

Lawrence Berkeley National Laboratory

Recent Work

Title

THERMCOYNAMICS OF GAS SOLUBILITY. RELATION BETWEEN EQUATION-OF-STATE AND ACTIVITY-COEFFICIENT MODELS

Permalink

<https://escholarship.org/uc/item/6cf3m3mc>

Author

Bender, E.

Publication Date

1983-12-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

Materials & Molecular Research Division

FEB 21 1984

LIBRARY AND
DOCUMENTS SECTION

To be submitted for publication

THERMODYNAMICS OF GAS SOLUBILITY. RELATION BETWEEN
EQUATION-OF-STATE AND ACTIVITY-COEFFICIENT MODELS

E. Bender, U. Klein, W.P. Schmitt, and
J.M. Prausnitz

December 1983

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-17152
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THERMODYNAMICS OF GAS SOLUBILITY.

RELATION BETWEEN EQUATION-OF-STATE AND ACTIVITY-COEFFICIENT MODELS

Eberhard Bender[†], Udo Klein, Wolfgang Ph. Schmitt
Departments of Mechanical and Chemical Engineering
University of Kaiserslautern,
F.R. Germany

and

John M. Prausnitz
Molecular and Materials Research Division
Lawrence Berkeley Laboratory
and Department of Chemical Engineering
University of California
Berkeley, CA 94720

This work was supported by the Director, Office of Energy Research,
Office of Basic Energy Sciences, Chemical Sciences Division of the
US Department of Energy.

[†] Deceased, December 22, 1982

Revised July 1983

Abstract

The Krichevsky-Ilinskaya equation for gas solubility is derived from an equation of state. First, the ratio of fugacity to mole fraction for the solute is obtained by calculating the fugacity coefficient of the solute at infinite dilution. Then, the logarithm of this ratio is expanded in a double Taylor series with respect to pressure and composition. Only first-order terms are retained. Using a simple equation of state with conventional mixing rules, an experimental value for Henry's constant is used to obtain the equation-of-state's characteristic binary parameter. The remaining parameters in the Krichevsky-Ilinskaya equation (partial molar volume and Margules constant) are then obtained from the equation of state.

To illustrate, results are given for the solubility of hydrogen in ethylene diamine and for the solubilities of methane in n-hexane and in water.

Many high-pressure processes in the chemical industry are concerned with mixtures containing supercritical gases and nonpolar or polar liquids. For the design of such processes, accurate gas solubilities in the liquid phase are essential. Recent developments in coal-gasification and heavy-fossil-fuel processes have renewed interest in experimental data for gas solubilities, especially at higher temperatures and pressures.

As for all fluid-phase equilibria, either one of two common methods can be applied for correlating and calculating gas solubilities at moderate and high pressures. For mixtures of simple, nonpolar fluids, many equations of state correlate gas solubilities reasonably well. But these (mostly generalized) equations of state with common mixing rules predict poorly fluid-phase equilibria of systems with highly polar components or with components which differ significantly in size and shape.

The other method, using activity coefficients referred to standard-state fugacities in an ideal dilute solution, yields the well-known equation of Krichevsky-Ilinskaya where the liquid-phase fugacity of the solute is a simple function of $H_{2,1}$, Henry's constant (at the solvent's saturation pressure); \bar{v}_2^∞ , the partial molar volume of the solute at infinite dilution, and a suitably normalized activity coefficient given by a two-suffix Margules equation with parameter A (Prausnitz, 1969):

$$\ln \frac{f_2(T, P, x_2)}{x_2} = \ln H_{2,1}(T, P_i^s) + \frac{\bar{v}_2^\infty(T)}{RT} (P - P_i^s) + \frac{A(T)}{RT} [(1-x_2)^2 - 1] \quad (1)$$

For some binary systems, Henry's constants and their temperature dependence can be roughly correlated by scaled-particle theory, [See, for example, Schulze (1981) and Schaffer (1981)]. There are also some data and estimation techniques for the partial molar volumes of gases dissolved in liquids [see for example, Handa and Benson (1982)]. However, often the accuracies of these correlations are low.

The composition correction provided by Margules parameter A has been reported for only a few systems [see, for example, Orentlicher (1964)]; therefore, the Krichevsky-Ilinskaya equation is often not useful for predicting gas solubilities at high pressure.

Data reduction and correlation of isothermal, high-pressure solubility measurements using the Krichevsky-Ilinskaya equation is difficult because the effects of pressure and composition are not easily separated as discussed for example, by Orenlicher (1964) and by Mathias and O'Connell (1981). Without further information, there is no way to obtain correctly both partial molar volume and Margules parameter A from solubility data alone. On the other hand, Henry's constant can be evaluated accurately from reliable solubility measurements.

We show here that there is a direct relation between an equation-of-state model and an activity-coefficient model for calculating gas solubilities at high pressures. We propose a new data-reduction method for typical solubility data using both models.

Relation Between Equation-of-State and Activity-Coefficient Models

The best way to derive the Krichevsky-Ilinskaya equation is to write it as an isothermal Taylor series about mole fraction x_2 of the solute in the liquid phase and about $P = P_1^S$, the saturation pressure of the solvent. With $Y = \ln(f/x)_2$, we write

$$Y(T, P, x_2) = Y(T, P_1^S, 0) + \left(\frac{\partial Y}{\partial P} \right)_{T, P_1^S} \cdot (P - P_1^S) + \left(\frac{\partial Y}{\partial x_2} \right)_{T, 0} \cdot x_2 \quad (2)$$

The right-hand side of this equation has three parts. The first one is

$$Y(T, P_1^S, 0) = \ln H_{2,1}(T, P_1^S) \quad (3)$$

with Henry's constant $H_{2,1}$ of solute 2 in solvent 1. The second is

$$\left(\frac{\partial Y}{\partial P} \right)_{T, P_1^S} \cdot (P - P_1^S) = \frac{\bar{V}_2^\infty (P - P_1^S)}{RT} \quad (4)$$

where ∞ stands for infinite dilution, and the third one is

$$\left(\frac{\partial Y}{\partial x_2}\right)_{T,0} \cdot x_2 = \frac{A}{RT} \left[(1-x_2)^2 - 1 \right] \quad (5)$$

or

$$\left(\frac{\partial Y}{\partial x_2}\right)_{T,0} = - \frac{2A}{RT} \quad (6)$$

Now we can use an equation of state for the mixture and evaluate at infinite dilution the liquid-phase fugacity coefficient of the solute and its derivatives. The liquid-phase fugacity coefficient of the solute is

$$\phi_2^L = \frac{f_2^L}{x_2 P} \quad (7)$$

At $x_2 = 0$ and $P = P_1^s$, Henry's constant follows according to Eq. 3:

$$\ln H_{2,1}(T, P_1^s) = \ln \left[P_1^s \phi_2^{L\infty}(T, P_1^s) \right] \quad (8)$$

We can also calculate the partial molar volume at infinite dilution from an equation of state

$$\bar{v}_2^\infty = \left[\left(\frac{\partial V}{\partial n_2} \right)_{T, P, n_1} \right]_{n_2=0} = - \left[\frac{(\partial P / \partial n_2)_{V, T, n_1}}{(\partial P / \partial V)_{T, n_1, n_2}} \right]_{n_2=0} \quad (9)$$

which follows from

$$\left(\frac{\partial V}{\partial n_2} \right)_{T, P, n_1} \cdot \left(\frac{\partial n_2}{\partial P} \right)_{V, T, n_1} \cdot \left(\frac{\partial P}{\partial V} \right)_{T, n_1, n_2} = - 1 \quad (10)$$

Here n stands for the number of moles.

