Values of α and β are given in Table IV. Since the relative partial molal heat capacity, $(\overline{C}_p - \overline{C}_{p0})$, may be computed by the equation

$$(\overline{C}_p - \overline{C}_{p0}) = 2\beta T \qquad (8)$$

the data in the table afford a very brief method of expressing all the heat data.

TABLE IV

PARAMETERS OF EQUATIONS (7) AND (8)

m	$(-\alpha)$	$\beta \times 10^3$	m	α	$\beta \times 10^3$
0.005	77	2.08	0.2	298	8.08
.007	77	2.54	.3	435	10.15
.01	72	2.77	.5	682	13.84
.02	77	3.46	.7	871	16.84
.03	87	3.93	1	1156	21.23
.05	87	4.38	1.5	1517	27.23
.07	96	4.85	2	1753	32.07
.1	144	5.54	3	2013	39.46

Summary

1. Electromotive forces of the cells

H_2 | HCl (m), Dioxane (20%), H_2O (80%) | AgCl-Ag

have been obtained at 5° intervals from 0 to 50°, and from 0.005 to 3 M concentrations.

2. From these and the results at lower concentrations obtained by Harned and Morrison, the activity coefficient, relative partial molal heat content and heat capacity of hydrochloric acid in this solvent have been computed over these ranges of temperature and concentration.

NEW HAVEN, CONN. RECEIVED NOVEMBER 9, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, THE UNIVERSITY OF WISCONSIN]

The Joule-Thomson Effect in Mixtures of Helium and Nitrogen

BY J. R. ROEBUCK AND H. OSTERBERG

The measurements on the Joule-Thomson effect in air,[1,2] in helium,[3,4] in argon[5] and in nitrogen,[6] are here extended to four mixtures of helium and nitrogen. The work on mixtures of helium and air[3] had shown an unexpected situation which increases one's interest in the physics of these mixtures. Reference is made to the above articles for details of apparatus and methods. These measurements cover our usual pressure range of 1 to 200 atm., but the temperature range here of −100 to 250° is somewhat reduced. The experimental work was done in the fall of 1933 but the press of other work has delayed publication.

Liquefaction

In all the work with helium mixtures, whenever there was reason to believe that a liquid phase was present anywhere in the apparatus, the data simultaneously became unmanageably erratic. This occurred both when making readings near the condensing conditions of one constituent and when using the regenerative purifier.[2] This difficulty was not observed with pure air, due doubtless to the similarity of the condensing conditions of oxygen and nitrogen. We attribute the erratic readings to variation in composition of the mixture when the liquid phase consists largely of the more condensable constituent. The difficulties involved both in the experiments and in the subsequent use of the data, led us to avoid this situation. For this reason the experimental readings usually were not carried below −100°. This is distinctly unfortunate because data on gas mixtures in equilibrium with their liquid phases would be of great value for the study of the liquid-vapor relations.

Gas Supplies.—The helium was part of that supplied by the Bureau of Mines for the previous work on pure helium.[3] It was purified before use by passage over activated coconut charcoal cooled by liquid air as in the earlier work.[3]

The nitrogen was purchased from the Air Reduction Company. As in our previous work with pure nitrogen[6] it was used without further purification.

The mixture compositions are given in Table I. Since the air-helium mixture work had shown that the Joule-Thomson effect varied more rapidly

TABLE I

HELIUM-NITROGEN MIXTURES

No.	Helium, %	Nitrogen, %
0[3]	*100*	*0*
1	75.5	24.5
2	51.0	49.0
3	33.2	66.8
4	16.6	83.4
5[6]	*0*	*100*

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(1) Roebuck, *Proc. Am. Acad. Arts. Sci.*, **60**, 537 (1925).

(2) *Idem.*, **64**, 287 (1930).

(3) Roebuck and Osterberg, *Phys. Rev.*, **43**, 60 (1933).

(4) *Idem.*, **45**, 332 (1934).

(5) *Idem.*, **46**, 785 (1934).

(6) *Idem.*, **48**, 450 (1935).

with composition for the air-rich mixtures, these helium–nitrogen mixtures were crowded somewhat toward the pure nitrogen side. Sufficient of each mixture for the projected work was made up at once so that the compositions should be very constant. To avoid excess loss of nitrogen, the lubricating water was discharged only near atmospheric pressure where the dissolved helium and nitrogen are both small in quantity.

The mixtures were made up by admitting the desired measured quantities of the constituent gases to the flow system and mixing thoroughly. The mixtures were analyzed carefully by absorbing the nitrogen in liquid-air cooled charcoal.[3] The two methods of ascertaining the composition agree well and the analytical data are given in Table I.

TABLE II

MIXTURE NO. 1

No.	p_2	t_2	No.	p_2	t_2	No.	p_2	$-t_2$
	250° Curve	Plug 52		100° Curve	Plug 52		−50° Curve	Plug 43
1	4.3	263.60	1			1	2.0	44.53
2	19.0	262.70	2	18.8	109.71	2	16.1	44.86
3	41.8	261.28	3	41.6	108.47	3	42.2	45.53
4	65.8	259.68	4	65.4	107.16	4	66.8	46.17
5	88.8	258.20	5	88.4	105.87	5	88.8	46.89
6	113.3	256.61	6	113.0	104.49	6	113.5	47.63
7	135.0	255.20	7	136.5	103.17	7	134.9	48.37
8	158.8	253.63	8	159.5	101.87	8	158.6	49.24
9	180.6	252.00	9	180.9	100.63	9	178.6	49.93
10	201.9	251.02	10	201.9	99.44	10	201.9	50.94
	200° Curve	Plug 52		50° Curve	Plug 43		−100° Curve	Plug 43
1	3.7	212.91	1	1.4	60.20	1	2.3	98.09
2	18.6	212.07	2	18.6	59.46	2	18.5	97.88
3	40.9	210.80	3	41.9	58.32	3	41.2	97.96
4	65.7	209.12	4	66.8	57.04	4	66.4	98.03
5	89.6	207.67	5	90.1	55.84	5	90.9	98.22
6	113.3	206.14	6	113.3	54.64	6	113.5	98.49
7	136.5	204.71	7	135.5	53.47	7	135.0	98.83
8	159.9	203.23	8	158.2	52.32	8	158.0	99.28
9	180.8	201.52	9	184.4	50.81	9	180.0	99.73
10	201.9	200.69	10	201.9	50.01	10	201.9	100.51
	150° Curve	Plug 52		0° Curve	Plug 43		−124° Curve	Plug 43
1	4.0	161.86	1	1.7	8.78	1		
2	19.2	161.02	2	18.9	8.15	2	19.2	123.61
3	40.0	159.80	3	42.2	7.22	3	40.9	123.11
4	65.7	158.29	4	66.8	6.14	4	66.7	122.73
5	89.0	156.89	5	89.1	5.19	5	90.2	122.56
6	113.0	155.43	6	113.3	4.09	6	114.6	122.54
7	136.6	154.03	7	135.0	3.11	7	135.2	122.62
8	158.5	152.72	8	158.3	2.03	8	158.0	122.82
9	180.8	151.28	9	183.7	0.83	9	181.5	123.04
10	201.9	150.22	10	201.9	−0.13	10	201.9	123.78

Experimental Results

The data for mixtures 1–4 are given in Tables II–V. The individual runs are referred to by their approximate bath temperatures. The last temperature and pressure readings in a run are, respectively, the bath temperature and the inlet high pressure. The temperatures are in degrees centigrade and the pressures in atmospheres absolute.

