Table II. Pair Potential Parameters Used in Calculations for Table I

	Set A		Set B	
Substance	σ, Å	ε/k, K	σ, Å	ε/k, K
CH_4	3.70[a]	157[a]	3.81[b]	144[b]
CF_4	4.66[a]	134[a]	4.70[b]	152[b]
n-Hexane	5.92[c]	517[c]	5.91[d]	413[d]
n-Heptane	6.25[c]	573[c]	6.33[d]	416[d]
n-Octane	6.54[c]	611[c]	6.61[d]	438[d]
Isooctane	6.52[c]	602[c]	6.52[e]	402[e]

[a] Ref. *10.* [b] Ref. *3.* [c] Ref. *14.* [d] Ref. *9.* [e] Estimated from $\epsilon/k = 0.74\ T_c$ and $\sigma^3 = 0.59\ V_c$.

CF_4, a consistent set for the *n*-alkanes from Nelson and DeLigny (*9*), and the values for isooctane were estimated. The agreement (average deviation) for all systems with CH_4 was 5.5% for Set A and 2.0% for Set B. The agreement with CF_4 was 13% for Set A and 10% for Set B. Considering the great variations reported in the literature for ϵ/k and σ values (see ref. *3*, for example), we find the agreement between experimental and calculated values of D_{12} to be reasonable.

The much greater difference for the systems with CF_4 is certainly beyond experimental error. An ϵ/k for CF_4 of about 70K would give about 1% agreement between experimental and theory. This is of the order one would expect if Kihara core potentials were used. We intend examining the situation in more detail in a subsequent paper when we have more data available.

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LITERATURE CITED

(1) Dreisbach, R. R., *Advan. Chem. Ser.*, **15**, 3–536 (1955).
(2) Dreisbach, R. R., *ibid.*, 22, 3–491 (1959).
(3) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," Wiley, New York, N.Y., 1964.
(4) Kohn, J. P., Romero, N., *J. Chem. Eng. Data*, **10**, 125 (1965).
(5) Marrero, T. R., PhD thesis, University of Maryland, College Park, Md., 1970.
(6) Marrero, T. R., Mason, E. A., "Gaseous Diffusion Coefficients," NSRDS-NBS 38 (1971).
(7) Mason, E. A., Marrero, T. R., *Adv. At. Mol. Phys.*, **6**, 155 (1970).
(8) Nagata, I., Hasegawa, T., *J. Chem. Eng., Japan*, **3**, 143 (1970).
(9) Nelson, W. D., DeLigny, C. L., *Rec. Trav. Chim.*, **87**, 623 (1968).
(10) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," 2nd ed., McGraw-Hill, New York, N.Y., 1966.
(11) Romero, N., MS thesis, University of Notre Dame, Notre Dame, Ind. (1962).
(12) Stefan, J. *Wien. Akad. Sitzungber.*, **63**, 63 (1871).
(13) Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Elsevier Amsterdam, 1950.
(14) Wilhelm, E., Battino, R., *J. Chem. Phys.*, **55**, 4012 (1971).

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Excess Enthalpy of Gaseous Mixtures of Nitrogen and Carbon Dioxide

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The excess enthalpies of binary mixtures of nitrogen and carbon dioxide have been measured for six isotherms in the temperature range 10–80°C at pressures up to 110 atm over the complete range of compositions.

A number of methods can be used to obtain information regarding the dependence of the enthalpy of mixtures on pressure, temperature, and composition. A direct method is the determination of the excess enthalpy (heat of mixing). The excess enthalpy, H^E is defined by:

$$H^E \equiv \left\{ H_m - \sum_i x_i H_i \right\}_{P,T} \quad (1)$$

where H_m is the enthalpy of the mixture, H_i the enthalpy of pure component i, and x_i the mole fraction of component i in the mixture.

Many studies have been made of the excess enthalpy of liquid mixtures, but only a few workers have applied this method to gases. The earliest work on gases was performed by Beenakker and co-workers (*1, 2, 5*) on the systems H_2–N_2, H_2–Ar, Ar–N_2, CH_4–H_2, and CH_4–Ar. Later Van Eijnsbergen and Beenakker (*7*) studied the systems CH_4–N_2, He–CH_4, and He–Ar as well as extended the range of data in some of the systems studied earlier. Hejmadi (*3*) obtained some data in the systems N_2–CO_2, N_2–C_2H_6, and N_2–O_2, and Klein et al. (*4*) made extensive measurements in the system CH_4–N_2. Earlier in this laboratory, the system N_2–CO_2 was studied in a flow calorimeter at 40°C (*6*). In the present work results in this system have been obtained along six isotherms between 10° and 80°C at pressures up to 110 atm.