Margules parameter A can be calculated from an equation of state:

$$A = - \frac{RT}{2} \frac{\partial}{\partial x_2} \left(\ln \phi_2^L + \ln P \right)_{T, x_2=0} \quad (11)$$

These relations illustrate the powerful advantages of an equation of state, provided that this equation, its parameters and mixing rules, hold for the pure components and their mixtures.

These relations illustrate the powerful advantages of an equation of state, provided that this equation, its parameters and mixing rules, hold for the pure components and their mixtures. However, in our work here, we require only that the equation of state be valid for the solvent and for dilute solutions of a solute in that solvent. In addition to equation-of-state parameters, we also use the saturated molar volume v_1^S of pure solvent in Eqs. 8, 9 and 11.

Application of Two-Parameter Cubic Equations of State

To illustrate the calculations outlined above, we use a simple two-parameter cubic equation of state such as the Redlich-Kwong (1949) or Peng-Robinson (1976) equations.

Proper evaluation of optimum equation-of-state parameters is essential. Parameters b_2 and a_{22} for the nonpolar solute can be evaluated by the well-known generalized corresponding-states formula; they have only minor influence on the accuracy of the method. The only solute parameter in Eqs. 8 and 9 is b_2 but Eq. 11 also contains a_{22} . For accurate work, however, we must take care in evaluating the constants of the solvent. The best way is to fit parameters a_{11} and b_1 to the experimental vapor pressure and to the experimental saturated liquid volume for the pure solvent at system temperature. The conditions of phase equilibrium for the pure solvent are:

$$f_1^L(T, v_1^S, b_1, a_{11}) = f_1^V(T, v_1^V, b_1, a_{11}) \quad (12)$$

$$P_1^S = P(T, v_1^S, b_1, a_{11}) \quad (13)$$

$$P_1^S = P(T, v_1^V, b_1, a_{11}) \quad (14)$$

To solve these nonlinear equations for the three unknowns v_1^V , b_1 and a_{11} , we use a multidimensional regula-falsi method.

The binary constant a_{12} of the mixture is calculated from the experimental Henry's constant at system temperature, as shown in Appendices A and B, Eqs. A4 and B4. Now all parameters of the equation of state are known at system temperature and we can calculate \bar{v}_2^∞ and Margules parameter A in the Krichevsky-Ilinskaya equation. We can also test this correlation and the mixing rules of the equation of state if we have gas-solubility data for an appreciable range of x_2 corresponding to $P > P_1^S$.

Appendix A contains all required relations using the Redlich-Kwong equation of state and Appendix B those using the Peng-Robinson equation of state.

Evaluation of Henry's Constant from Gas-Solubility Measurements

Before we look at some results, we discuss the evaluation of Henry's constant from solubility measurements, that is, from data for x_2 and P at constant T . We are here concerned with higher temperatures where the vapor pressure of the solvent $P_1^S > 1$ bar.

Nonideality in the gas phase is expressed by an interaction second virial coefficient B_{12} , leading to fugacity f_2 on the left side of the Krichevsky-Ilinskaya equation.

The equilibrium conditions in the gas-liquid system are

$$f_1^L(T, P, x_2) = f_1^V(T, P, y_2) \quad (15)$$

$$f_2^L(T, P, x_2) = f_2^V(T, P, y_2) \quad (16)$$

where y_2 is the mole fraction of the solute in the gas phase. Eq. 15 for the solvent is

$$\phi_1(1 - y_2) P = (1 - x_2) P_1^S \phi_1^{SPC} \quad (17)$$

where PC is the Poynting correction. Using a virial equation with second virial coefficients only for fugacity coefficients ϕ_1 , and ϕ_1^S , and the Margules equation for γ_1 with parameter A, it follows from Eq. 17 (Prausnitz, 1969):

$$\exp \left[\frac{P}{RT} y_2^2 (B_{11} + B_{22} - 2B_{12}) - \frac{(P - P_1^S)}{RT} (v_1^S - B_{11}) \right] (1 - y_2) P = (1 - x_2) P_1^S \exp (A x_2^2 / RT) \quad (18)$$

This relation gives a first estimate for y_2 using $A = 0$ and known values B_{11} , B_{22} , B_{12} . With this estimate, fugacity f_2^L can be calculated from Eq. 16:

$$f_2^L = f_2^V = \exp \left[\frac{P}{RT} \left(B_{22} + (1 - y_2)^2 (2B_{12} - B_{11} - B_{22}) \right) \right] y_2 P \quad (19)$$

Values of $\ln(f/x)_2$ depend on $P - P_1^S$. By numerical or graphical interpolation and extrapolation to $P = P_1^S$, we obtain an approximate Henry's constant. After evaluating parameter a_{12} of the equation of state and calculating the terms of the Krichevsky-Ilinskaya equation as shown above, Eqs. 18 and 19, can be used again with $A \neq 0$. This iteration converges rapidly.

Results

We tested the proposed correlation method for three binary systems. Isothermal $x_2 - P$ data were measured by Schmitt in a newly established apparatus using the static synthetic method [Schmitt (1982)]; he measured the solubility of hydrogen in ethylene diamine in the temperature range 32 to 165°C with x_2 from 0.12 to 1.17 mole % and the solubility of methane in n-hexane from 32 to 200°C with x_2 from 1.0 to 10.8 mole %. The molar volumes of the solvents were also measured in these temperature ranges

for various pressures; by extrapolation to the vapor pressure, the saturated liquid volumes v_1^S were determined. Solubility data for methane in water were taken from Michels et al (1936) and from Culberson and McKetta (1951).

We fitted both the Redlich-Kwong equation and the Peng-Robinson equation to the measurements, as explained above. We found that the results are essentially the same for both equations of state. The results depend mainly on accurate v_1^S data. Tables 1 and 2 give necessary constants for the system ethylene diamine-hydrogen.

For the solubility of hydrogen in ethylene diamine, Figure 1 compares the measurements of Schmitt with results of phase-equilibrium calculations using the RK or PR equation. Agreement is very good; mean deviations between calculated and measured pressures are within $\pm 5\%$. The gas solubility rises with temperature, as expected for hydrogen/high-boiling solvent systems.

Figure 2 gives the temperature dependence of Henry's constant in a plot of $\ln H_{2,1}$ versus $1/T$; the plot is a straight line. Previous values of Moore and Otto (1972) and Brunner (1978) agree well with those of this work. Figure 3 gives the saturated liquid molar volume of pure ethylenediamine and the partial molar volume of hydrogen at infinite dilution, calculated by the RK or PR equation of state. The partial molar volumes differ by $2.5 \text{ cm}^3/\text{mol}$ or 2 to 8%. The values given by Brunner (who neglected composition correction in data-reduction), are much smaller.

Results from the correlation of Brelvi and O'Connell (1972) are compared with those from the equations of state. The characteristic volume $v_1^* = 193.5 \text{ cm}^3/\text{mol}$ for the highly polar ethylene diamine was fitted to the \bar{v}_2^∞ value given by the PR equation at 32°C . The temperature dependence of the Brelvi-O'Connell correlation agrees well with the results of this work.

Figure 4 shows the temperature dependence of Margules parameter A ; the larger differences between the RK and the PR equation are due to differences in \bar{v}_2^∞ . Finally, Figure 5 gives the Krichevsky-Ilinskaya plot. There are practically no differences between the results of the KI equation using parameters from either equation of state. These results agree also with $\ln(f/x)_2$ as calculated directly with the equations of state (by VLE-calculations). In this diagram the scatter of experimental data due to experimental errors is especially evident, indicating that it is very difficult to correlate these measurements with the Krichevsky-Ilinskaya equation without the help of an equation of state or volumetric data for the mixture.

The experimental results shown in Figure 5 were calculated using second virial coefficients and Eq. 19 for fugacity f_2 .