TABLE III

MIXTURE NO. 2

No.	p_2	t_2	No.	p_2	t_2
	250° Curve	Plug 52		150° Curve	Plug 52
1	3.5	260.94	1	3.5	156.76
2	16.4	260.40	2	16.6	156.48
3	40.8	259.20	3	40.9	155.78
4	66.4	257.93	4	66.4	154.97
5	90.1	256.76	5	89.0	154.28
6	113.6	255.54	6	113.3	153.47
7	135.5	254.39	7	135.5	152.59
8	157.9	253.15	8	158.0	151.67
9	180.9	251.83	9	181.9	150.50
10	201.9	251.02	10	201.9	150.22
	200° Curve	Plug 52		100° Curve	Plug 52
1	3.2	209.12	1	4.8	103.77
2	18.9	208.65	2	18.9	103.62
3	40.5	207.79	3	40.3	103.35
4	66.5	206.74	4	65.8	102.94
5	90.0	205.78	5	88.7	102.50
6	113.0	204.72	6	113.6	101.95
7	135.6	203.72	7	135.2	101.40
8	158.0	202.69	8	157.3	100.80
9	183.3	201.29	9	181.6	100.09
10	201.9	200.69	10	201.9	99.44
	50° Curve	Plug 43		−51° Curve	Plug 43
1	1.9	51.85	1	2.3	60.05
2	19.6	51.98	2	17.3	58.70
3	40.9	52.00	3	41.8	56.78
4	66.3	51.90	4	65.5	55.24
5	90.3	51.75	5	88.8	54.00
6	113.2	51.49	6	113.0	52.95
7	135.2	51.18	7	135.3	52.17
8	158.6	50.79	8	158.3	51.58
9	182.4	50.25	9	181.6	51.07
10	201.9	50.01	10	201.9	50.94
	0° Curve	Plug 43		−100° Curve	Plug 43
1	1.9	−2.38	4	65.1	108.94
2	18.9	−1.84	5	87.8	106.90
3	41.5	−1.23	6	111.1	105.04
4	66.0	−0.65	7	117.0	104.53
5	88.4	−0.27	8	139.5	103.06
6	111.7	−0.04	9	163.7	101.71
7	134.6	+0.10	10	201.9	100.51
8	158.0	+0.09			
9	181.1	+0.06			
10	201.9	−0.13			

TABLE IV

MIXTURE No. 3

No.	p_2	t_2	No.	p_2	t_2
250° Curve		Plug 52	150° Curve		Plug 52
1	4.4	257.71	1	4.8	152.33
2	18.8	257.35	2	18.9	152.31
3	39.3	256.77	3	41.2	152.29
4	66.3	255.94	4	65.1	152.17
5	89.9	255.16	5	87.9	152.01
6	113.2	254.32	6	112.5	151.74
7	135.8	253.48	7	135.9	151.33
8	159.7	252.51	8	159.4	150.95
9	181.1	251.66	9	181.7	150.50
10	201.8	251.02	10	201.8	150.22
200° Curve		Plug 52	100° Curve		Plug 52
1	4.5	205.40	1	5.4	98.25
2	18.9	205.22	2	18.5	98.62
3	41.4	204.85	3	41.4	99.09
4	65.6	204.36	4	64.8	99.46
5	89.2	203.84	5	88.6	99.72
6	113.2	203.25	6	112.3	99.85
7	135.7	202.64	7	136.1	99.88
8	159.3	201.94	8	157.5	99.82
9	180.2	201.30	9	180.5	99.66
10	201.8	200.69	10	201.8	99.44
50° Curve		Plug 52	0° Curve		Plug 43
1	7.1	44.41	1	1.9	12.73
2	19.5	45.09	2	18.4	10.92
3	41.0	46.21	3	42.0	8.59
4	65.8	47.24	4	66.4	6.68
5	89.3	48.09	5	89.5	4.87
6	112.6	48.72	6	112.8	3.52
7	136.2	49.25	7	135.7	2.37
8	201.6	50.01	8	163.6	1.24
			9	179.9	0.65
			10	201.8	0.13
50° Curve		Plug 43	−50° Curve		Plug 43
1	1.9	43.95	1	1.9	74.02
2	18.5	44.89	2	15.9	71.01
3	41.5	46.11	3	42.1	66.19
4	67.0	47.20	4	66.2	62.47
5	88.6	47.98	5	89.2	59.53
6	111.9	48.63	6	112.5	57.00
7	133.9	49.13	7	134.0	55.02
8	156.5	49.53	8	156.3	53.35
9	179.9	49.79	9	182.4	51.55
10	201.8	50.01	10	201.8	50.94

