Ω_4 = dimensionless Sisko model non-Newtonian viscosity coefficient, $= (r_o^3 g/24)^{1/2} (\rho/\beta) (2r_o/3g)^{\frac{m-1}{2}}$

λ_1 = stress relaxation time constant in 3 constant Oldroyd model, sec.

λ_2 = rate of shear retardation time constant in 3 constant Oldroyd model, sec.

τ_{rz} = shear stress, force in a direction in plane perpendicular to radial direction, dynes/sq. cm.

τ^*_{rz} = dimensionless shear stress, defined in Equation (9)

$< >$ = average over area of tube

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Joule-Thomson Effects for Nitrogen-Ethane Mixtures

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In the chemical processing industry it is vital to know enthalpies of gas mixtures for economic designs of thermal equipment. In most cases the lack of reliable data forces one to predict the required values. In the absence of contrary information it is reasonable to expect a mixture to behave similarly to the components of which it is composed. Therefore one normally derives estimates of mixture values by some rule which combines the known enthalpies of the individual components. Methods by which this has been done are well known and have recently been compared by Brewer and Geist (2). It is apparent that only a method which will adequately describe the interactions of different molecular species can be seriously considered as an acceptable combination rule. Thus the problem at hand is essentially twofold: a need for increased knowledge concerning the interaction of unlike molecules, and a need for dependable data with which existing and subsequent theories for predicting mixture results can be checked. The purpose of this research therefore was to provide a useful stepping stone for this large problem.

The authors decided to investigate Joule-Thomson effects for mixtures of nitrogen and ethane in the region straddling the critical states of the components. It was presumed that data taken in this region would allow a severe test of mixture theories to be made. The nitrogen-ethane system provided desirable ranges of temperature (25° to −100°C.) and pressure (up to 2,500 lb./sq.in.) in which to operate. Joule-Thomson effects were chosen to be measured inasmuch as it was required only to measure two intensive properties, temperature and pressure, and these could be measured with a good deal of accuracy. The measurements were sufficient to define the temperature-pressure loci of constant enthalpy from which enthalpy data can be derived. It was necessary to develop a suitable apparatus on which to make these measurements; its description and a discussion of its operation follows. Finally the data obtained are presented, and the results of zero-pressure Joule-Thomson coefficient estimates are discussed.

APPARATUS

A flow diagram of the experimental equipment is shown in Figure 1. System gas is drawn from a 2 cu.ft. storage tank through a filter to the diaphragm compressor. This unit is a two-stage, V type of compressor with 3.5 std. cu. ft./min. capacity and maximum discharge pressure of 3,600 lb./sq. in. gauge. This compressor was specifically purchased to eliminate oil contamination previously encountered with a piston compressor. The high-pressure gas passed through a silica gel dryer and then was cooled by returning low-pressure gas in a countercurrent heat exchanger. The precooled gas flowed through a coil of ⅛-in. finned copper tubing immersed in the cryostat bath and was cooled to within 1°C. of the bath temperature.

The cryostat bath fluid was a nonflammable, eutectic mixture of halogenated hydrocarbons (8). It was contained in a stainless steel Dewar of approximately 2 gal. capacity. Cooling of the bath was accomplished by evaporating liquid nitrogen in a submerged heat exchanger. Agitation was provided by a

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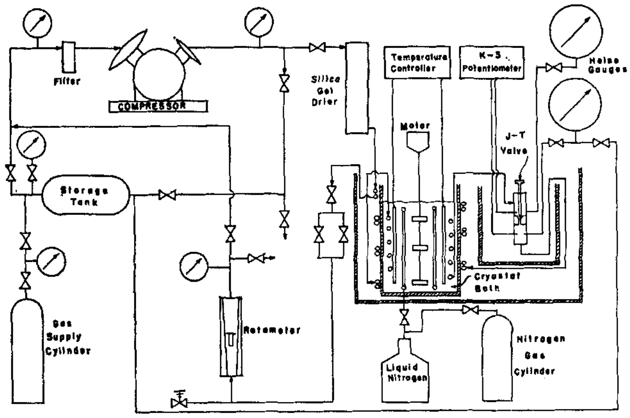

Fig. 1. Diagram of Joule-Thomson apparatus.

stirrer. The bath temperature was controlled to ± 0.01°C. by a precision temperature controller. The instrument sensed temperature fluctuations with a resistance thermometer, and adjusted the voltage to a small electric immersion heater.

