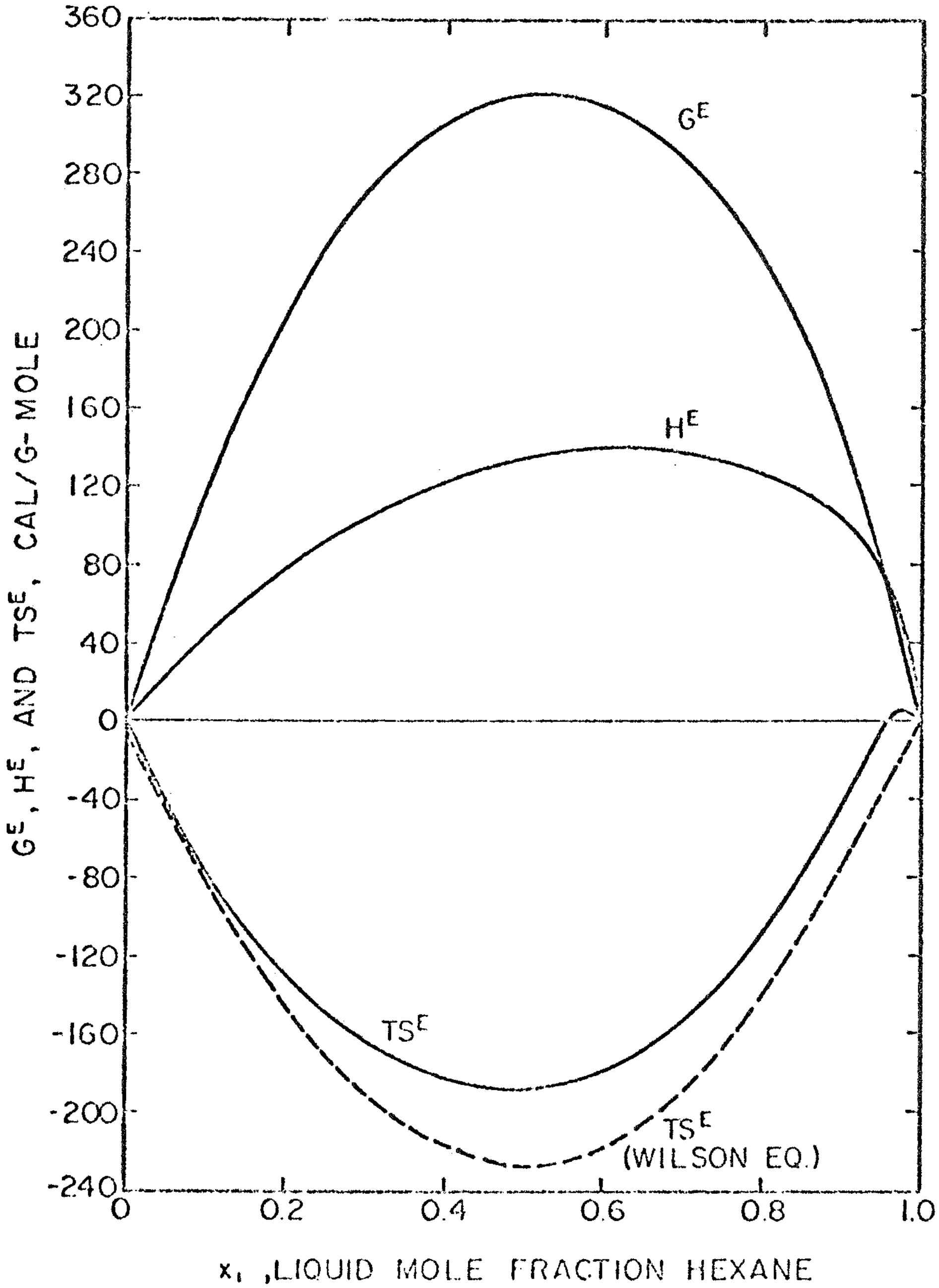


Figure 12. Excess Thermodynamic Properties at 25° C for the System n-Hexane-Ethanol