THERMODYNAMIC RELATIONS

The first law of thermodynamics, applied to a flow calorimeter in which two pure gases mix, reduces to:

$$H_m(T_2,P_2) - xH_1(T_1,P_1) - (1-x)H_2(T_1,P_1) = \frac{\dot{Q} - \dot{W}}{F} \quad (2)$$

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where $\dot{Q}$ is the rate of heat leak, $\dot{W}$ is the rate of electrical energy transfer, F is the mass flow rate, and x is the mole fraction of component 1. Changes in kinetic and potential energy are assumed negligible. In a well-designed flow calorimeter, operation at a sufficiently high mass flow rate makes $\dot{Q}$ small, T_1 is equal to T_2, and the pressure drop is negligible. Equation 2 then becomes:

$$H^E = \{H_m - xH_1 - (1 - x)H_2\}_{T,P} = \frac{-\dot{W}}{F} \tag{3}$$

EXPERIMENTAL

The experimental apparatus differs somewhat from that used previously (*6*). The two gases to be mixed are stored in standard gas cylinders. The gases flow independently through high-pressure regulators and metering valves to heat exchanger coils immersed in the calorimeter bath. The gases pass through the vacuum jacket and enter the mixing chamber. Here they mix and since the mixing is usually endothermic the outlet temperature would tend to drop. However, energy is supplied by the resistance heater and is adjusted to the amount required for temperature equality between the inlet and outlet. The mixture of gases exits from the calorimeter and is passed to a high-temperature bath before being throttled to atmospheric pressure. The gases pass through a rotameter for flow indication purposes and through a calibrated orifice meter for accurate flow rate determination.

The mixing chamber contains three concentric aluminum shells, with insulated Nichrome heating wire (40 B&S) wrapped bifilarly on the inner two shells. These shells serve to reverse the flow of the mixture, ensure complete mixing, and prevent the formation of hot spots.

The temperature difference across the calorimeter was monitored by six-junction copper-constantan thermopiles. The pressure drop across the calorimeter was determined by a differential pressure transducer and was negligible (<10 torr). The absolute pressure was measured by a Heise bourdon tube gauge which had been calibrated against a dead-weight tester. The electrical energy for the heater was supplied by a dc power supply, and the potential difference and current were determined using standard resistors. The temperature of the calorimeter bath was determined by a calibrated platinum resistance thermometer. All voltage measurements were made using a Hewlett-Packard Model 3450A digital voltmeter. The composition of the mixed gases was determined by gas chromatography. A sample of the flowing mixture was taken after the orifice meter and analyzed using a silica gel column. The chromatograph was calibrated by the analysis of standard mixtures prepared gravimetrically.

The error in the excess enthalpy depends directly upon the errors in the determination of the mass flow rate and the power input. Errors in the temperature, pressure, and composition result in uncertainty in the state at which the measurement was made. The heat leak, $\dot{Q}$, is presumed negligible since results obtained over a four-fold range of flow rates agreed within 0.5%. The accuracy of the results, however, is not of this magnitude.

For a variable Z which is a function of n independent variables z_i, the fractional error in Z can be estimated from the equation:

$$\frac{e(Z)}{Z} = \sum_{i=1}^{n} \left| \frac{1}{Z} \left(\frac{\partial Z}{\partial z_i} \right)_{z_j} e(z_i) \right| \tag{4}$$

Uncertainty in the determination of the mass flow rate estimated from the flow meter calibration is about 2%. From calibrations and specifications of the instruments used in determining the power input, the estimated uncertainty is 0.2%. Since the functional form of the dependence of the excess enthalpy upon pressure, temperature, and composition is not known, the partial derivatives involving these variables in Equation 4 were estimated from the experimental data. The contribution of each term in the summation is given in Table III.

The gases were obtained from commercial suppliers and were used as received. The purity of the gases was as follows: N_2 99.993 mol %, CO_2 99.9 mol %.