The compressed, cold gas passed directly to the Joule-Thomson valve located in another insulation filled, stainless steel Dewar. The Joule-Thomson valve is shown in Figure 2 (*1*). Its design was an extensive modification of that of a valve originally built by H. L. Johnston (*7*). The valve had two principal parts, the body containing the valve stem and seat and the barrel containing the downstream flow guide, joined together with a threaded connection. Both parts were constructed of Monel to minimize conduction effects and yet provide the strength necessary to hold 3,000 lb./sq.in. pressure. The valve stem, seat, and downstream flow guide were made of lucite to prevent conduction of heat from the upstream to the downstream gas. Kinetic energy of the expanded gas was dissipated by passing it through a coiled length of thermocouple wire before it reached the thermocouple tip. Within the valve the gas expanded at constant enthalpy to a lower pressure and temperature. Upstream and downstream temperatures were measured with calibrated 30 gauge copper-constantan thermocouples whose tips were immersed in the gas stream to about 6 in. A potentiometer was used to obtain millivolt indications. Corresponding pressures were measured with calibrated 12-in. diameter Heise gauges. Both thermocouple leads and pressure lines passed through the cryostat bath to eliminate conduction effects.

After leaving the Joule-Thomson valve the gas was warmed in the countercurrent heat exchanger. It then passed through a rotameter and returned to the compressor.

The Dewars containing the cryostat bath and the Joule-Thomson valve were surrounded with rockwool insulation. All cold lines were covered by at least 6 in. of insulation.

PROCEDURE

After several purgings and evacuations of the system, premixed gas was fed from a cylinder to the storage tank. The gas was gradually fed to the compressor and circulated through the apparatus. As pressure was being built up, the cryostat bath was brought to the desired temperature and there maintained by the controller.

Upstream and downstream pressures were adjusted to desired levels by regulating the Joule-Thomson valve and other control valves on the inlet and outlet lines. After steady state operation had been achieved, measurements were recorded for the upstream and downstream pressures and temperatures. This process was repeated for given upstream conditions, varying the downstream pressure until the whole pressure range was covered. The series of points obtained defined one isenthalp. Different isenthalps were obtained by varying upstream conditions of temperature and pressure.