UNCERTAINTIES IN INTERMOLECULAR PAIR POTENTIAL PARAMETERS DETERMINED FROM MACROSCOPIC PROPERTY DATA
I. VIRIAL COEFFICIENTS

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ABSTRACT

The effect of experimental variables (temperature range, experimental uncertainty, and number of data points) on the uncertainties in intermolecular pair potential parameters derived from second virial coefficient data is described. A knowledge of these uncertainties is required when conclusions regarding combination rules for prediction of the unlike pair potential are made from comparison of "experimental" and predicted unlike pair parameters.

I. INTRODUCTION

At the present time, the <u>ab initio</u> calculation of the pair potential function has not been accomplished for cases involving atoms more complex than helium[1]. Although theoretical work has furnished valuable practical information regarding specific portions of the potential[2-5], empirical models are still required for the complete description of the potential curve.

Numerous empirical potential models (Lennard-Jones, Kihara, exp-6, Morse, etc.) have been proposed and thoroughly studied. Such models, containing two or more adjustable parameters, can be related to the low pressure equilibrium and transport properties of gases by well established theoretical relationships[6]. In practice, these theoretical relationships are employed to determine values of the potential parameters from experimental equilibrium or transport data. The empirical potentials so determined can serve several useful functions, including interpolation of data, prediction of a property from a potential based on data on a second property[7,8], and prediction of mixture properties based on pure component data[9], through the use of appropriate combination rules for the potential parameters.

Alternatively, sets of potential parameters have been employed to compare (or force agreement of) the parameters with values based on theoretical calculations[10,11], and to investigate the validity of various combination rules for prediction of unlike-molecule potential parameters from pure component values[12-16].

In comparisons of the type described above, conclusions must be tempered by a knowledge of the uncertainties in the potential parameters employed and the relation of these uncertainties to the uncertainty in the experimental data on which they are based. Only when such uncertainties are known can meaningful conclusions be reached from comparison of potential parameters.

II. EVALUATION OF PARAMETER UNCERTAINTIES

In past studies where potential parameters have been determined, any attention to the associated uncertainties is rare; at best, some off-hand comment is given (e.g., ϵ is thought to be known to $\pm 10\%$, σ to $\pm 1\%$). There are notable exceptions[8,17,18], particularly the work of DiPippo and Kestin[8]. In attempting to evaluate combination rules for prediction of mixture viscosities, they acknowledged that they "are hampered by the inherent uncertainties these (parameter) values which are conditioned by the uncertainties in the measurements" and that "this matter has received scant attention in the literature"[8]. They then provided a simple and approximate error analysis as follows. Two viscosity data at separate reduced temperatures, T_1^* and T_2^*, were considered, each datum being uncertain by an equal amount $\Delta\mu$. Using simple maximum error propagation analysis and the Lennard-Jones 6-12 model, they calculated $\Delta\epsilon/\epsilon$ as a function of T_2^* ($=kT_2/\epsilon$) for a fixed $T_1^* = 2.36$. Similar treatment was done for the distance parameter, σ. From their study, DiPippo and Kestin concluded

i) Data taken over a small temperature range lead to large uncertainties in potential parameters, even for rather precise data.

ii) The percentage error in the energy parameter ϵ, is an order of magnitude larger (10 to 100% in $\Delta\epsilon/\epsilon$) than in the distance parameter, σ, since "σ^2 appears explicitly (in the equation for μ) whereas ϵ is computed from the inverse of the function $\Omega^{(2,2)*}(T^*)$"[8].

They point out the above could account for the diversity of ϵ values that are present in the literature for a given molecular specie.

In view of the scant prior attention to this subject, a more detailed analysis of the parameter uncertainty problem in terms of statistical least squares regression and error propagation theories seems warranted. Using certain simplifications, a rather generalized relationship among the parameter uncertainties (i.e., estimated standard errors in regression coefficients[19]) and pertinent independent variables may be established.