TABLE V

MIXTURE No. 4

No.	p_2	t_2	No.	p_2	t_2
250° Curve		Plug 52	150° Curve		Plug 52
1	3.7	253.70	1	4.6	146.48
2	19.2	253.68	2	19.3	147.09
3	41.6	253.60	3	41.0	147.88
4	65.8	253.39	4	65.4	148.62
5	90.3	253.14	5	89.3	149.18
6	113.6	252.79	6	111.9	149.60
7	134.7	252.42	7	135.0	149.85
8	158.6	251.88	8	157.5	150.02
9	181.4	251.47	9	181.4	150.12
10	201.9	251.02	10	201.9	150.22
200° Curve		Plug 52	100° Curve		Plug 52
1	4.8	200.57	1	5.1	91.29
2	19.3	200.85	2	19.0	92.31
3	41.5	201.15	3	40.0	93.73
4	66.0	201.35	4	66.5	95.25
5	90.3	201.46	5	88.4	96.31
6	113.0	201.45	6	112.3	97.32
7	135.5	201.35	7	135.3	98.08
8	158.2	201.17	8	158.6	98.68
9	179.9	200.85	9	179.6	99.09
10	201.9	200.69	10	201.9	99.44
50° Curve		Plug 52	0° Curve		Plug 43
1	4.8	35.68	1	1.9	24.95
2	19.0	37.38	2	18.7	21.51
3	40.4	39.80	3	42.0	17.20
4	66.2	42.31	4	65.4	13.40
5	87.7	44.15	5	87.9	10.27
6	112.3	45.92	6	113.1	7.28
7	134.9	47.30	7	135.8	5.05
8	158.1	48.54	8	157.4	3.13
9	176.3	49.28	9	179.8	1.46
10	193.5	50.01	10	201.8	0.13
			−51° Curve		Plug 43
			1	1.9	90.85
			2	16.5	85.34
			3	41.7	77.18
			4	65.1	70.77
			5	87.6	65.80
			6	112.8	61.14
			7	135.5	57.75
			8	157.4	55.05
			9	179.1	52.63
			10	201.8	50.94

In the early work duplication of each run with another plug having a different rate of flow was used to prove the negligibility of heat leaks and kinetic energy of flow effects. This has involved so much labor and the duplication has been so uniformly satisfactory, that it was not considered necessary here. The plugs employed had all given normal data in their previous use with nitrogen or helium. One curve, that at 50° was duplicated. It was considered that the uniformity with which the points lie on the curve, the consistency of the family of curves and of the family of their derivatives, gives sufficient assurance of the reliability of the data.

Isenthalpic Curves

The data of Tables II–V are plotted, respectively, in Figs. 1–4 with temperature as ordinate and pressure as abscissa. The coincidence of the points with the curves in the accurate plots from which these figures were traced, leaves very little to be desired.

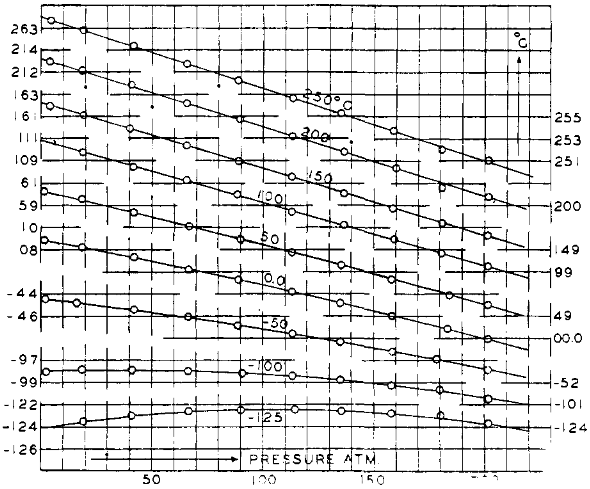

Fig. 1.—Isenthalpic curves, Mixture No. 1, He 75.5%. N 24.5%. Pressure in atm. (absolute), and temperature in °C.

The corresponding curves for pure helium[3] and for pure nitrogen[6] should be considered together with these four groups of curves for the four mixtures. In the resulting six figures, a comparison of the isenthalpic curves for any one bath temperature shows how the straight lines of negative slope for pure helium shift regularly to the concave-downward curves of large positive slope for ni-

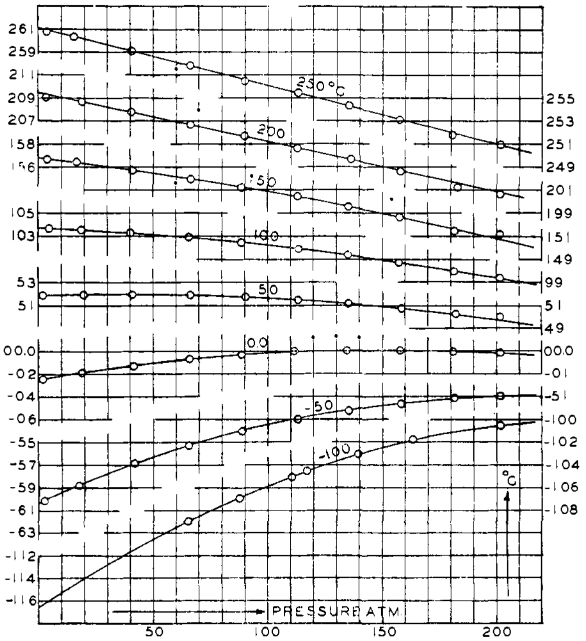

Fig. 2.—Isenthalpic curves: Mixture No. 2, He 51.0%, N 49.0%. Pressure in atm. (absolute) and temperature in °C.

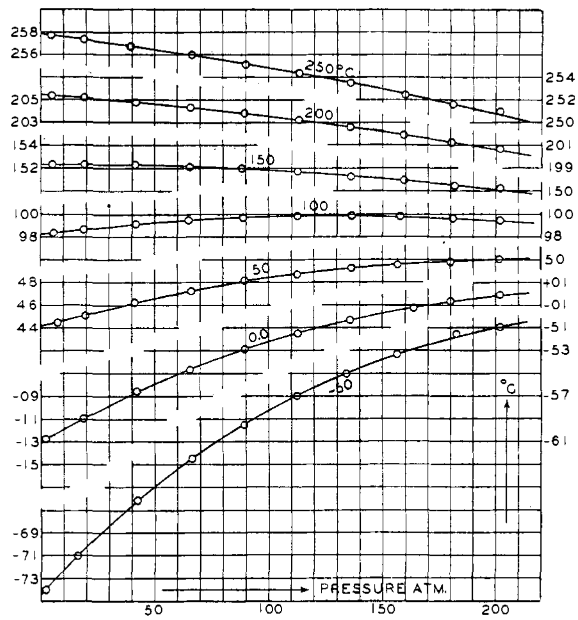

Fig. 3.—Isenthalpic curves: Mixture No. 3, He 33.2%, N 66.8%. Pressure in atm. (absolute) and temperature in °C.