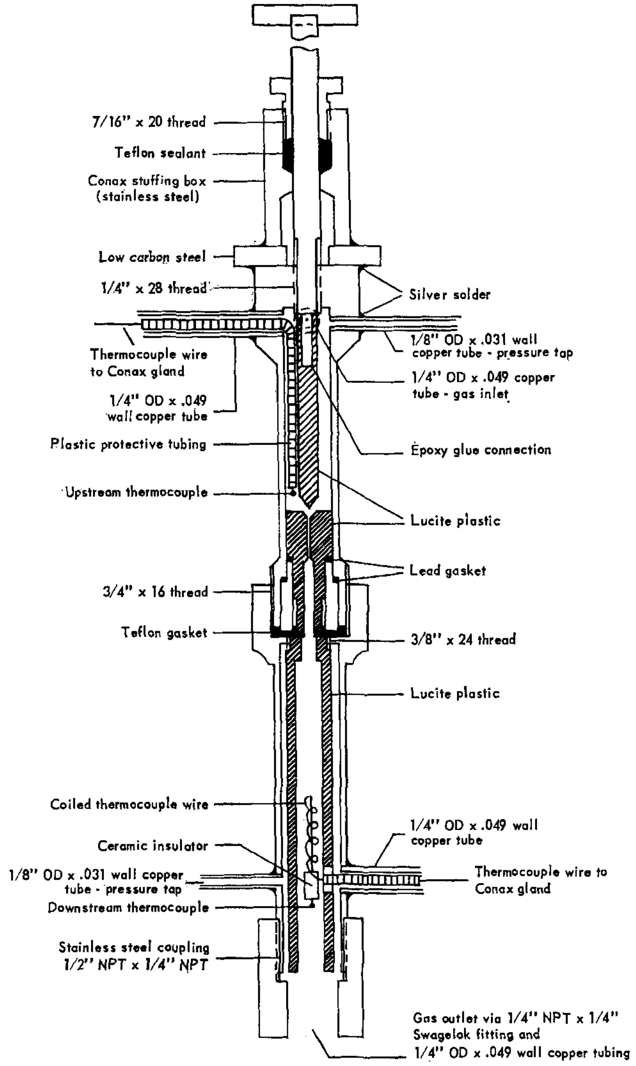

Fig. 2. Joule-Thomson valve. All parts monel except as indicated.

DISCUSSION AND RESULTS

The objectives of the program called for development of an apparatus capable of measuring Joule-Thomson effects at low temperatures, and obtaining data on the nitro-

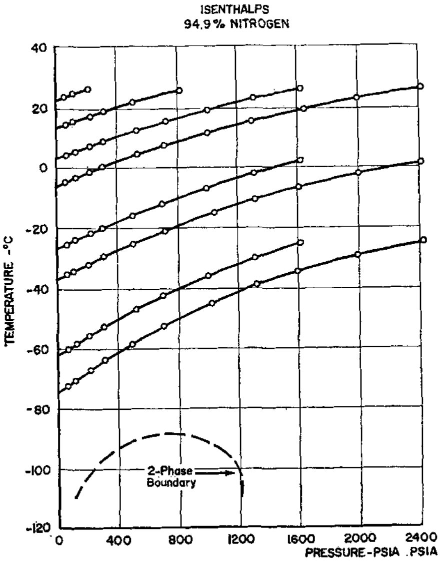

Fig. 3. Isenthalps 94.9% nitrogen.

TABLE 1. JOULE-THOMSON EFFECT IN NITROGEN

		Joule-Thomson Effect, t°C		
Pressure drop from 2,000 lb./sq. in. abs. to	Flow rate ——→	1.5 std. cu. ft./min.	3.5 std. cu. ft./min.	2.5 std. cu. ft./min.
	Date ——→	11-15-60	11-15-60	10-17-61
	t°C. @ 2,000 lb./sq. in. abs.	19.07	18.86	19.10
1,600 lb./sq. in. abs.		3.37°C.	3.48°C.	3.48°C.
1,200		7.74	7.87	7.85
800		13.09	13.15	13.11
400		19.42	19.31	19.26
0		26.75	26.41	26.30

gen-ethane system in the region adjacent to the vapor-liquid phase boundary.

The authors' activities in the development of an aparatus were motivated by the desire to be able to obtain large quantities of reliable data quickly and economically. The ease of operation and flexibility offered by the expansion valve device were very attractive characteristics. Thus it was decided to construct and test a system centered around a Joule-Thomson expansion valve. Some may criticize this decision on theoretical grounds that the jet kinetic energy of the fluid passing through a valve cannot be converted adequately to thermal energy. The authors recognized that this problem and others of a general heat leakage nature are hazards of Joule-Thomson work regardless of the device used, and that a valve may be more susceptible to such errors. However they felt these sources of error could be reduced to insignificant levels, and indeed they believe the experimental results justify their decisions.

In order to evaluate the performance of the apparatus the Joule-Thomson effect in nitrogen at room temperature was measured over a range of flow rates. Analysis of calibration temperature measurements showed a standard deviation of 0.02°C.; the pressure measurements were accurate to about 0.1%. Table 1 gives the estimates of Joule-Thomson effects for minimum and maximum operating conditions; also included are results obtained nearly a year later in order to demonstrate the degree of reproducibility.