In the present paper, we choose to demonstrate the effect of experimental variables on the parameter uncertainties for the situation where parameters are based on second virial coefficient data and the Lennard-Jones 6-12 model. (Similar techniques can be applied to other properties and/or other potential models[20]). The Lennard-Jones model for the intermolecular pair potential, U(r), as a function of molecular separation, r, is

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{1}$$

and U is related to the second virial coefficient, B(T), by the following equation

$$B(T) = 2\pi\tilde{N}\int_0^\infty \left[1-\exp(-U/kT)\right]r^2 dr \tag{2}$$

If B(T) data are used to establish the parameters ϵ and σ by least-squares fit of the calculated to experimental B(T) values, the parameter uncertainties, s_ϵ and s_σ, may be evaluated by usual statistical procedures[21].

(Here s^2 is the parameter variance.) Detailed description of the calculation scheme is given in the Appendix. The general features of the present analysis are

i) The 6-12 model is assumed to be the correct model for the data (i.e., lack-of-fit is neglected in the calculations).

ii) The virial coefficient data are assumed to be evenly spaced with respect to temperature and to have an uncertainty, s_B, which is independent of temperature.

iii) The number of observations, n, is assumed to be large so that in the statistical error propagation equations for s_ϵ and s_σ all sums over n of terms proportional to ΔB_i are negligible. This follows from the fact that ΔB is a random variable of mean zero by i) and ii).

Under these assumptions, the uncertainties in ϵ and σ may be expressed as functions of the uncertainty in the virial coefficients, s_B, the extreme values of reduced temperature of the data, T^*_{min} and T^*_{max}, and the number of data points, n, i.e.,

$$s_\epsilon = s_\epsilon(s_B, T^*_{min}, T^*_{max}, n) \tag{3}$$

with a similar relation for s_σ. The relations were evaluated from tabulated values of B^* vs T^{*6} as described in the Appendix and results are given in Figures 1 through 3.

III. DISCUSSION

The results presented in Figures 1 and 2 may be interpreted as showing the effect of the temperature range of the data on the ratio of the fractional parameter uncertainty (s_ϵ/ϵ or s_σ/σ) to the virial coefficient uncertainty (expressed as a fraction of the hard-sphere value, $b_o = \frac{2}{3}\pi\tilde{N}\sigma^3$), for a fixed number of data points. These results show that in general the parameter uncertainty is directly proportional to the data uncertainty, s_B, and to $n^{\frac{1}{2}}$, as might be anticipated; however, the effect of temperature range on the parameters is less obvious. Particular information which may be drawn from the figures includes

i) For small temperature ranges, the parameter uncertainty increases rapidly as the range decreases[22].

ii) For a given initial temperature, T^*_{min}, there is an optimum final temperature for minimizing the uncertainty in a given parameter. The optimum value of T^*_{max} is, in general, different for the two parameters ϵ and σ. Spacing a given number of data points over as wide a T^* range as possible does not minimize the parameter uncertainty (as it would in the case in linear regression).

iii) The energy parameter, ϵ, becomes very uncertain when based on high temperature data, due to decreased influence of potential bowl depth at high temperatures, i.e., the approach to hard sphere behavior at high temperatures.

iv) For a given parameter, the most sensitive temperature range occurs in the region where the sensitivity to the other parameter is low. Thus, for precise values of ϵ, the range of T^* from 3 to 4 seems optimum ($\partial B^*/\partial\sigma = 0$ at $T^* = 3.4$, the Boyle point[23]) and for σ the optimum range is about 20 to 35 ($\partial B/\partial\epsilon = 0$ at $T^* = 26.2$, the inversion point in B).

v) Figure 3 shows that the relative percentage uncertainties in the two parameters depend on the experimental temperature range. Furthermore, in the most common range of temperatures, $T^* < 10$, either of the two parameters might be the more precise by as much as an order of magnitude, depending on the temperature range covered.

vi) In studies of mixtures of dissimilar components, the less certain of the two pure component parameters, ϵ and σ, may in fact differ from component to component[24].