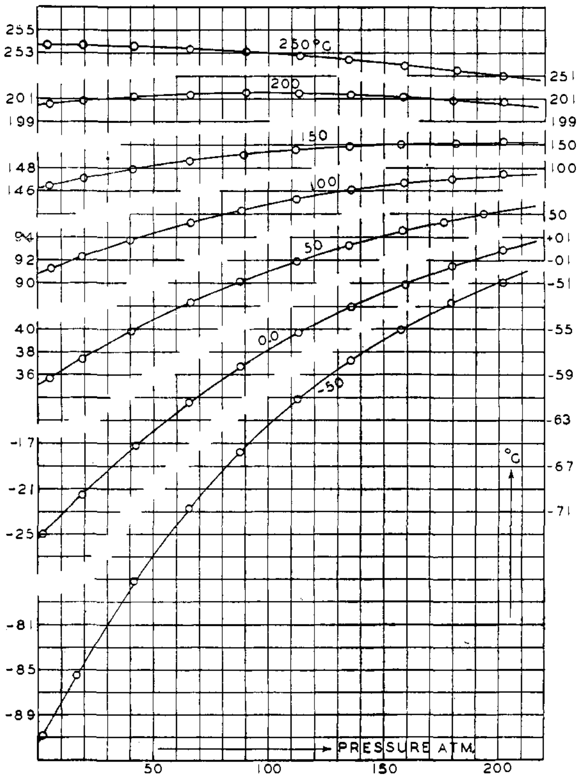

Fig. 4.—Isenthalpic curves: Mixture No. 4, He 16.6%, N 83.4%. Pressure in atm. (absolute) and temperature in °C.

trogen. The situation is the same as first observed in our mixture work with air in helium.[3]

To observe the effect of the composition and temperature on the total drop, the Δt for a pressure drop from 200 to 15 atm. was read off from these isenthalpic curves of Figs. 1–4. In Fig. 5 these values of Δt are plotted against composition, giving a set of curves one for each bath temperature. The four curves all have the same general character as Fig. 5 in the helium[3] article. The curve at 50° starts from the pure helium side practically horizontally and falls all the way to the nitrogen side. The curves at 250 and 150° show a slight increase in the temperature rise and at −50° a slight fall with the first additions of nitrogen to the pure helium.

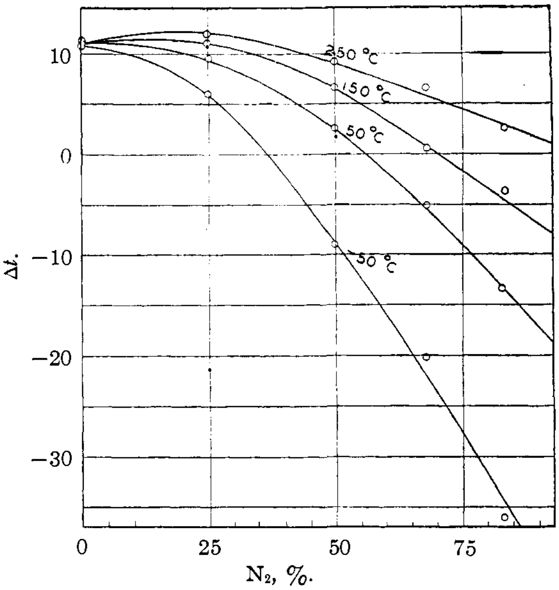

Fig. 5.—Δt for a ΔP of 200 to 15 atm., as a function of composition at a series of initial temperatures.

These slight rises and falls undoubtedly occur also in the helium–air case and modify the previous conclusions as to the allowable air impurity in the helium measurements. As now proves fortunate, air was kept out of the helium as perfectly as possible. The amount present at any time was so small that errors in the helium measurements, from these slight rises or falls, were much less than the errors from other causes.

The maximum slope on each of the curves of Fig. 5 falls at the pure nitrogen side and this maximum slope increases steadily with falling temperature. This latter trend will probably reverse at temperatures lower than those in Fig. 5 since the similar trend in pure nitrogen[6] reverses at these lower temperatures.

One is struck by the similarity between the family of isenthalpic curves for one gas (*e. g.*, for nitrogen) at a series of bath temperatures, and the family of curves corresponding to a series of compositions all at the same bath temperature. The shift down in temperature with the pure gas produces much the same series of changes as the increase in proportion of the higher critical temperature constituent.

Joule–Thomson Coefficient, $\mu = (dt/dp)_h$

As in previous work, the numerical values of μ are obtained by taking the ratio of the successive and corresponding differences of temperature and of pressure for each experimental run. These values of μ were plotted against the corresponding average pressure to give a set of isenthalpic curves for each mixture. In the large scale plot (25 × 40 cm.) the experimental points drop on smooth curves at least as well as with the nitrogen data, leaving in both cases only small irregularities to be smoothed out. It has not seemed necessary to reproduce these curves.

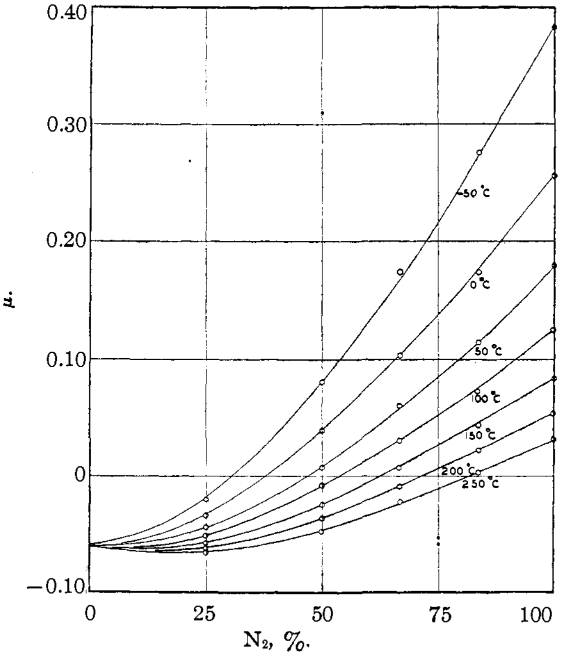

Fig. 6.—μ at 1 atm. as a function of composition at a series of temperatures.