Nearly the same conclusions hold for the second system, n-hexane - methane. The measurements of Schmitt are compared in Figure 6 with results from the fitted RK and PR equations of state. Agreement is good. However, the pressures calculated by the generalized Redlich-Kwong-Soave equation of state with $k_{12} = 0.0422$ [Doring et al. (1982)] differ significantly from experiment.

For the system methane-water, similar results are obtained as shown in Figures 7, 8 and 9.

Conclusion

We have presented a new method for reduction and correlation of high-pressure gas-solubility data, using both the Krichevsky-Ilinskaya equation and a two-parameter cubic equation of state. The results are nearly independent of the particular form of the equation of state. Our proposed data-reduction procedure makes it possible to determine one binary parameter of an equation of state using isothermal, high-pressure gas-solubility measurements. This binary parameter, coupled with pure-component parameters, can be used to calculate Henry's constant as well as the partial molar volume of the solute at infinite dilution and Margules parameter A , all at system temperature.

Acknowledgment

J.M. Prausnitz is grateful to the National Science Foundation for financial support.

Figure Captions

Figure	Caption
1	Solubility of Hydrogen in Ethylenediamine
2	Henry's Constants for Hydrogen in Ethylenediamine
3	System Ethylenediamine/Hydrogen
4	System Ethylenediamine/Hydrogen
5	Krichevsky-Ilinskaya Diagram for Ethylenediamine/Hydrogen
6	Solubility of Methane in n-Hexane
7	Henry's Constants for Methane in Water
8	System Water/Methane
9	System Water/Methane

Literature Cited

- Brelvi, S.W. and J.P. O'Connell, AIChE J. 18, 1239 (1972).
- Brunner, E., Z. Phys, Chem. (Frankfurt/M.) 82, 798 (1978).
- Culberson, O.L. and J.J. McKetta, Petroleum Transactions AIME 195 223 (1951).
- Döring, R., H. Knapp, L.R. Oellrich, U.J. Plöcker and J.M. Prausnitz, Vapor-Liquid Equilibrium Data Collection, Mixtures of Low Boiling Substances, DECHEMA Chemistry Data Series Vol. VI, Frankfurt/M., 1982.
- Handa, Y.B. and G.C. Benson, Fluid Phase Equilibria 8, 161 (1982).
- Mathias, P.M. and J.P. O'Connell, Chem. Eng. Sci. 36, 1123 (1981).
- Moore, R.G. and F.D. Otto, Canad. J. Chem. Eng. 50, 355 (1972).
- Michels, A., Gerver, J. and A. Bijl, Physica III, No. 8 797 (1936).
- Orentlicher, M. and J.M. Prausnitz, Chem. Eng. Sci. 19, 775 (1964).
- Peng, D.Y. and D.B. Robinson, Ind. Eng. Chem. Fund. 15, 59 (1976).
- Prausnitz, J.M., Molecular Thermodynamics of Fluid-Phase Equilibria. Prentice-Hall, Englewood Cliffs, New Jersey, 1969.
- Redlich, O. and J.N.S. Kwong, Chem. Rev. 44, 233 (1949).
- Schaffer, S.K. and J.M. Prausnitz, AIChE J. 27, 844 (1981).
- Schmitt, W. P., Dissertation, Institute for Technical Thermodynamics, Universität Kaiserslautern (1982).
- Schulze, G. and J.M. Prausnitz, Ind. Eng. Chem. Fund. 20, 175 (1981).

Table 1

SATURATED VOLUMES OF ETHYLENE DIAMINE

TEMPERATURE, °C	v_1^s , cm ³ /mole
32.0	67.79
51.3	69.24
75.9	71.21
100.2	73.31
125.4	75.72
150.2	78.32
165.0	79.95

Table 2

EQUATION-OF-STATE CONSTANTS FOR ETHYLENE

DIAMINE (1)-HYDROGEN (2)

TEMPERATURE °C	b_1		$a_{11} \cdot 10^{-7}$		$a_{12} \cdot 10^{-7}$	
	RK	PR	RK	PR	RK	PR
32.0	59.13	59.67	44.0	2.85	2.09	0.109
51.3	59.41	59.98	44.0	2.77	1.98	0.0992
75.9	59.73	60.32	44.0	2.67	1.91	0.0926
100.2	59.96	60.56	43.9	2.58	1.85	0.0864
125.4	60.16	60.75	43.7	2.49	1.75	0.0786
150.2	60.25	60.79	43.4	2.40	1.76	0.0770
165.0	60.23	60.71	43.2	2.35	1.77	0.0765

b_1 is in $\text{cm}^3 \text{mole}^{-1}$

a_{11} and a_{12} (RK) are in $\text{bar cm}^6 \text{K}^{0.5} \text{mole}^{-2}$

a_{11} and a_{12} (PR) are in $\text{bar cm}^6 \text{mole}^{-2}$

Appendix A: Redlich-Kwong equation of state

Equation of state:

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RT^{3/2}(v+b)} \quad (A1)$$

with

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (A2)$$

$$b = \sum_i x_i b_i \quad (A3)$$

Binary interaction parameter a_{12} from Henry's constant $H_{2,1}$:

$$\begin{aligned} \frac{a_{12}}{RT^{3/2}} = & - \frac{b_1}{2} \left[\ln \frac{H_{2,1}(v_1^S - b_1)}{RT} - \frac{b_2}{v_1^S - b_1} \right. \\ & \left. - \frac{a_{11} b_2}{RT^{3/2} b_1^2} \left\{ \ln \frac{v_1^S + b_1}{v_1^S} - \frac{b_1}{v_1^S + b_1} \right\} \right] \left[\ln \frac{v_1^S + b_1}{v_1^S} \right]^{-1} \quad (A4) \end{aligned}$$

Partial molar volume of the solute at infinite dilution:

$$\begin{aligned} \bar{v}_2^\infty = & \frac{\frac{1}{v_1^S - b_1} + \frac{b_2}{(v_1^S - b_1)^2} - \frac{2a_{12}}{RT^{3/2} v_1^S (v_1^S + b_1)} + \frac{a_{11} b_2}{RT^{3/2} v_1^S (v_1^S + b_1)^2}}{\frac{1}{(v_1^S - b_1)^2} - \frac{a_{11} (2v_1^S + b_1)}{RT^{3/2} [v_1^S (v_1^S + b_1)]^2}} \quad (A5) \end{aligned}$$

Margules parameter k :

$$\begin{aligned} A = & - \frac{RT}{2} \left\{ \frac{v_1^S (b_2 - b_1) - v^1 b_2}{v_1^S (v_1^S - b_1)} - \frac{v^1 b_2 - b_2 (b_2 - b_1)}{(v_1^S - b_1)^2} \right. \\ & - \frac{2b_1 (a_{22} - a_{12}) - 2a_{12} (b_2 - b_1)}{RT^{3/2} b_1^2} \ln \frac{v_1^S + b_2}{v_1^S} \\ & - \frac{2a_{12} [v_1^S (b_2 - b_1) - v^1 b_1]}{RT^{3/2} b_1 v_1^S (v_1^S + b_1)} - \frac{v^1}{v_1^S} \\ & + \frac{2b_1 b_2 (a_{12} - a_{11}) - 2a_{11} b_2 (b_2 - b_1)}{RT^{3/2} b_1^3} \left[\ln \frac{v_1^S + b_1}{v_1^S} - \frac{b_1}{v_1^S + b_1} \right] \\ & \left. + \frac{a_{11} b_2}{RT^{3/2} b_1^2} \left[\frac{v_1^S (b_2 - b_1) - v^1 b_1}{v_1^S (v_1^S + b_1)} - \frac{v_1^S (b_2 - b_1) - v^1 b_1}{(v_1^S + b_1)^2} \right] \right\} \quad (A6) \end{aligned}$$

with

$$v^1 = \left(\frac{\partial v}{\partial x_2} \right)_{x_2=0} = \bar{v}_2^\infty - v_1^S \quad (A6a)$$