Analysis of the results given in Table 1 shows there are no significant differences due to changes in flow rate within the range 1.5 to 3.5 std. cu. ft./min. It is therefore concluded that errors attributable to kinetic energy effects had been successfully minimized. Most of the data reported herein were collected in the 2.5 to 3.5 std. cu. ft./min. range.

In order to test the accuracy of their results the authors compared their estimates with values obtained from the work of Roebuck and Osterberg (*13*). The mean difference between the authors' pooled estimates from Table 1 and Roebuck's values is 0.13°C.; the standard error of this difference was calculated to be 0.20°C. It is therefore concluded that no significant difference exists between results obtained by two different methods, and consequently any bias due to heat leakage across the valve must also have been successfully minimized. Additional data taken on nitrogen at temperatures to −170°C. generally showed good agreement with Roebuck's data.

Joule-Thomson effects were measured for ethane and five nitrogen-ethane mixtures in the temperature range 25° to −100°C. and at pressures up to 2,400 lb. sq. in. abs. Compositions of the mixtures studied were determined by chromatographic analysis to be 94.9, 85.7, 77.5, 56.9, and 27.9% nitrogen, ± about 0.5%. The results of the Joule-Thomson measurements are shown in Figures 3 to 8 in the form of isenthalpic curves.* The liquid-vapor phase boundaries shown in these figures were estimated from equilibrium data available on the nitrogen-ethane system (*6*).

In the experimental region above the two-phase area the curves reflect the expected behavior. All the Joule-Thomson effects were positive and increased with lower temperatures and pressures. Increasing amounts of ethane also increased Joule-Thomson effects. Temperature differences up to 75°C. were recorded for the maximum pressure drop of about 2,350 lb./sq. in. The density of points in the low-pressure region may be noted. This was done in order to facilitate the extrapolation to zero pressure

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* Tabular material has been deposited as document 7971 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

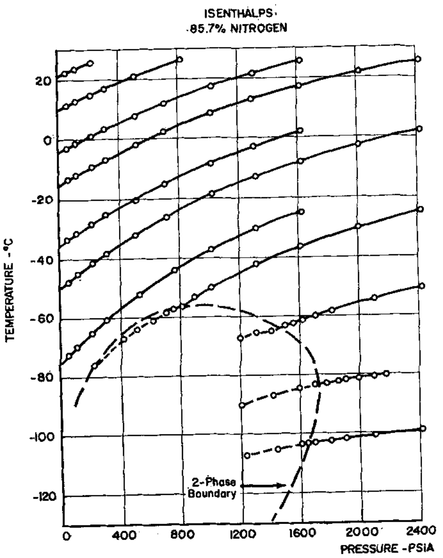

Fig. 4. Isenthalps 85.7% nitrogen.

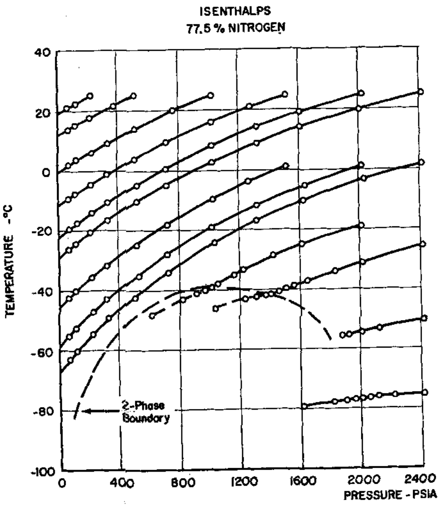

Fig. 5. Isenthalps 77.5% nitrogen.