The basis for the above analysis may be questioned from several views, perhaps most obviously from the dependence of the results on the 6-12 potential. This model was used because it has the general qualitative features desired and, in spite of its well-known limitations[25], it remains to date the most widely-used model in calculations and discussions of transport[7,12,13,26,27] and equilibrium[9,16,28] properties. A second point of concern is the use of a value of s_B independent of T^*[29]. Certainly at low temperatures s_B should be expected to increase as experimental problems increase. However, alternative simple descriptions of s_B also invite criticism (e.g., a constant percentage uncertainty fails at the region of the Boyle point, where $B=0$).

In spite of the above limitations, the qualitative behavior of the parameter uncertainties is reasonably described. Exact numerical results would vary from potential to potential. Nonetheless, any model consistent with two parameter corresponding states, $U = \epsilon f(\sigma/r)$, would show the qualitative features displayed. A knowledge of these features should be of value both to experimentalists planning a study using virial coefficients to establish potential parameters, and persons comparing potential parameters for testing combination rules.

In general, the testing of combination rules by using comparisons of the experimental and calculated unlike-molecule parameters is less meaningful than direct comparisons of experimental data with property values calculated using parameters based on a given combination rule[30-32]. Any combination rules which can reproduce the data within experimental uncertainty must be viewed as acceptable. Often, a considerable range of parameter pairs may be adequate, due to the insensitivity of the predicted B values to the parameters in certain temperature regions.

The analysis given above should not be viewed as furnishing information regarding the <u>selection</u> of a potential function. The use of equilibrium and transport properties to differentiate between potential functions is well described elsewhere[18,33]. Rather, the present work is restricted to evaluation of uncertainties in parameter values based on a <u>specified</u> potential.

IV. CONCLUSIONS

Calculations have been made which illustrate the qualitative effects of experimental variables, including temperature, number of data points, and experimental uncertainty, on the intermolecular pair potential parameters determined from virial coefficient data. Results are based on the 6-12 potential, but the qualitative conclusions should apply to any potential consistent with the two-parameter corresponding states principle.

V. ACKNOWLEDGEMENTS

We wish to thank Dr. Leroy Folks for helpful discussions. Financial support of the National Science Foundation through its Grant No. GK-2807 is gratefully acknowledged.

APPENDIX

Let the functional relationship

$$F(B^c, T, \theta_1, \theta_2) = 0 \tag{4}$$

describe the second virial coefficient calculated from a specific potential model of the form $U(r) = \theta_1 f(T/\theta_2)$. In addition, consider a set of experimental data pairs

$$B_i, T_i \ (i = 1,n) \tag{5}$$

be known. These data may serve to establish the values of θ_1, θ_2 by employing the usual least-squares criterion

$$\sum_{i=1}^{n} (B_i^c - B_i)^2 = \sum_{i=1}^{n} (\Delta B_i)^2 = \text{minimum} \tag{6}$$

At the least-squares solution for θ_1, θ_2, the parameter variances and co-variances may be evaluated from the theory of error propagation to yield[21]

$$s^2_{\theta_i \theta_j} = s_B^2 \left\{ b_{ij} - \sum_{s=1}^{2} \sum_{t=1}^{2} b_{is} b_{jt} \sum_{k=1}^{n} \Delta B_k \left(\frac{\partial^2 \Delta B_k}{\partial \theta_s \partial \theta_t} \right)_{T_k, B_k} \right\} \tag{7}$$

where

$$[b_{ij}]_{2,2} = A^{-1} = [a_{ts}]^{-1}_{2,2} \tag{8}$$

A = coefficient matrix of normal equations

$$a_{ts} = \sum_{k=1}^{n} \left\{ \left(\frac{\partial \Delta B_k}{\partial \theta_s} \right)_{T_k, B_k, \theta_{t \neq s}} \left(\frac{\partial \Delta B_k}{\partial \theta_t} \right)_{T_k, B_k, \theta_{s \neq t}} + \Delta B_k \left(\frac{\partial^2 \Delta B_k}{\partial \theta_s \partial \theta_t} \right)_{T_k, B_k} \right\} \tag{9}$$