RESULTS

Data were obtained in the temperature range 10–80°C over the complete range of compositions. Above 31°C, the critical temperature of CO_2, data were obtained at pressures up to 110 atm, while below this temperature the maximum pressure was limited by the vapor pressure of CO_2. The experimental results are presented in Table I which has been deposited with the ACS Microfilm Depository Service. The raw data were smoothed with respect to composition by plotting $H^E/4x(1 - x)$ against x. At low densities, where only binary interactions are important, this function is independent of x and even at high densities, the dependence on x is weak so that interpolation to even values of composition can be done accurately. An example of this smoothing plot is given in Figure 1 where the curve is drawn by eye. In most cases the small number of data points made it inappropriate to construct a least-squares polynomial. The smoothed results are plotted, together with the original experimental data in Figure 2, which shows all the experimental results at 20°C. Smoothing was also performed with respect to temperature and pressure. The results are presented in Table II.

Table II. Smoothed Excess Enthalpies H^E in J/g-mol for N_2–CO_2 Mixtures

		x								
T, °C	P/atm	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
10	10	21	37	47	54	59	53	44	34	18
	20	55	93	120	135	138	131	111	85	47
	30	140	215	265	285	277	255	213	157	87
	40	292	410	477	505	495	458	388	292	164
	43	400	530	602	620	594	534	450	335	190
20	10	19	34	43	49	53	48	40	30	17
	20	44	80	103	118	121	114	98	73	40
	30	91	155	199	220	222	197	167	127	63
	40	185	286	346	371	363	328	270	205	112
	50	403	597	664	662	613	537	439	322	179
32	10	16	30	39	44	47	43	35	26	16
	20	38	65	87	98	101	99	83	60	32
	30	73	128	166	185	188	165	138	102	55
	40	129	219	270	280	275	252	205	153	85
	50	234	389	452	460	439	396	329	240	133
	60	389	605	732	732	670	598	495	354	186
	70	937	1160	1265	1282	1200	1050	831	560	285
	80	4190	4400	4130	3650	3200	2665	2080	1400	720
	85	3980	4340	4170	3740	3240	2705	2085	1405	725
	90	3810	4310	4210	3790	3310	2965	2115	1410	730
	100	2995	3910	3970	3750	3300	2720	2080	1400	720
40[a]	10	15	27	36	41	44	40	33	24	15
	20	36	61	83	93	97	93	77	57	29
	30	65	117	149	165	170	150	124	92	45
	40	111	187	235	256	255	230	189	130	69
	50	169	297	355	386	365	320	274	204	113
	60	278	461	552	577	544	481	400	288	160
	70	492	748	859	862	818	715	570	393	197
	80	1021	1292	1416	1370	1243	1097	904	668	364
	90	2349	2764	2823	2604	2319	2010	1680	1262	700
	100	2891	3418	3478	3204	2816	2423	1998	1469	819
	110	2404	3341	3431	3249	2880	2423	1860	1263	649
	120	1883	2940	3291	3244	2879	2391	1787	1138	541

(Continued on next page)

Table II. *(Continued)*

T, °C	P/atm	x 0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
50	10	13	25	32	38	40	37	30	22	13
	20	32	54	74	84	87	84	69	51	25
	30	57	100	130	146	151	134	111	82	42
	40	93	156	200	225	220	195	160	115	60
	50	133	235	295	320	310	275	230	170	95
	60	200	350	430	465	440	398	325	235	131
	70	310	500	620	660	625	560	450	333	178
	80	490	720	870	890	845	760	620	465	257
	90	760	1050	1180	1220	1160	1045	880	660	370
	100	1260	1570	1700	1690	1600	1470	1250	980	565
60	10	11	22	29	35	38	35	28	21	11
	20	29	48	66	76	79	76	62	45	23
	30	51	85	114	128	130	121	101	74	39
	40	80	132	172	192	190	170	147	100	54
	50	110	190	243	261	252	230	200	150	80
	60	171	272	340	370	360	325	275	200	115
	70	237	377	460	490	480	430	360	267	150
	80	390	540	625	658	640	560	462	347	195
	90	540	750	873	888	841	739	600	440	240
	100	712	1042	1190	1210	1100	955	780	556	295
	110	1010	1420	1550	1520	1410	1230	995	680	350
70	10	10	20	27	32	35	32	26	19	10
	20	25	45	58	69	72	69	56	41	22
	30	44	76	100	113	115	110	92	68	37
	40	69	112	149	168	165	155	132	97	53
	50	95	165	210	235	225	205	175	135	72
	60	137	230	285	315	305	270	225	170	92
	70	187	310	380	415	400	350	290	215	115
	80	260	415	500	525	510	450	365	265	140
	90	360	555	650	675	650	565	460	320	170
	100	498	752	865	920	850	735	580	400	200
80	10	9	18	24	30	32	30	24	18	9
	20	22	37	51	63	66	63	51	36	21
	30	39	65	86	100	105	100	85	63	34
	40	56	96	127	146	150	142	125	94	50
	50	82	135	176	198	203	190	164	125	67
	60	115	185	236	270	267	245	212	160	87
	70	151	245	309	348	343	310	265	198	107
	80	203	320	396	438	425	383	326	240	130
	90	262	412	500	540	530	470	390	285	156
	100	335	540	643	670	640	555	457	335	182