To investigate somewhat further the quantitative effect on μ of the composition, data for μ at each of three pressures, 1, 100 and 200 atm. were collected for the four mixtures and also for

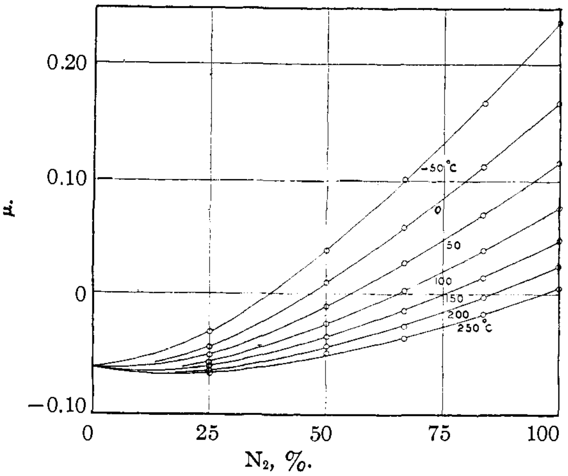

Fig. 7.—μ at 100 atm. as a function of composition at a series of temperatures.

pure helium and pure nitrogen. These data are plotted in Figs. 6, 7 and 8 as isothermals on a μ

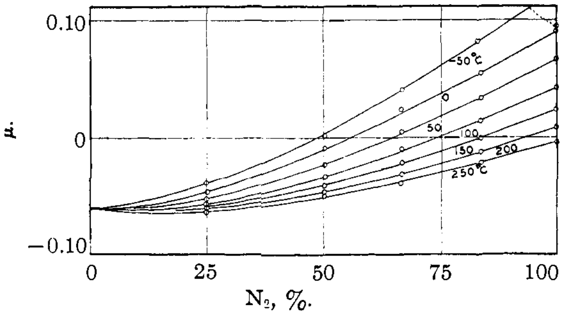

Fig. 8.—μ at 200 atm. as a function of composition at a series of temperatures.

versus composition diagram, one figure for each pressure. The points fall excellently on a very regular family of curves. The most notable characteristic of the families is that for all three pressures, and at the higher temperatures, the first additions of nitrogen to the helium make μ more negative. For the one atmosphere case at 250° it takes 37% N to restore the initial negative value of μ. In all three families the effect continues down to about 50°. This increased warming is also shown in Fig. 5 and was considered there. Until pv and C_p data are available for these mixtures, one cannot predict how the free-expansion coefficient, η, will be affected. Such data probably will suggest further refinements in the kinetic theory of gaseous mixtures.

From the unpublished curves referred to above values of μ for a series of selected pressures were read off and the corresponding temperatures read off from the isenthalpic curves of Figs. 2–5. These values of μ and t were then plotted as isopiestics. The four families of curves, one family for each mixture, are reproduced in Figs. 9–12.

The abscissa scale is the same in all four figures but the ordinate scale of 9 and 10 differs by a factor of two from that of 11 and 12. The four families resemble each other so greatly that it would appear possible to superpose them by a proper choice of both scales for each family. These four families of curves also resemble greatly the higher temperature portions of the corresponding families for air,[1] argon[5] and nitrogen.[6] All these resemblances suggest the extension of the theorem of corresponding states to cover gas mixtures.

The previous observation for the isenthalpic curves of Figs. 1–4, that the effect of a change in composition resembles greatly the effect of a change in temperature, holds again as regards μ in the curves of Figs. 9–12.

Numerical data for μ have been picked off the large scale plots from which Figs. 9–12 were traced and are collected in Tables VI–IX. The negative values for the higher temperatures with mixture 1 are definitely larger numerically than the corresponding value $\mu = -0.061$ for pure helium.[3] Nevertheless the inversion temperature is much higher for the mixture, *e. g.*, at 1 atm. 186°K. for mixture 1 and 23.6°K. for helium.

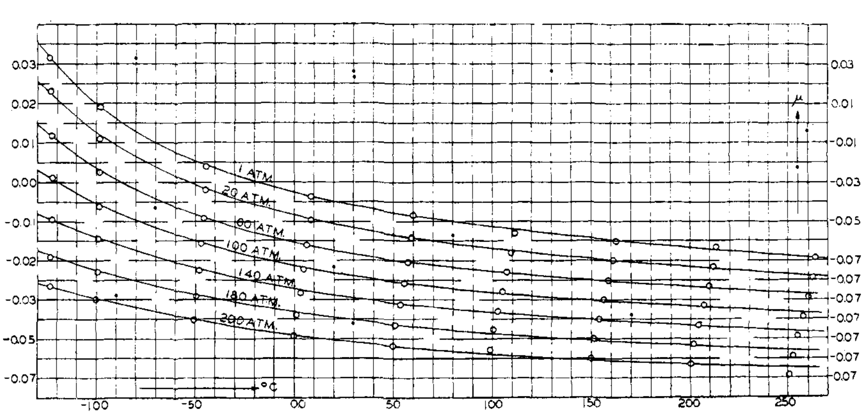

Fig. 9.—Mixture No. 1, μ as function of temperature at a series of pressures.

It is also curious that at the lowest temperature

TABLE VI

$\mu \times 10^2$; Mixture 1; He 75.5%; N_2 24.5%

t, °C.	p......1	20	60	100	140	180	200
250	−6.73	−6.68	−6.62	−6.61	−6.59	−6.56	−6.45
200	−6.31	−6.30	−6.32	−6.32	−6.32	−6.32	−6.27
150	−5.84	−5.90	−6.00	−6.01	−6.02	−6.08	−6.04
100	−5.26	−5.40	−5.57	−5.64	−5.66	−5.71	−5.76
50	−4.52	−4.68	−5.00	−5.10	−5.18	−5.28	−5.36
0	−3.50	−3.66	−4.07	−4.29	−4.44	−4.63	−4.79
− 50	−2.11	−2.21	−2.61	−3.00	−3.39	−3.72	−3.97
−100	+0.98	+0.52	−0.28	−1.03	−1.81	−2.49	−2.92
−125	+3.50	+2.66	+1.46	+0.32	−0.86	−1.69	−2.28

TABLE VII

$\mu \times 10^2$; Mixture 2; He 51.0%; N_2 49.0%

t, °C.	p......1	20	60	100	140	180	200
250	−4.82	−4.77	−4.89	−4.89	−4.91	−5.03	−5.05
200	−3.68	−3.71	−4.00	−4.23	−4.41	−4.61	−4.70
150	−2.46	−2.51	−2.98	−3.39	−3.72	−4.04	−4.18
100	−0.80	−1.03	−1.65	−2.27	−2.80	−3.28	−3.48
50	+1.21	+0.87	+0.10	−0.77	−1.50	−2.10	−2.39
0	+3.93	3.41	2.48	+1.26	+0.24	−0.56	−0.97
− 50	8.01	7.21	5.78	4.00	2.62	+1.41	+0.89
− 87.5	13.01	11.51	9.08	6.70	4.82	3.29	2.63

TABLE VIII

$\mu \times 10^2$; Mixture 3; He 33.2%; N_2 66.8%

t, °C.	p......1	20	60	100	140	180	200
250	−2.26	−2.42	−3.00	−3.54	−3.77	−4.02	−4.02
200	−0.93	−1.22	−1.84	−2.53	−2.81	−3.08	−3.22
150	+0.78	+0.38	−0.34	−1.19	−1.55	−1.98	−2.23
100	+2.97	+2.52	+1.52	+0.56	−0.11	−0.63	−1.02
50	6.00	5.34	4.03	+2.83	+1.86	+0.86	+0.41
0	10.28	9.38	7.44	5.93	4.36	2.78	2.03
− 50	17.42	15.84	12.63	10.08	7.73	5.00	4.00
− 87.5	26.65	24.03	18.76	14.58	10.87	6.91	5.62