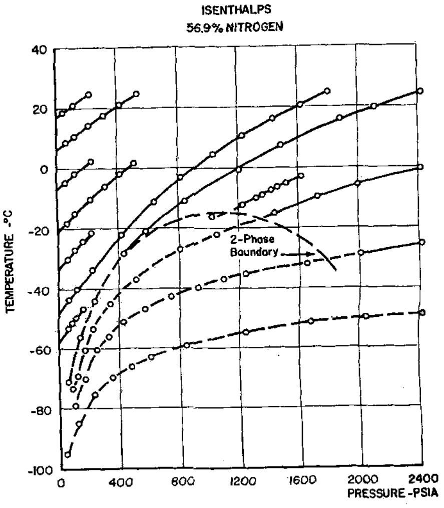

Fig. 6. Isenthalps 56.9% nitrogen.

Table 2. Comparison of Zero Pressure Joule-Thomson Coefficients for Ethane, °C./atm.

°C.	Stockett and Wenzel	Eucken and Parts (*3*)	Tester (*14*)	Mc Glashan and Potter (*11*)
20	1.17	1.23	1.23	1.13
0	1.46	1.47	1.47	1.36
—20	1.79	1.77	1.76	1.67
—40	2.15	2.25	2.08	2.10

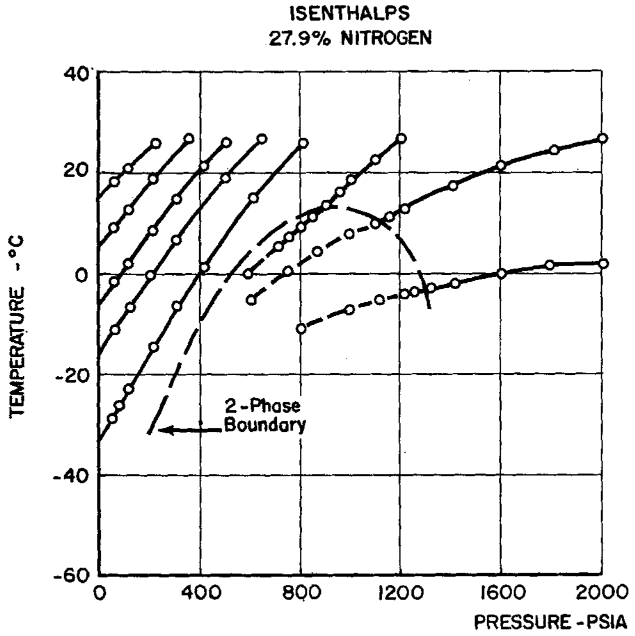

Fig. 7. Isenthalps 27.9% nitrogen.