[a] The values at 40°C are from the previous work (*6*), adjusted slightly within the experimental error.

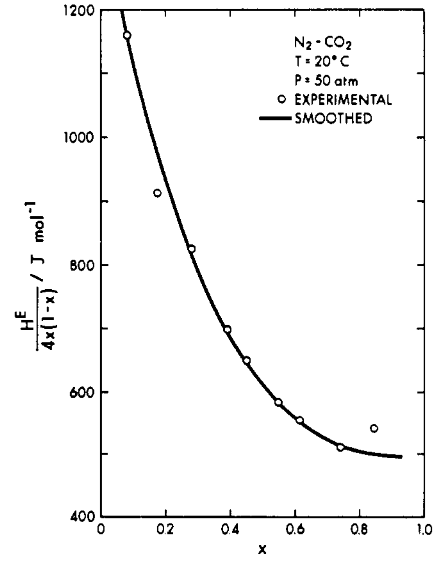

Figure 1. Smoothing plot

Table III

Item	% Error
Mass flow rate	2.0
Power input	0.2
Pressure	0.07–0.2
Temperature	0.01–0.1
Composition	0.00–2.0
Total	2.28–4.5

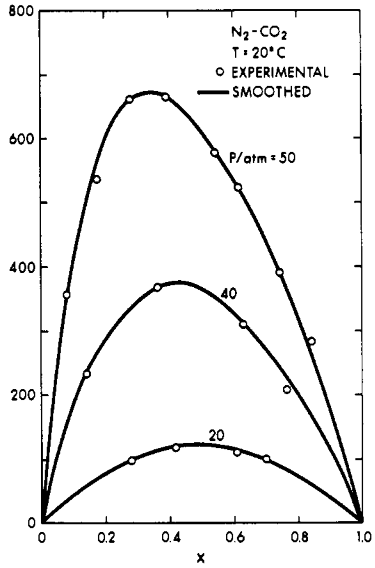

Figure 2. Smoothed results at 20°C plotted against the original experimental data

The only experimental data for H^E in the N_2–CO_2 system are those of Hejmadi (*3*) at 31° and 40°C. The previous work at 40°C (*6*) agreed well. Interpolated values from the present experiments were compared with the data at 31°C. The data agree within 2%, well within the expected accuracy of both sets (Table III).

NOMENCLATURE

e = absolute error
F = mass flow rate
H = enthalpy
P = pressure
$\dot{Q}$ = rate of heat transfer
T = temperature
$\dot{W}$ = rate of work transfer
x = mole fraction nitrogen

SUPERSCRIPTS

E = excess property

SUBSCRIPTS

m = mixture property
i = component i

LITERATURE CITED

(1) Beenakker, J. J. M., Coremans, J. M. J., "Prog. Int. Res. Thermo. Transport Prop.," Symp. Thermophys. Properties, 2nd, Princeton, N.J., p 3 (1962).

(2) Beenakker, J. J. M., Van Eijnsbergen, B., Knoester, M., Taconis, K. W., Zandbergen, P., "Advan. Thermophys. Prop. at Extreme Temperatures and Pressures," Symp. Thermophys. Properties, 3rd, Lafayette, Ind., p 114 (1965).
(3) Hejmadi, A. V., PhD thesis, University of Michigan, 1970.
(4) Klein, R. R., Bennett, C. O., Dodge, B. F., *A.I.Ch.E. J.*, **17**, 958 (1971).
(5) Knoester, M., Taconis, K. W., Beenakker, J. J. M., *Physica*, **33**, 389 (1967).
(6) Lee, J. I., Mather, A. E., *J. Chem. Thermodynam.*, **2**, 881 (1970).
(7) Van Eijnsbergen, B., Beenakker, J. J. M., *Physica*, **39**, 499 (1968).