To facilitate the presentation in a general form of the dependence of the parameter uncertainties in terms of experimental variables, the following assumptions have been employed

i) The potential model, Eq. (1), is the correct model for the data considered i.e., there is no "lack of fit" associated with the regression.

ii) The experimental data contain random errors in the B values, the magnitude of which is independent of T and of variance s_B^2; the T values are without error.

iii) From the above assumptions, the ΔB_k values are random variables of mean zero when B_k^c is evaluated at the exact least-squares values of Θ_1, Θ_2. We employ the limit of large numbers of data points, n, so that all sums over n (in Eqns. (7) and (9)) of terms proportional to ΔB_k may be neglected due to the random nature of the ΔB_k values.

The above assumptions result in the following expressions for the parameter variances

$$(s_\sigma^2/s_B^2)(b_o/\sigma)^2 = S_1/9(S_1S_3 - S_2^2) \tag{10}$$

$$(s_\epsilon^2/s_B^2)(b_o/\epsilon)^2 = S_3/(S_1S_3 - S_2^2) \tag{11}$$

$$S_1 = \sum_{i=1}^{n} (B_1^*)_i^2 \tag{12}$$

$$S_2 = \sum_{i=1}^{n} (B^*B_1^*)_i \tag{13}$$

$$S_3 = \sum_{i=1}^{n} (B^*)_i^2 \tag{14}$$

where B^* and B_1^* (= $T^*\, dB^*/dT^*$) have been tabulated as functions of T^* for the 6-12 potential[6]. As n increases, the sums S_1, S_2 and S_3 over a fixed T^* range become proportional to n, so the left sides of Eqs. (10) and (11) become proportional to n^{-1}.

for the data con [illegible]

fit" associated with [illegible]

ii) The experimental data [illegible]

B values, the [illegible]

T and of variance s_B^2 [illegible]

iii) [illegible]

[illegible]

nature of the [illegible]

The above [illegible]

parameter variances [illegible]

$$(s_\sigma^2/s_B^2)\ [illegible]$$

$$(s_\epsilon^2/s_B^2)\ [illegible]$$

$$S_1 = \sum_{i=1}^{n} [illegible]$$

$$S_2 = \sum^{n} [illegible]$$

FIGURE CAPTIONS

1. The Effect of Experimental Variables on Uncertainty in the Pair Potential Energy Parameter, ϵ.
2. The Effect of Experimental Variables on Uncertainty in the Pair Potential Distance Parameter, σ.
3. Relative Fractional Uncertainties in the Pair Potential Parameters, ϵ and σ as a Function of the Temperature Range of the Virial Coefficient Data.

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22. This conclusion agrees with that of DiPippo and Kestin[8] regarding viscosity; similar results seem reasonable for other equilibrium and transport properties.

23. Michels[17] has previously commented on the uncertainty of σ near the Boyle point.

24. For example, in the He-Kr system in the range 350-500°K, one would find for He: $s_\sigma/\sigma \approx 0.03\ s_\epsilon/\epsilon$, and for Kr: $s_\sigma/\sigma \approx 1.38\ s_\epsilon/\epsilon$ (based on ϵ values from reference 6).