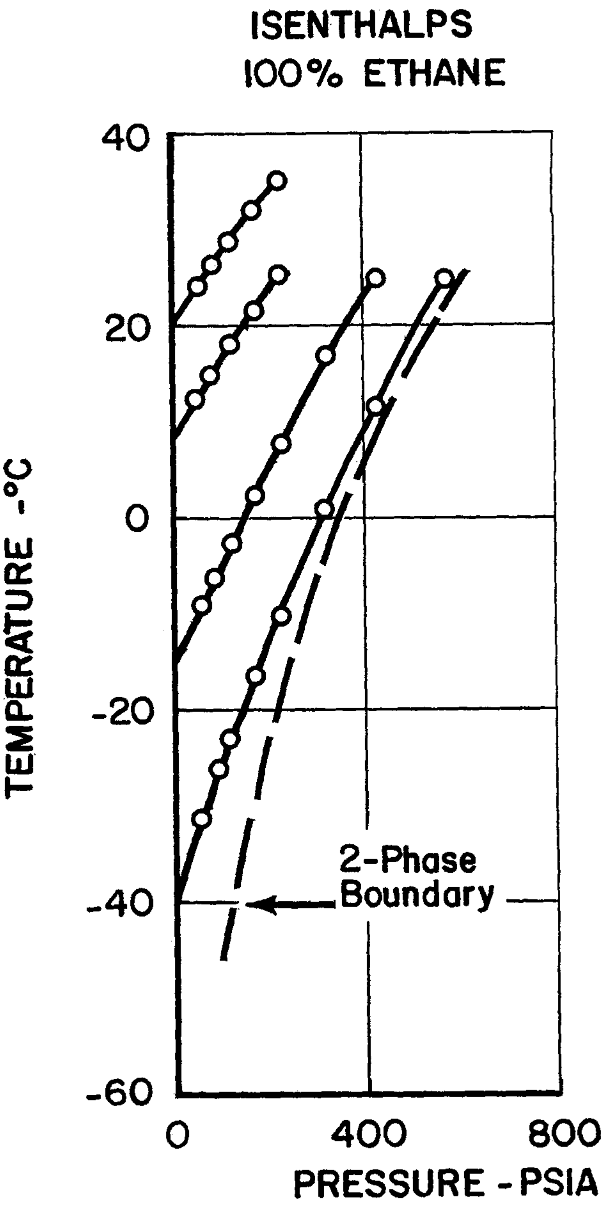

Fig. 8. Isenthalps 100% ethane.

discussed below. The incomplete appearance for the 56.9 mixture (Figure 6) was due to an insufficient amount of gas remaining to reach higher pressures. Operation of the equipment in this region was smooth and steady with pressure control within ± 2 lb./sq. in. abs.

In contrast the curves shown penetrating the two-phase region were accompanied by wide fluctuations in pressure, amounting at times to as much as 100 lb./sq. in. The data shown represent measurements taken as close to steady state as possible, but they are no doubt subjected to larger than normal errors. Nonetheless around the dome or critical part of the two-phase area a definite discontinuity appears to occur in the isenthalp. In most cases the points were closely spaced in an attempt to clearly define the point of discontinuity. The usefulness of such an effect for establishing phase behavior could be considered. The discontinuities in the curves disappeared as the curves themselves became less steep, beyond the critical state.

To obtain estimates of zero-pressure Joule-Thomson coefficients it was necessary to extend the isenthalpic

Table 3. Zero-Pressure Temperature Intercepts °C. and Joule-Thomson Coefficients °C./atm. for Nitrogen-Ethane Mixtures

Percent nitrogen

94.9		85.7		77.5		56.9		27.9	
t	μ^0	*t*	μ^0	*t*	μ^0	*t*	μ^0	*t*	μ^0
22.84	0.260	21.04	0.349	19.30	0.436	16.90	0.539	14.31	0.839
13.51	0.263	9.93	0.343	12.11	0.417	6.40	0.585	5.26	0.931
3.17	0.280	—4.55	0.384	—0.27	0.462	—7.29	0.696	—6.45	1.098
—6.04	0.315	—15.43	0.426	—11.76	0.503	—21.12	0.772	—16.47	1.207
—26.77	0.336	—35.73	0.506	—22.04	0.549	—34.01	0.932	—33.81	1.406
—37.22	0.380	—50.16	0.598	—28.78	0.590	—48.64	1.060		
—62.16	0.488	—75.00	0.725	—45.15	0.689	—57.17	1.162		
—74.54	0.551			—58.02	0.764				
				—66.27	0.825				

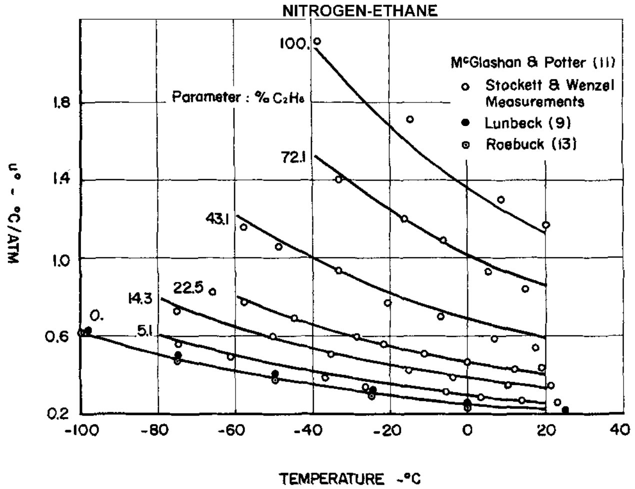

Fig. 9. Zero-pressure Joule-Thomson coefficients.

curves to zero pressure. The experimental data for each curve were fitted by the model

$$t = Bo + \sum_{i=1}^{n} Bi\ p^i \qquad (1)$$

to within about 1%. This model provided the means to extrapolate the isenthalps to obtain zero-pressure temperature intercepts and also, by differentiation, zero-pressure Joule-Thomson coefficients.