Appendix B: Peng-Robinson equation of state

Equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (B1)$$

with

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (B2)$$

$$b = \sum_i x_i b_i \quad (B3)$$

Binary interaction parameter a_{12} from Henry's constant $H_{2,1}$:

$$\frac{a_{12}}{RT} = -\sqrt{2} b_1 \left[\ln \frac{H_{2,1}(v_1^s - b_1)}{RT} - \frac{b_1}{v_1^s - b_1} + \frac{a_{11} b_2 v_1^s}{RT b_1 [v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)]} \right. \\ \left. - \frac{a_{11} b_2}{2\sqrt{2} RT b_1} \ln \frac{v_1^s + 2.414 b_1}{v_1^s - 0.414 b_1} \right] \left[\ln \frac{v_1^s + 2.414 b_1}{v_1^s - 0.414 b_1} \right]^{-1} \quad (B4)$$

Partial molar volume of the solute at infinite dilution:

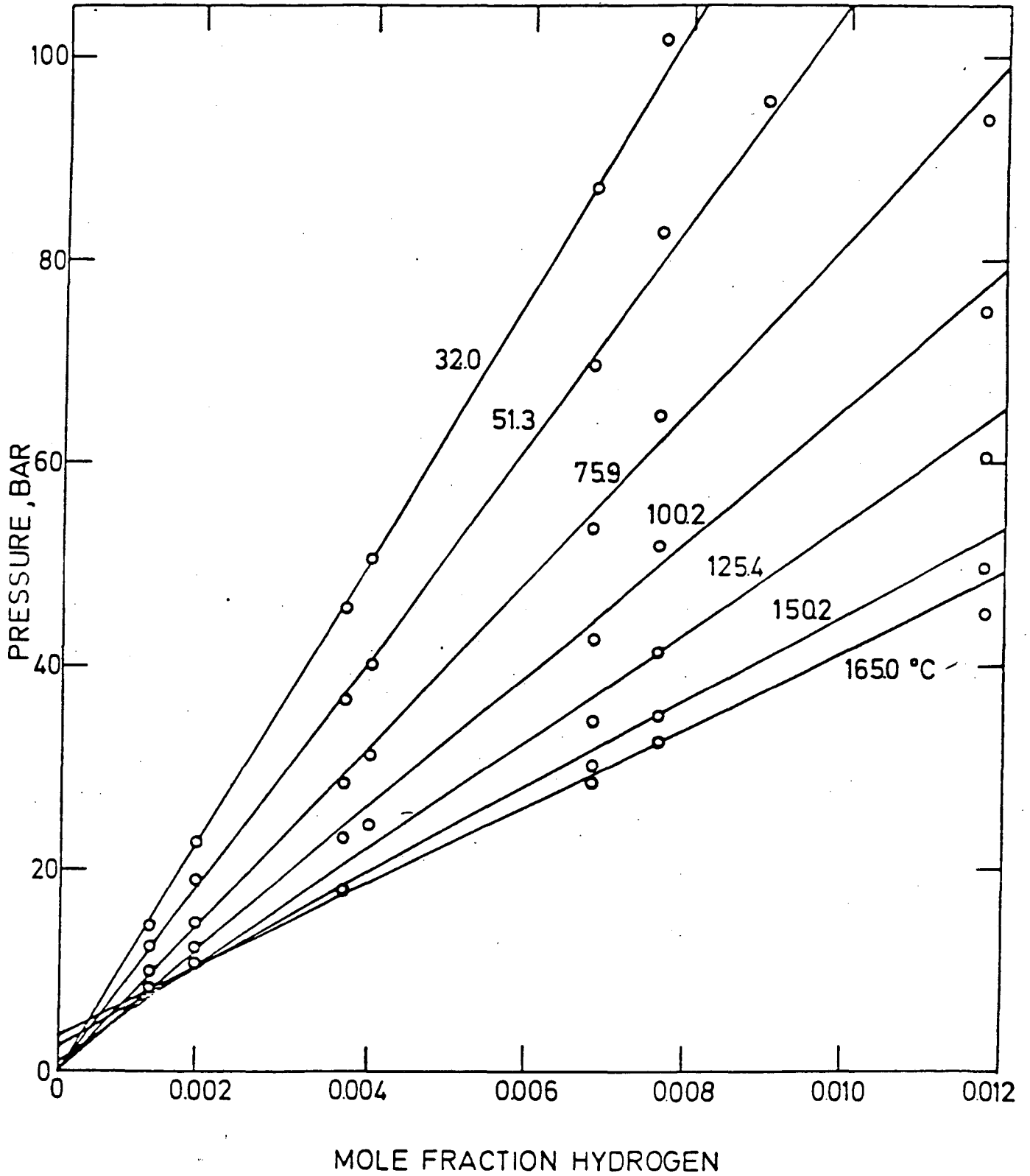
$$\bar{v}_2^\infty = \frac{RT[b_2 + v_2^s - b_1]}{(v_2^s - b_1)^2} - \frac{2a_{12}}{v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)} - \frac{2a_{11} b_2 (v_2^s - b_1)}{[v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)]^2} \\ \frac{RT}{(v_2^s - b_1)^2} - \frac{2a_{11}(v_2^s + b_1)}{[v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)]^2} \quad (B5)$$

Margules parameter A:

$$A = -\frac{RT}{z} \left\{ \frac{b_2(b_2 - b_1) - v^1 b_2}{(v_1^s - b_1)^2} - \frac{a_{11} b_2 v^1 + 2b_2 v_2^s (a_{12} - a_{11})}{RT b_1 [v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)]} - \frac{v^1 - (b_2 - b_1)}{v_1^s - b_1} \right. \\ \left. + \frac{a_{11} b_2 v_2^s [(b_2 - b_1) \{v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)\} + 2b_1 \{v^1(v_1^s + b_1) + (v_1^s - b_1)(b_2 - b_1)\}]}{RT \{b_1 [v_1^s(v_1^s + b_1) + b_1(v_1^s - b_1)]\}^2} \right. \\ \left. - \frac{2b_1(a_{12} - a_{11}) - a_{11}(b_2 - b_1)}{2\sqrt{2} RT b_1^2} \left(\frac{2a_{12}}{a_{11}} - \frac{b_2}{b_1} \right) \ln \frac{v_1^s + 2.414 b_1}{v_1^s - 0.414 b_1} \right. \\ \left. - \frac{a_{11}}{\sqrt{2} RT b_1} \left(\frac{a_{11}(a_{22} - a_{12}) - 2a_{12}(a_{12} - a_{11})}{a_{11}^2} + \frac{b_2(b_2 - b_1)}{2b_1^2} \right) \ln \frac{v_1^s + 2.414 b_1}{v_1^s - 0.414 b_1} \right. \\ \left. - \frac{a_{11}}{RT b_1} \left(\frac{2a_{12}}{a_{11}} - \frac{b_2}{b_1} \right) \frac{v_1^s(b_2 - b_1) - b_1 v^1}{(v_1^s + 2.414 b_1)(v_1^s - 0.414 b_1)} \right\} \quad (B6)$$