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Thermodynamics of Solutions

Low-Temperature Densities and Excess Volumes of *cis*-Pentene-2 and Mixtures

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Temperature-dependent densities were determined for *n*-pentane and *cis*-pentene-2 from 25°C down to approaching the triple points. Excess volumes at 25°C were determined for binary mixtures of *cis*-pentene-2 with *n*-pentane, acetonitrile, toluene, and diethyl ether; all showed negative deviations except the mixture with diethyl ether which was slightly positive. The densities as a function of temperature and excess volumes as a function of composition were correlated by empirical functions.

As part of a continuing program on thermodynamics of solutions, liquid density data were determined for *cis*-pentene-2, *n*-pentane, toluene, acetonitrile, and diethyl ether, and mixtures of the latter four components with *cis*-pentene-2. The work was concurrent with infrared shift measurements as a function of density to determine intermolecular field effects.

EXPERIMENTAL

Pycnometers. The type of pycnometer used for the room-temperature densities of the pure components and mixtures, and the method of use have been described previously (*9*). By calibration, the pycnometer used was determined to have a stem cross-sectional area of 0.002351 ml/cm and a volume of 30.65259 ml.

Two modified Lipkin bicapillary pycnometers (*2*) were used for the low-temperature measurements, and consisted of a bulb blown into a piece of capillary tubing with two vertical graduated sections, one rising from the top and the other making a bend from the bottom, and then rising vertically. The top of each capillary was fitted with a $^{7}/_{15}$ ground glass cap, to reduce vaporization loss and sample contamination. The graduated sections were 20 cm × 1 mm i.d. borosilicate glass capillary. The bulb volume and stem cross sections were; pycnometer #1, 4.12563 ml, 0.0096900 ml/cm; pycnometer #2, 3.72290 ml, 0.0096285 ml/cm.

Room-Temperature Bath. The volume measurements were made in a well-stirred water bath, controlled by a Melabs CTC-1A, proportional controller (*8*), using a 500-Ω platinum resistance sensing element and a 200-W electric heater. The temperature was measured with a short-range Kessler, precision mercury-in-glass thermometer, with 0.05°C smallest scale division. The liquid level in the pycnometer, and the mercury level in the thermometer were read by a cathetometer with a vernier scale.

Low-Temperature Bath. A constant-temperature refrigerated bath was used for the low-temperature densities. The system consists of an outer bath, a large strip-silvered glass dewar, and an inner bath made of a closed-off section of glass pipe. The pycnometer rests in the inner bath. The bath liquid (both baths) is a mixture of low-freezing point liquid hydrocarbons, a 60–40 mol % isopentane and 2-methylpentane.

The outer bath is cooled by flowing liquid nitrogen through coils in the bath. A copper-constantan thermocouple in the bath senses the temperature and provides a signal to an on-off temperature controller, which actuates a solenoid valve regulating the flow of liquid nitrogen. The temperature controller is a West Instrument Corp. Model JS-14 on-off controller (*14*), and the solenoid valve is an ITT model K27 35 psi, liquid nitrogen solenoid valve. The outer bath vessel is a pyrex vacuum dewar, 25 cm i.d. × 40 cm deep, with a $^{3}/_{4}$ in. wide unsilvered stripe.

The inner bath is cooled by the outer bath and heated by heat leakage into it. The temperature is controlled by a 250-W heater, actuated by a Melabs CTC-1A Proportional Temperature Controller (*8*) with a platinum resistance sensing element. The inner bath temperature can be maintained at some temperature above the mean outer bath temperature. The heater is a 50-Ω coil of #26 B&S Nichrome wire, 650 cm long, coiled into a multiple helix. The inner bath is a 10 cm i.d. × 36 cm deep section of glass pipe, closed off at the bottom. Each bath is stirred through a pulley and belt system by a Precision Scientific Co. 1525 rpm, 20-W motor, with a variable speed control.

The entire bath system is enclosed in an insulated box, with a port in the front for viewing the pycnometer. A small neon

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