For further comparison of the authors' procedures they checked their zero-pressure Joule-Thomson coefficients for ethane with values calculated from the equation of Eucken and Parts (*3*) for the second virial coefficient of ethane, also with values from the survey results of Tester (*14*) and with values calculated from the reduced correlation of McGlashan and Potter (*11*). These comparisons are presented in Table 2 which shows that the authors' values compare favorably with the literature.

The results of the authors' computations of zero-pressure Joule-Thomson coefficients for the five nitrogen-ethane mixtures are presented in Table 3. These results are also shown in Figure 9, which includes data on nitrogen from Lunbeck (9) and Roebuck (*13*) and the graphical representation of the reduced correlation of McGlashan and Potter (*11*).

Estimates of zero-pressure Joule-Thomson coefficients were calculated for the five mixtures with the pure component data from 20° to —40°C. The simple linear mixture rule below was used:

$$\mu_m{}^0 = X_1\mu_1{}^0 + X_2\mu_2{}^0 \qquad (2)$$

This model gave results higher than those measured by an average of 15.7%.

The useful relationship between Joule-Thomson coefficients and second virial coefficients has been discussed by Manning and Canjar (9). Hirschfelder et al. (5) describe a rule based on the virial method. The data were then fitted to the virial model

$$\mu_m{}^0 = \frac{C_{p1}{}^0\, \mu_1{}^0 X_1{}^2 + C_{p2}{}^0 \mu_2{}^0\, X_2{}^2 + 2A\, X_1\, X_2}{X_1\, C_{p1}{}^0 + X_2\, C_{p2}{}^0} \qquad (3)$$

Average values of *A* estimated from the data were represented by the expression

$$A = 4.34 - 0.024\ t \qquad (4)$$

(correlation coefficient = — .44) as shown in Figure 10. This model, by accounting for the interaction effect, substantially reduced the difference between calculated and measured results. The absolute average deviation was evaluated to be 4.6%, namely a value within the range of accuracy of the estimates.

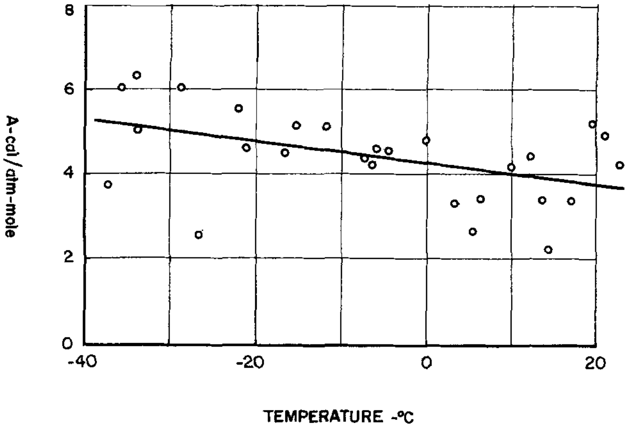

Fig. 10. Estimated function of interaction parameter A.

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NOTATION

A = interaction coefficient, $C_p{}^0{}_{1\,2} \cdot \mu^0{}_{1\,2}$
B_o, B_i = regression coefficients
$C_p{}^0$ = zero pressure heat capacity (*4*), (*12*)
$i.\ n$ = integer indexes
p = pressure, lb./sq.in.abs.
t = temperature, °C.
X = mole fraction
μ^0 = zero-pressure Joule-Thomson coefficient, °C./atm.

Subscripts

1 = nitrogen
2 = ethane
1 2 = interaction
m = mix

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