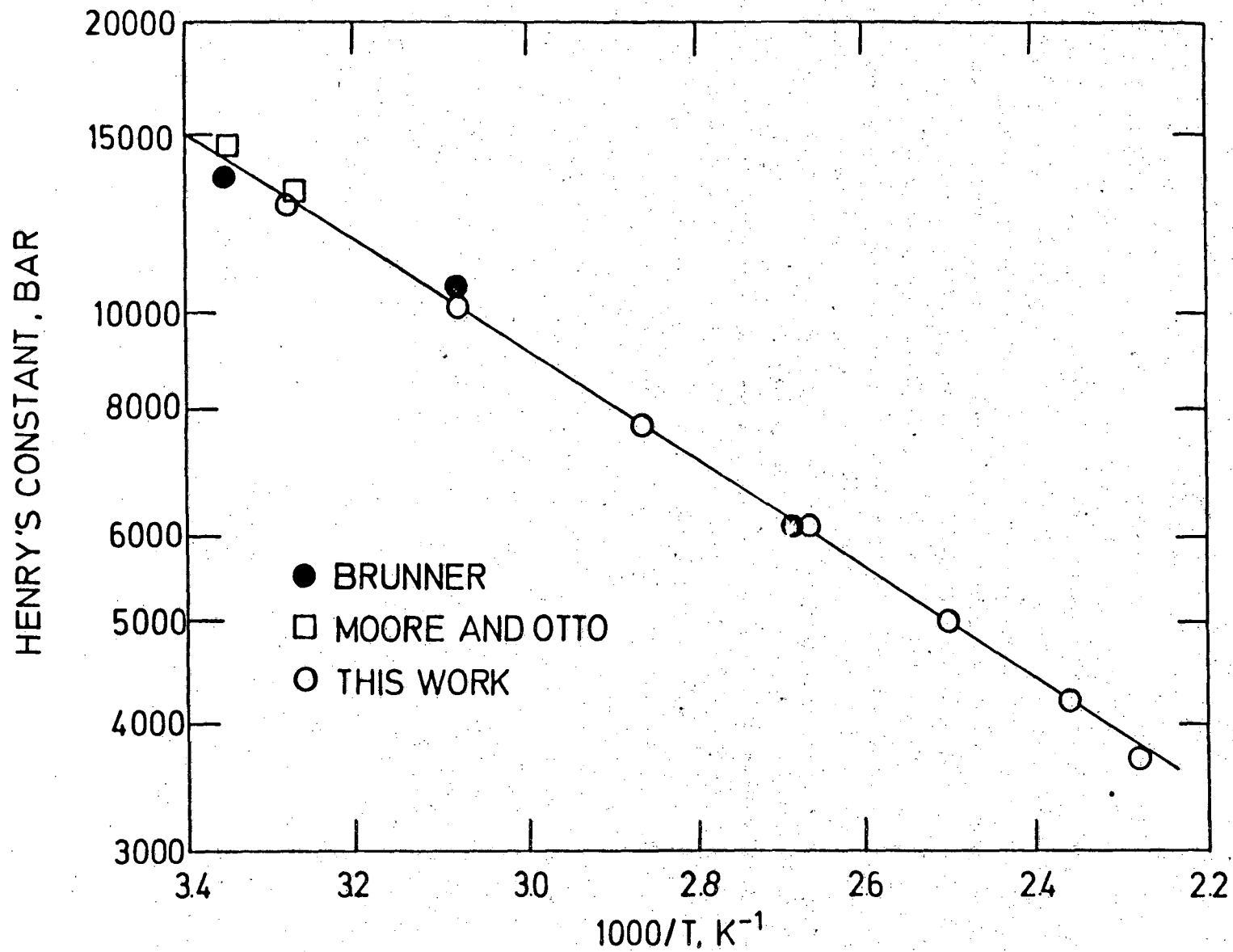
with

$$v^1 = \left(\frac{\partial v}{\partial x_2} \right)_{x_1=0} = \bar{v}_2^\infty - v_1^s \quad (B6a)$$