TABLE IX

$\mu \times 10^2$; Mixture 4; He 16.6%; N_2 83.4%

t, °C.	p......1	20	60	100	140	180	200
250	+0.26	−0.03	−0.76	−1.41	−1.94	−2.17	−2.25
200	2.18	+1.74	+0.80	0.00	−0.63	−1.18	−1.33
150	4.39	3.92	2.72	+1.64	+0.84	+0.18	−0.19
100	7.33	6.66	5.22	3.98	2.82	1.87	+1.34
50	11.39	10.56	8.68	7.02	5.38	3.96	3.21
0	17.39	16.27	13.71	11.14	8.59	6.40	5.43
− 50	27.60	25.41	21.00	16.60	12.59	9.56	8.11
− 87.5	40.67	36.79	28.41	21.57	15.95	12.19	10.35

(−87.5°) and highest pressure (200 atm.) + μ = 0.1035 for mixture 4 is markedly larger than μ = 0.076 for pure nitrogen. This is doubtless connected with the rapid decrease of μ for pure nitrogen at somewhat lower temperatures. At the lower pressures the values of μ for mixture 1 are smaller than those for pure nitrogen.

Inversion Curves, $\mu = 0$

In all four families of curves, Figs. 9–12, the isopiestics intersect the ordinate $\mu = 0$. These intersections correspond to the points of horizontal tangency in the curves of Figs. 1–4. The data for these points are plotted in Fig. 13. The points fall on the curves remarkably well in view of the difficulty of locating maxima on curves of such small curvature. The four curves show very slight curvature concave downward, and they strike zero pressure without any observable change of curvature. The slope and slight curvature agree with the observed situation for air[1] and for nitrogen,[6] in both of which the lower branch of the curve was also observed. The nitrogen data seemed to require an upward bend as the upper branch approached zero pressure. The four curves here show no indication of such a bend. This casts some doubt on the reality of the bend in the nitrogen case, as indicated in the nitrogen[6] article.

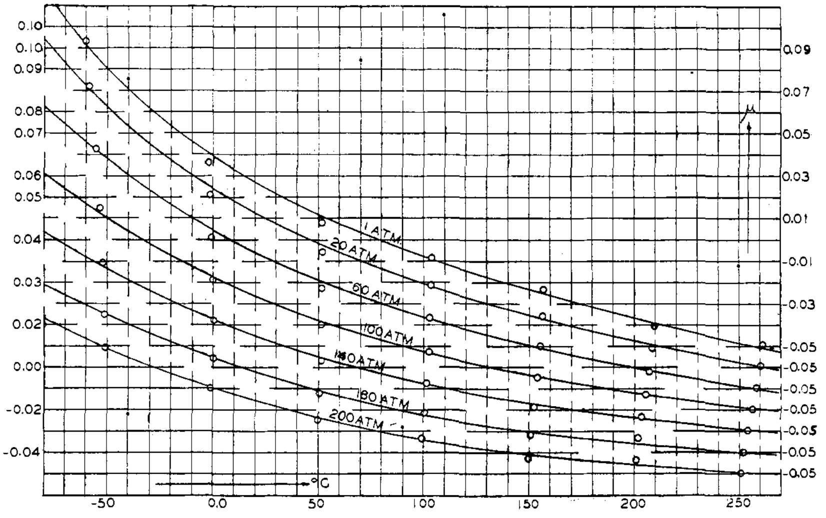

Fig. 10.—Mixture No. 2, μ as a function of temperature at a series of pressures.

The curves of Fig. 13 exhibit the shift of the maxima ($\mu = 0$) with pressure and temperature. In view of the behavior of pure gases, *e. g.*, nitrogen,[6] one would look for a lower branch of each of these curves as well as a maximum pressure.

To show its effect, composition is plotted in Fig. 14 as a function of temperature, for $\mu = 0$ and for $p = 1$, 100 and 200 atm. The resulting curves are almost straight and slope toward the higher nitrogen proportion at the higher temperature. The corresponding curves for the lower branch are estimated to be, of course, lower down on the temperature scale and somewhat less steep. The two series have to merge asymptotically into a common curve where the upper and lower branches of the inversion curves join.

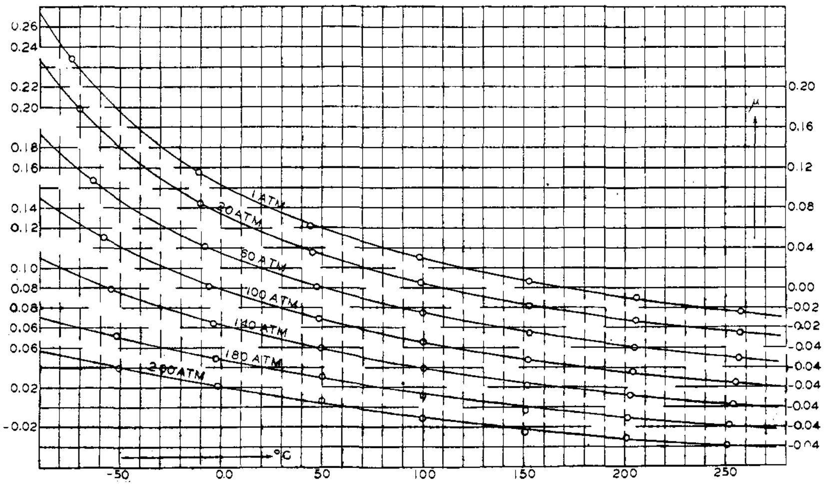

Fig. 11.—Mixture No. 3, μ as a function of temperature at a series of pressures.

In Fig. 14, curve for $p = 1$, the temperature at which $\mu = 0$ may be shifted between 0 and 100° as desired by adjustment of the composition. Equation 11 from an earlier publication[1]

$$\frac{V_{100}}{T_{100}} - \frac{V_0}{T_0} = -\int_{0^\circ\text{C.}}^{100} -\mu C_p \, dt^{-1} = I$$

may be written in the form

$$\frac{1}{\alpha} - T_0 = \frac{T_0(T_0 + 100)}{V_0 \, 100\alpha} I$$

where the integral I is a factor in the difference between the constant pressure gas thermometer reading, $1/\alpha$, of the ice point and its temperature reading T_0, on the Kelvin scale.[8] C_p in this integral is ordinarily a very slow function of the temperature. Hence this integral may be readily made zero by a suitable choice of composition. From the curve of Fig. 14 this composition will fall in the neighborhood of 46% by volume of nitrogen. With a constant pressure gas thermometer containing this mixture, the value of $1/\alpha$ is itself the Kelvin scale reading of the ice-point.