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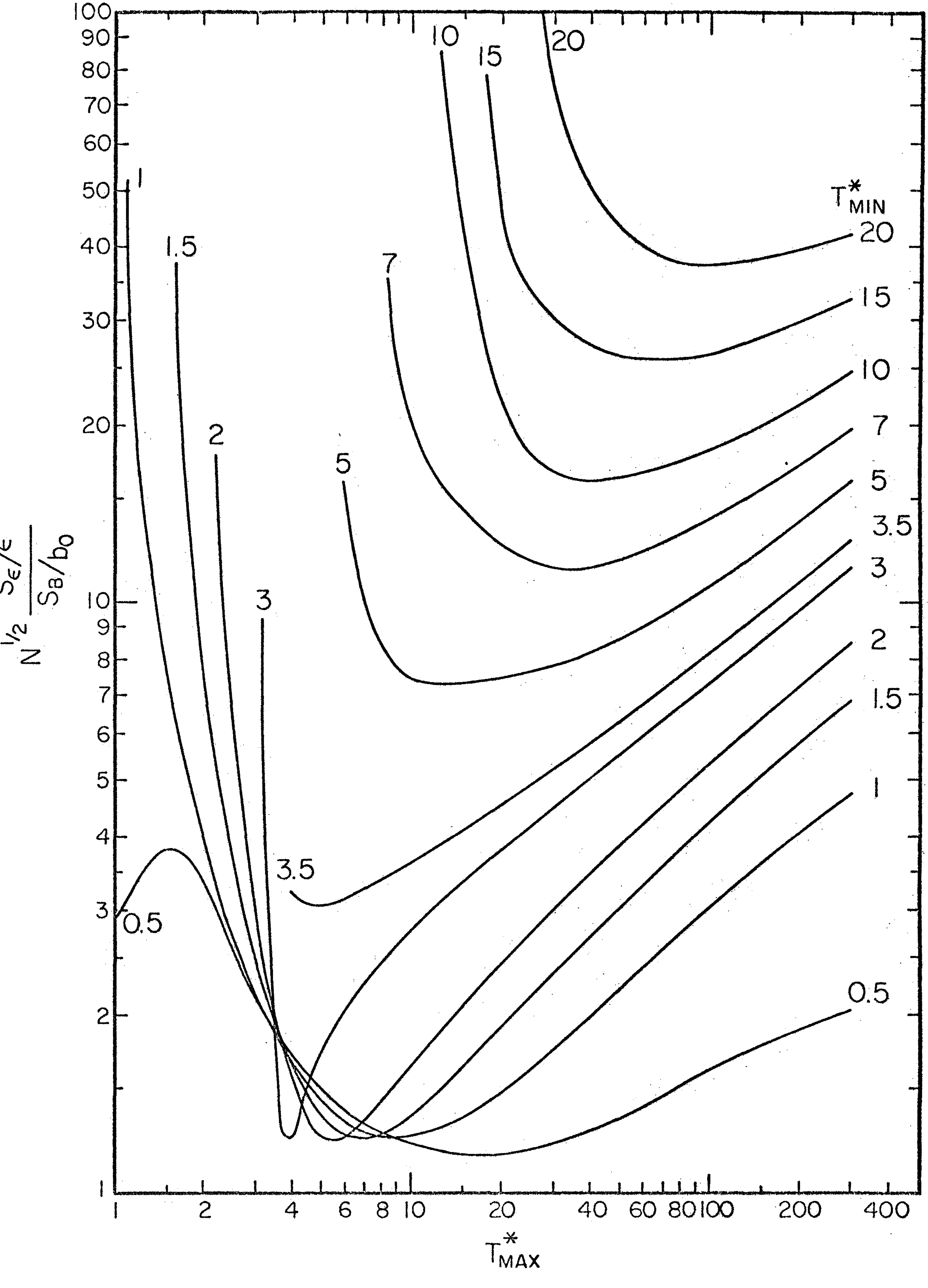
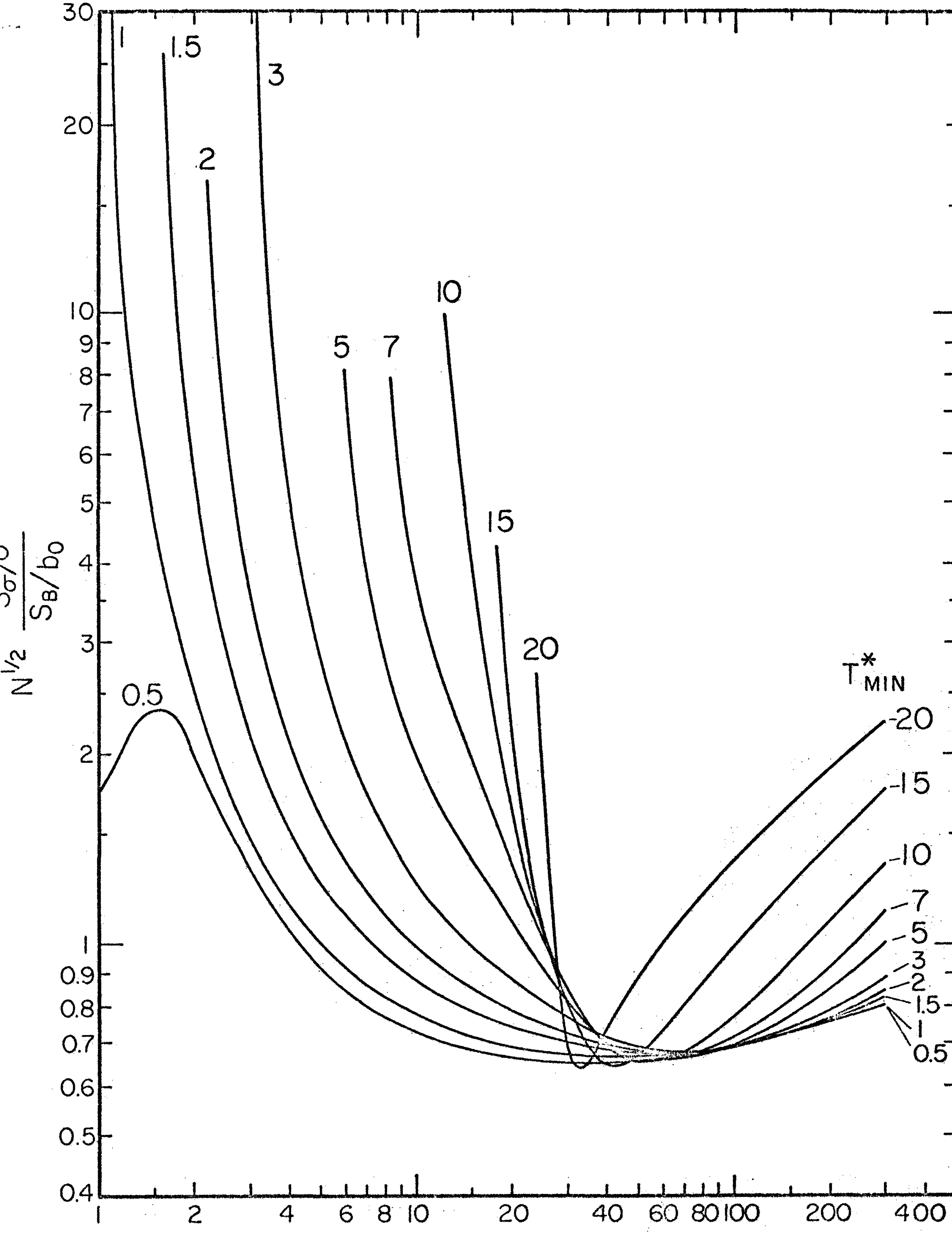


$N^{1/2} \dfrac{S_\epsilon/\epsilon}{S_B/b_0}$
T^*_{MAX}
T^*_{MIN}
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
1
2
4
6
8
10
20
40
60
80
100
200
400
0.5
1
1.5
2
3
3.5
5
7
10
15
20



$N^{1/2}\ \frac{S_\sigma/\sigma}{S_B/b_0}$
T^*_{MAX}
T^*_{MIN}
0.5
1
1.5
2
3
5
7
10
15
20