SOLUBILITY OF HYDROGEN IN ETHYLENEDIAMINE

Figure 1



HENRY'S CONSTANTS FOR HYDROGEN IN ETHYLENEDIAMINE

Figure 2

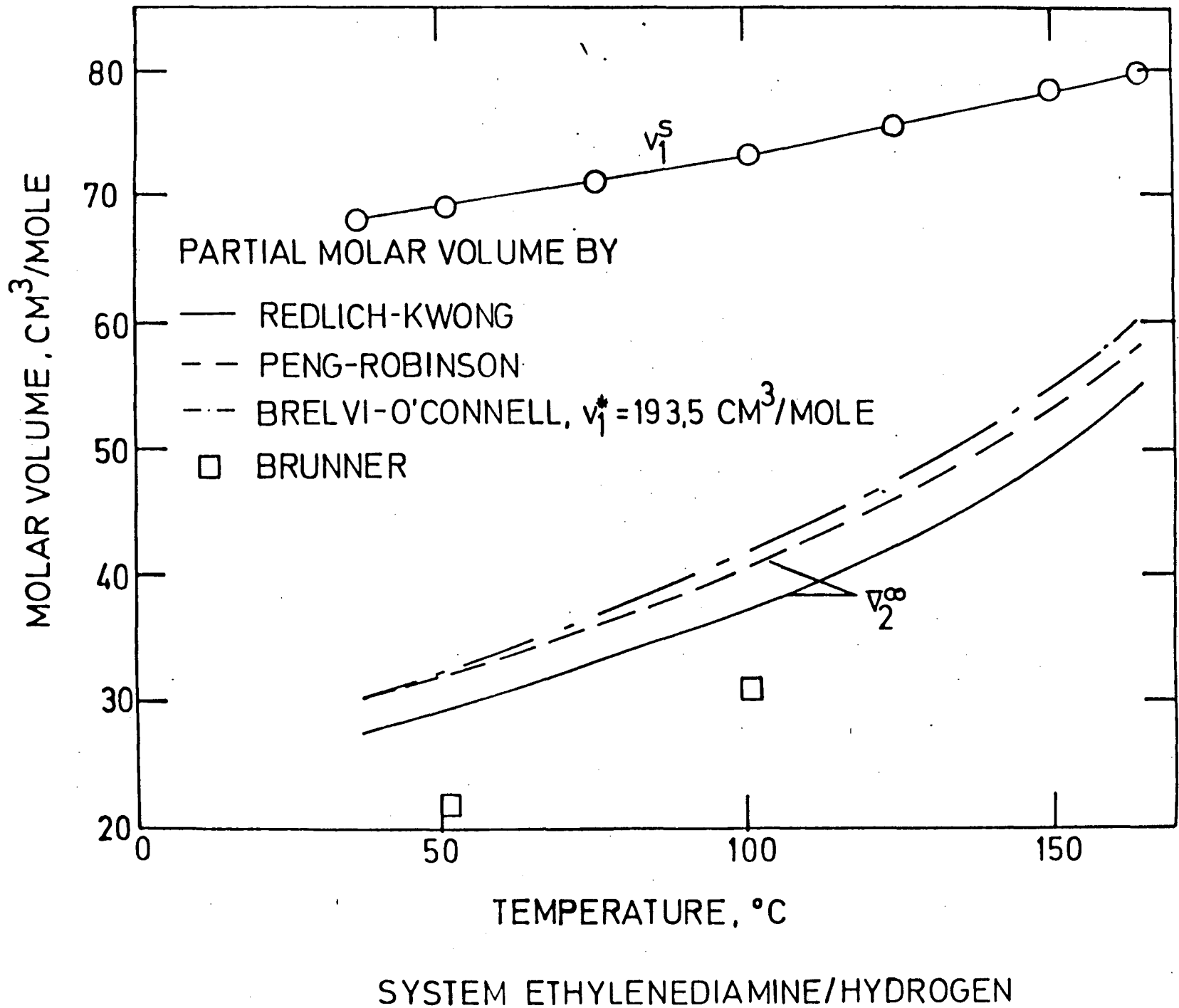
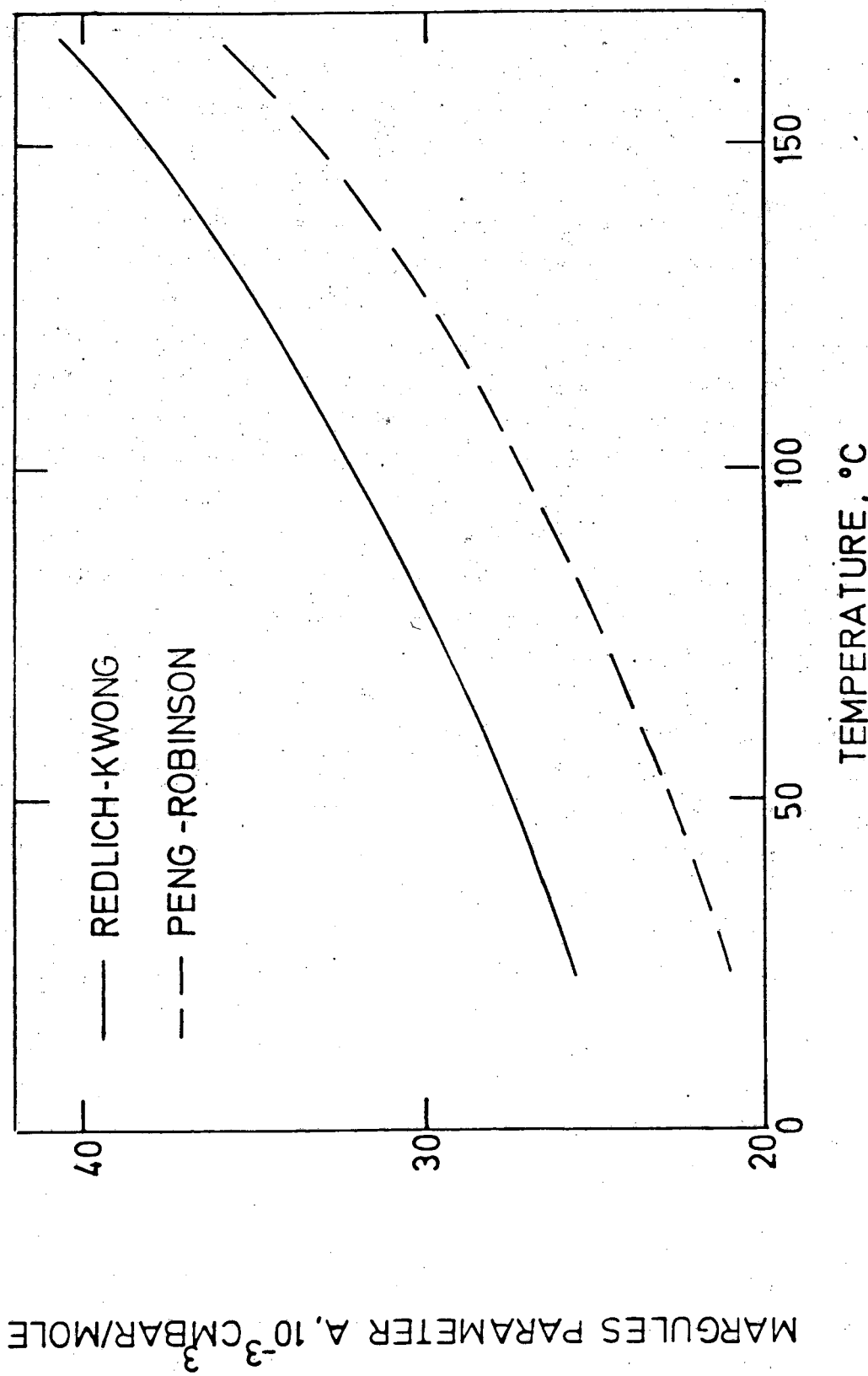
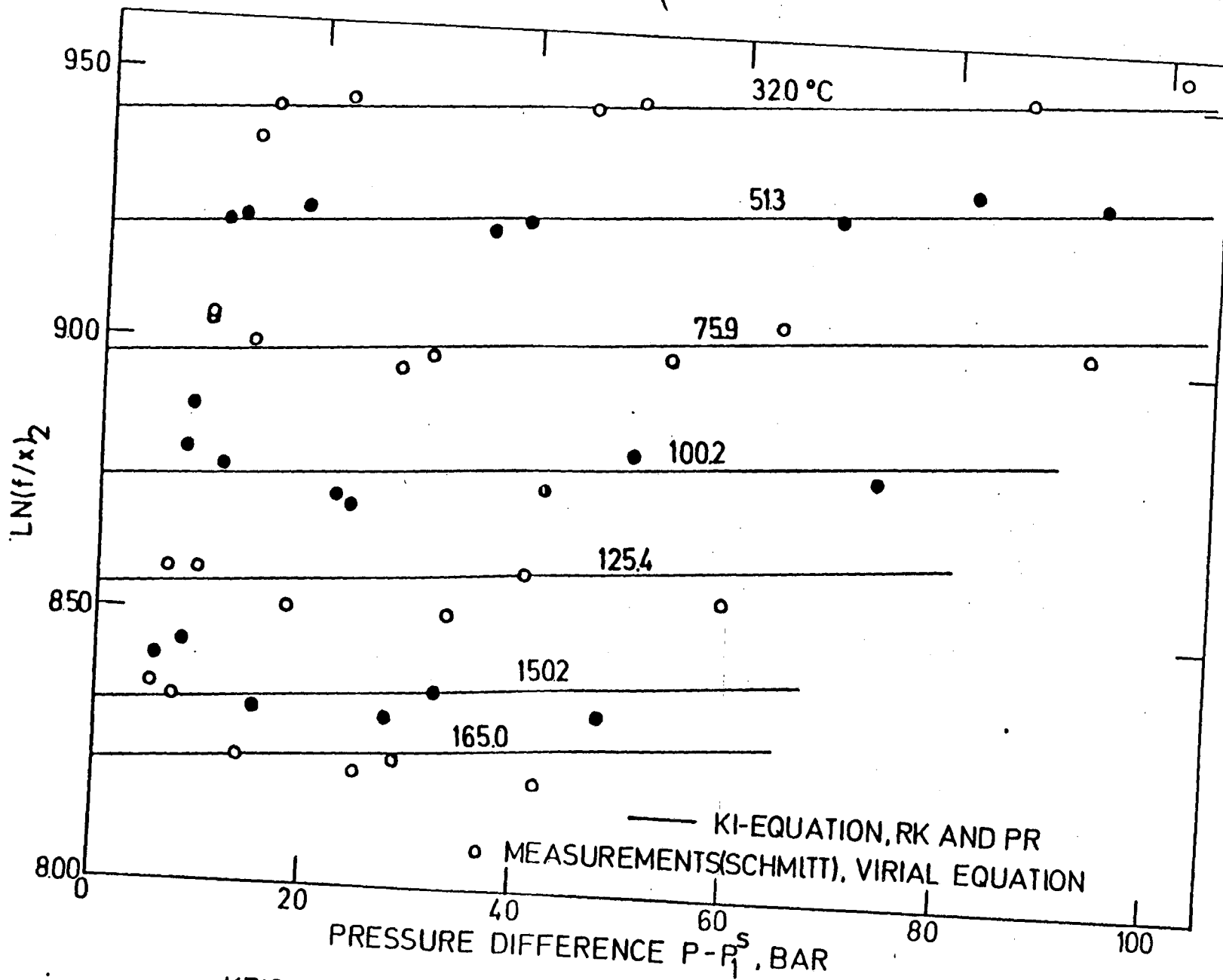