Wide Range Character of the Isenthalpic Curves for Any Gas

From the measurements already made upon the isenthalpic curves for air, helium, argon, nitrogen and some mixtures, together with the theorem of corresponding states, one can con-

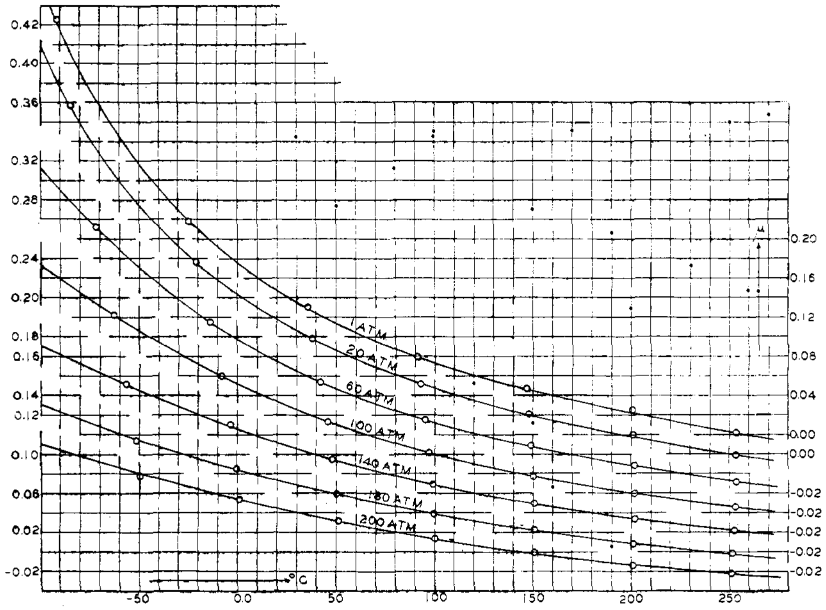

Fig. 12.—Mixture No. 4, μ as a function of temperature at a series of pressures.

struct a semiquantitative diagram, Fig. 15, of the family of isenthalpic curves covering a wide range of temperature and pressure. We have already measured helium at 111 times its critical temperature, T_c, and argon at 0.8 T_c. To represent the measured temperature range for helium on the same scale as used in Fig. 15 for the inversion curve would require over ten times the present height of the figure. To show the inversion curve in some detail, it is necessary to represent only a small part of the measured temperature range. The portion from 6 to 108 T_c is omitted.

At temperatures around 100 T_c—excluding cases involving ionization and chemical decomposition—the isenthalpic curves are nearly straight lines (probably slightly concave downward) of small negative slope. As one goes down in temperature the slopes remain negative and small in the whole field except within the boundary of the inversion curve (dashed-dotted line) which starts at about 5 T_c and $p = 0$, runs to the

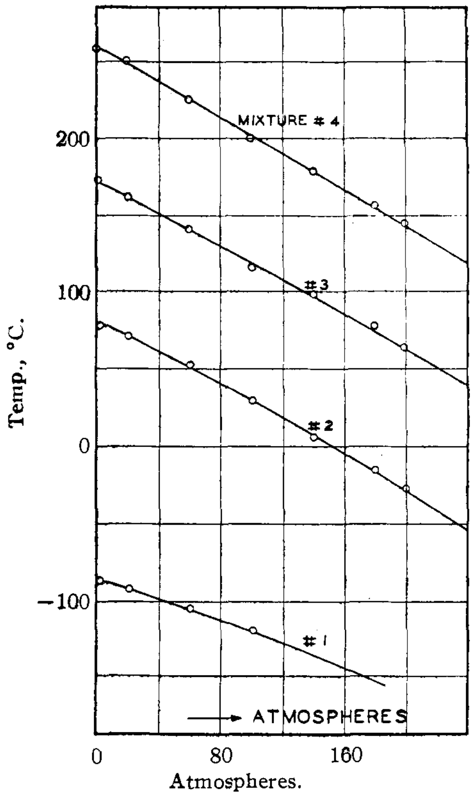

Fig. 13.—Inversion curves: temperature as a function of pressure for $\mu = 0$.

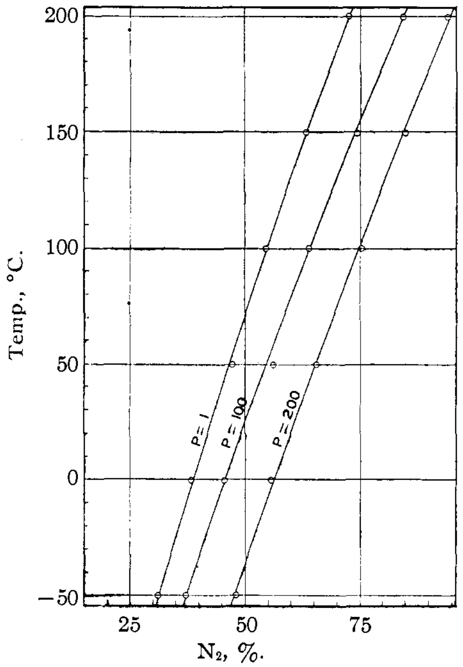

Fig. 14.—Temperature as a function of composition for $\mu = 0$ at 1, 100 and 200 atm. pressure.

right to about 2 × 5 T_c and 10 p_c and returns left to end at the vapor pressure curve a little below the point T_c p_c(C). The positive μ area within the inversion curve is but a very small part of the whole field. The predominant behavior of a gas is to warm on porous plug expansion. The whole field represented has been covered by the authors' experiments or by those of Bartlett and co-workers, reduced by Deming and Shupe.[10]