Figure 3

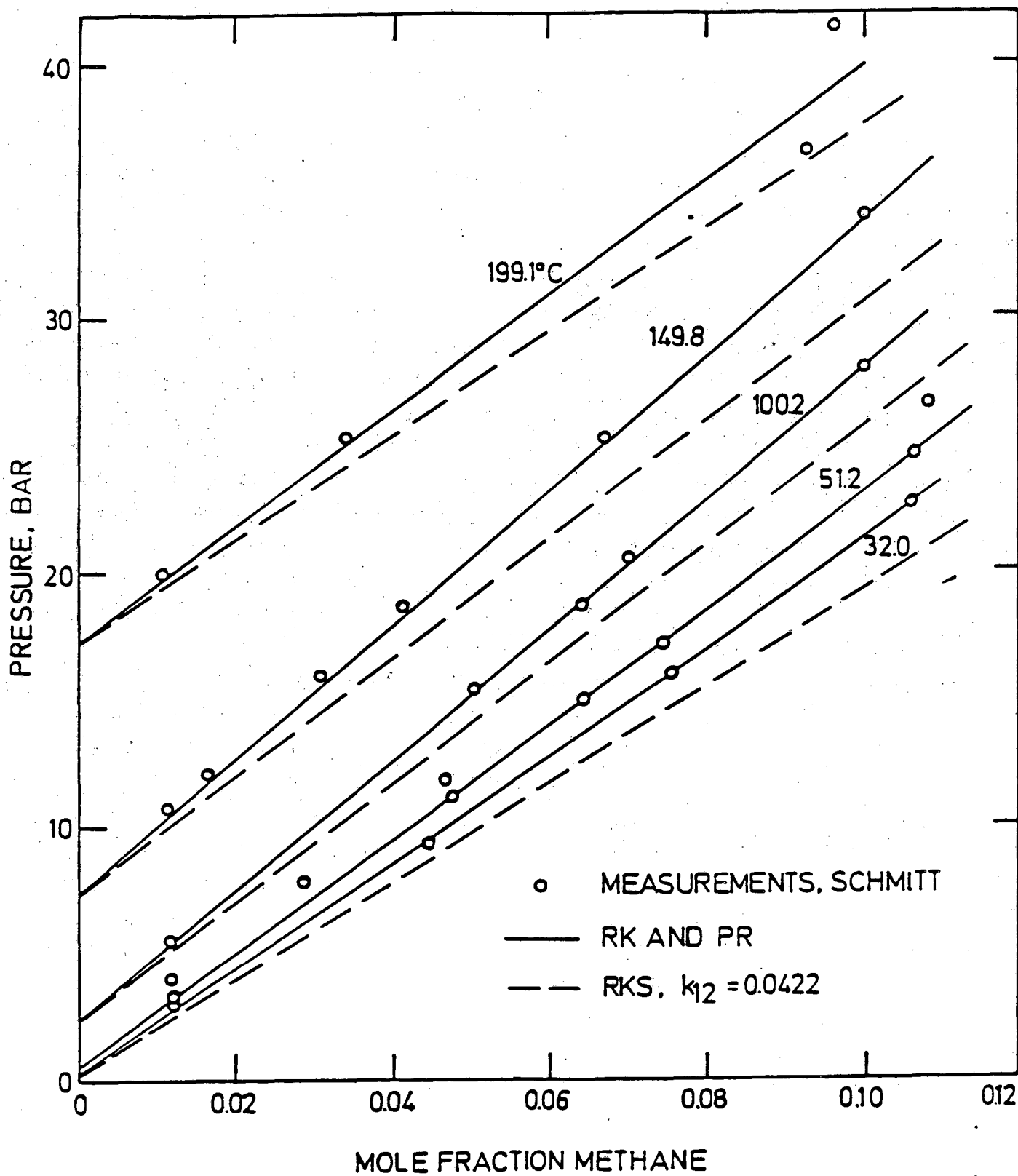


SYSTEM ETHYLENEDIAMINE/HYDROGEN

Figure 4



KRICHEVSKY-ILINSKAYA DIAGRAM FOR ETHYLENEDIAMINE/HYDROGEN
 Figure 5



SOLUBILITY OF METHANE IN *n*-HEXANE
Figure 6

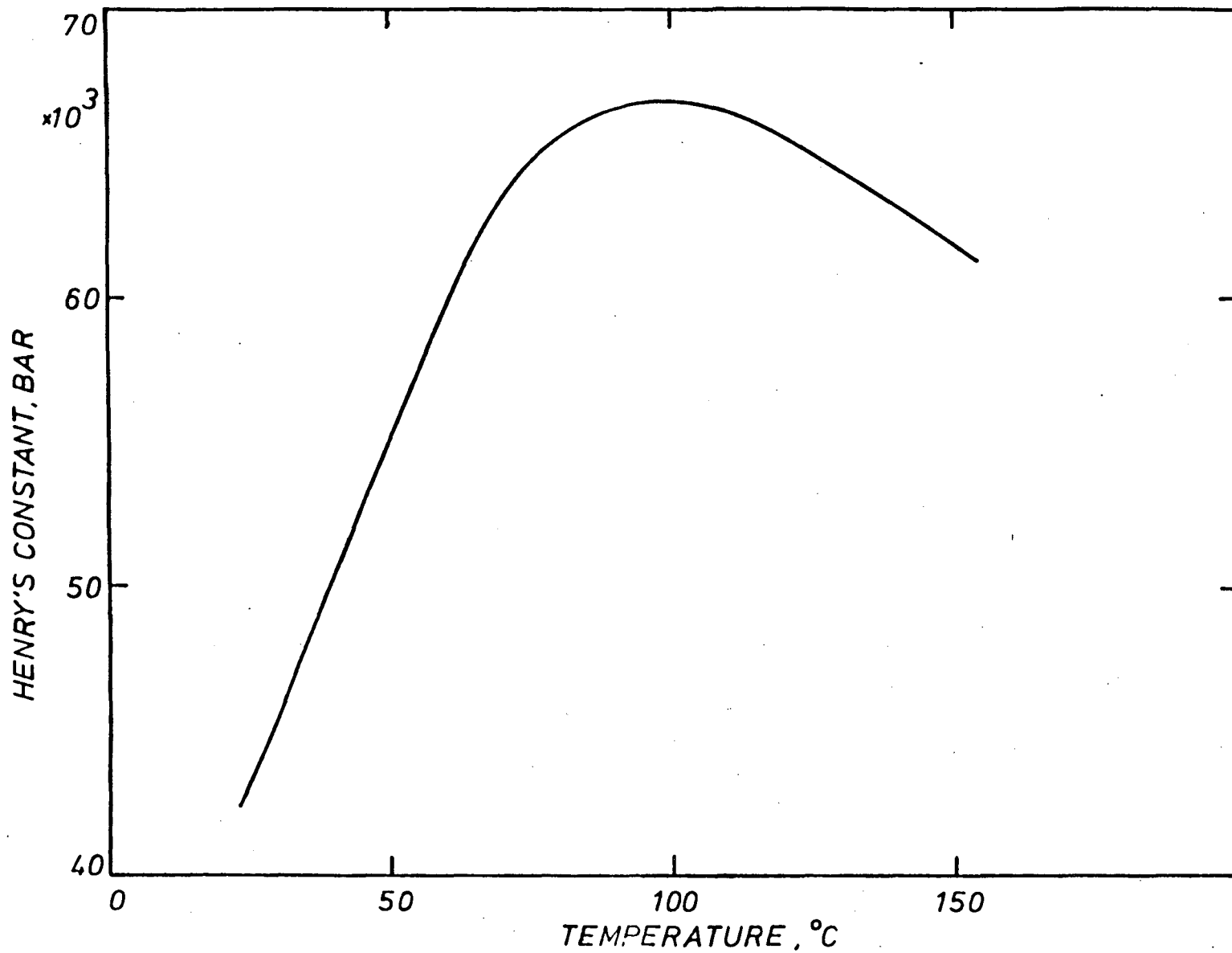


Figure 7

HENRY'S CONSTANTS FOR METHANE IN WATER

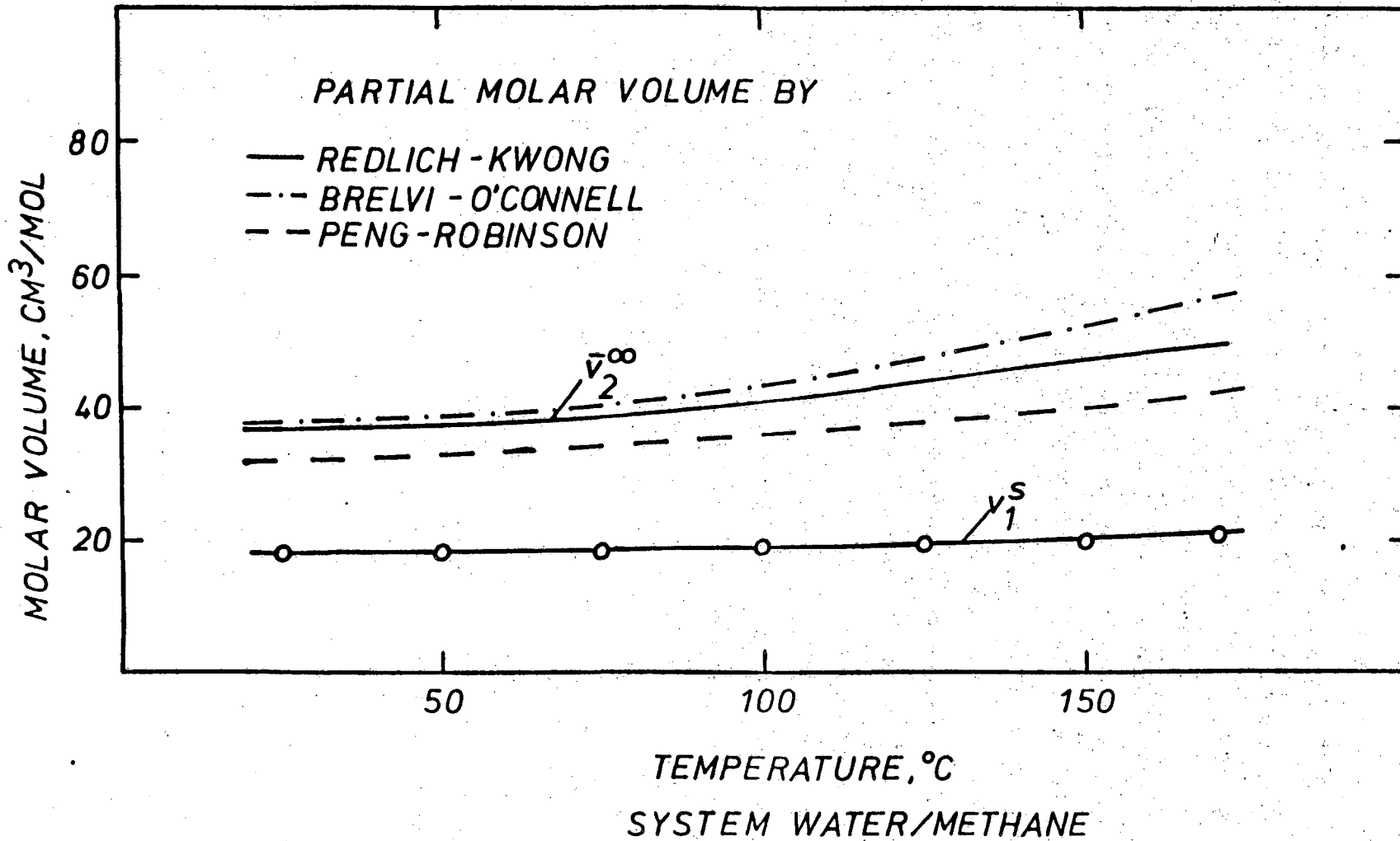


Figure 8

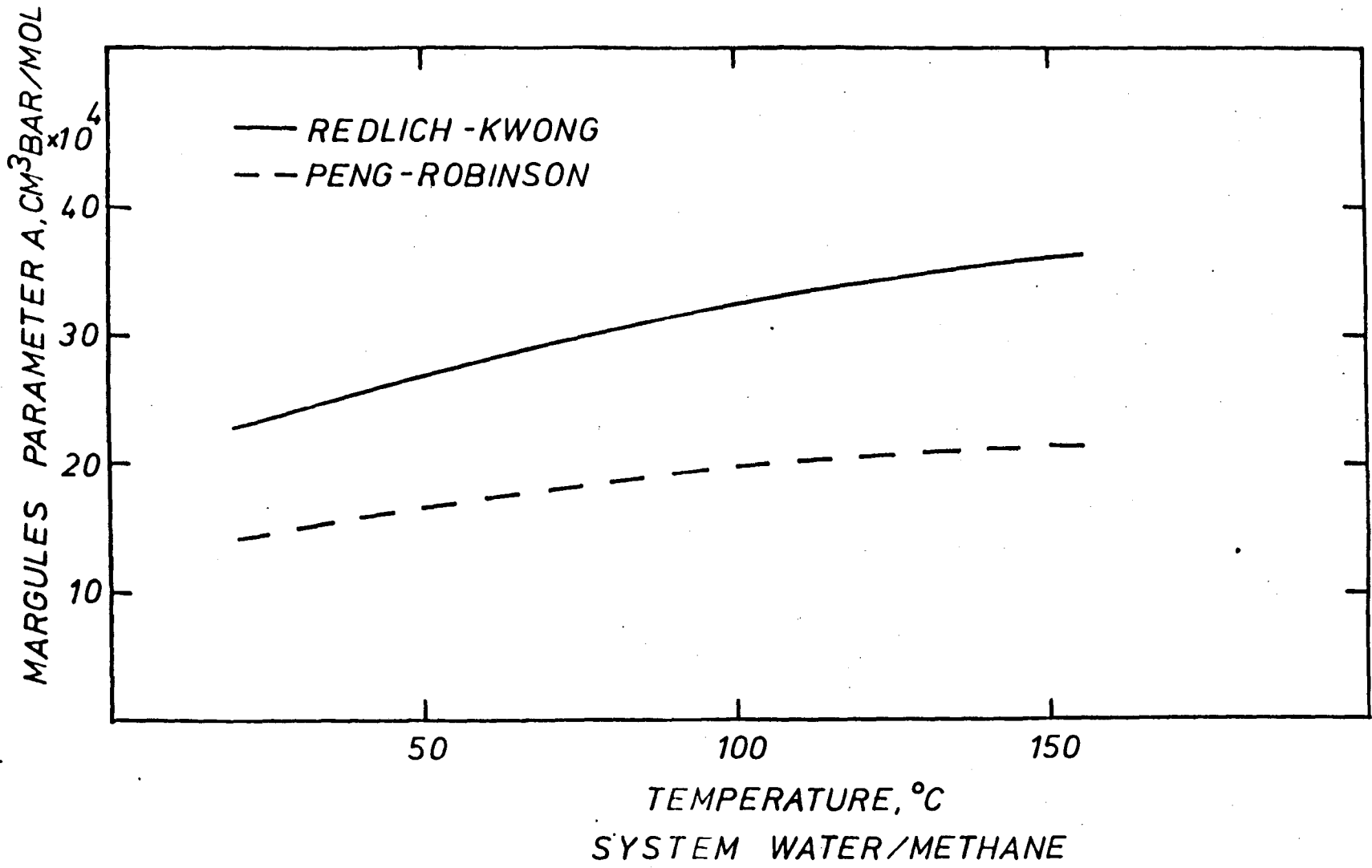


Figure 9

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720