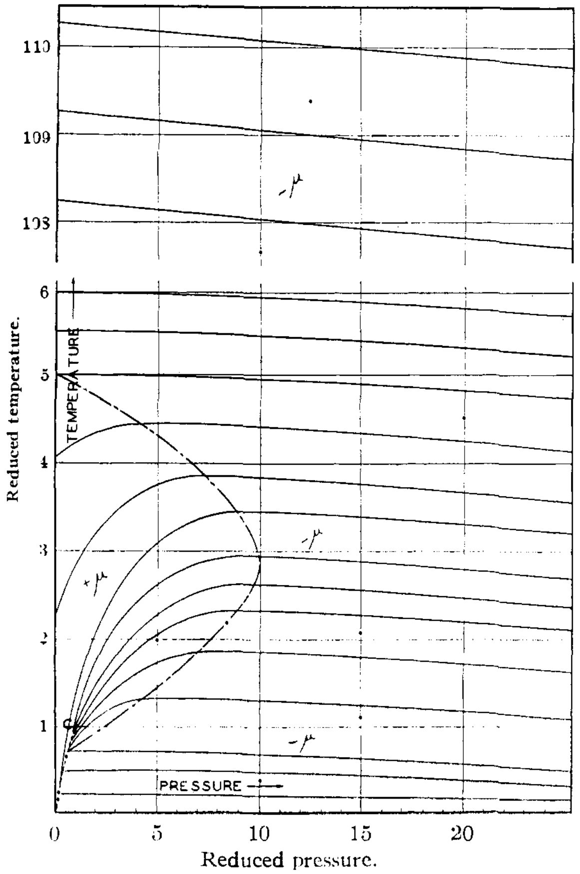

Fig. 15.—Isenthalpic curves over a wide range of temperature and of pressure for any gas. Reduced units.

Corresponding State Theorem for Mixtures

We will assume that the behavior of a mixture approximates that of an hypothetical pure (one molecular species) gas, whose critical temperature T_x is given by

$$T_x = T_1x + T_2(1 - x) \qquad (1)$$

where x is the proportion of constituent 1 in the mixture. That is we are assuming that the critical temperature of the hypothetical pure gas is a linear function of the difference of the critical temperatures of the constituents. We also assume that at any given reduced temperature and pressure, the slope of the isenthalpic curve is the same for all the mixtures, *i. e.*, the theorem of corresponding states is assumed to apply to the Joule–Thomson effect. Since the reduced temperature τ is equal to T/T_c, then as the critical temperature is raised from that of the first constituent of lower critical temperature, T_1, by admixture with the second constituent, the isenthalpic curves for the hypothetical pure gas corresponding to the mixture are shifted upward in actual temperature from those of the first constituent. That is, if the diagrams of isenthalpic curves, one diagram for each mixture, are arranged in order of increasing second constituent, the curve in each diagram for a given reduced temperature will fall at steadily higher actual temperatures. Or conversely, if one selects from each of these diagrams the isenthalpic curve taken at a particular actual temperature, and arranges the selected curves in the order of increasing proportion of second constituent, they will be in the order of decreasing reduced temperature and also in the order of increasing slope and curvature, particularly in the positive μ region. The rate of change of slope and curvature through the series is very small at first and increases with steadily increasing rapidity.

If now a pure gas of low critical temperature, *e. g.*, helium, is held at a high reduced temperature and there is steadily added at the same Kelvin temperature a gas of a much higher critical temperature, *e. g.*, nitrogen, the hypothetical critical temperature of the mixture moves steadily up the Kelvin scale. With this rise of critical temperature, the reduced temperature of the Kelvin temperature of mixing moves steadily down. Thus the character of the gas mixture, starting with isenthalpic curves of small negative slope and slight curvature, changes steadily down the reduced temperature diagram to stop finally at the pure second constituent of high critical temperature. The rate of change of character is at first very slow indeed, but accelerates till finally if the mixing temperature places the second constituent in the positive μ region, the rate becomes rapidly large. That is to say, small additions of nitrogen to helium at room temperature produce very small or unobservable changes in μ, while

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(7) Burnett, *Bull. Univ. Wisconsin*, **9**, No. 6, 77 (1926).

(8) Roebuck, *Phys. Rev.*, **50**, 370 (1936).

(9) M. Jakob, *Physik. Z.*, **22**, 67 (1921); A. Eucken, "Wien und Harmes Handbuch," Vol. VIII, part 1, p. 517.

(10) Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931).

small additions of helium to nitrogen produce large changes. This marked difference in the effect of the two constituents is the most outstanding characteristic of the experimental work described above for mixtures of helium and nitrogen, described in the paper[3] on helium for its mixtures with air, and to be described in a forthcoming paper on mixtures of helium and argon.

A quantitative test of Eq. (1) was obtained as follows. The hypothetical critical temperatures (t_c, °C. and T_c, °K.) were calculated for the mixtures of helium with air and with nitrogen. The results are presented in Table X along with the critical data for some pure gases. The upper inversion temperature for zero pressure has been observed for these gases, and the data are listed under t_i. For nitrogen[6] t_i is obtained by direct observation of the inversion curve; for air[1] it comes from a moderate extrapolation of the observed inversion curve; for argon[5] from a considerably more extensive extrapolation; for carbon dioxide[7] from a wide extrapolation by means of an empirical equation in Burnett's[7] work; and for hydrogen it comes from Jakob's[9] table and curves using the original data of Witkowski and Dalton. Witkowski's data for air do not agree with ours[1] by a considerable amount and it is doubtful whether his apparatus would give satisfactory data.

TABLE X

UPPER INVERSION TEMPERATURES FOR p = 0

Substance	t_c, °C.	T_c, °K.	t_i, °C.	T_i, °K.	τ_i	
N	−147.1	126.0	348	621	4.93	4.93
Air	−140.7	132.5	330	603	4.55	
Argon	−122.4	150.8	450	723	4.80	
CO_2	31.0	304.1			5.43	
H_2[9]	−240	33.2	− 78	195	5.89	
He + Air	−201.0	72.2	51.6	325	4.50	5.04
He + N_2 (1)	−237.8	35.40	− 87	186	5.25	
He + N_2 (2)	−207.6	65.60	78	351	5.35	
He + N_2 (3)	−187.0	86.15	171	444	5.15	
He + N_2 (4)	−166.5	106.7	257	530	4.97	

The reduced temperatures T_i of the inversion points for the pure gases (omitting hydrogen) run from 4.93 to 5.43 and are quite as close as the estimated precision of the measurements would lead one to expect. Evidently the theorem of corresponding states holds for the Joule–Thomson effect, at least within these limits.

The data for t_i in the air–helium mixture were obtained by an interpolation using the data given in the helium[3] article, with an estimated error of at least 5%. For the helium–nitrogen mixtures, the data of the present article fix t_i better than in any other known case.

The reduced temperatures T_i for the mixtures run from 4.50 to 5.35, that is, the spread is only slightly larger than that for the pure gases. For the He + N_2 case the spread is from 4.97 to 5.35, which is possibly a little larger than the estimated experimental error.

Thus within the limits of this constancy the theorem of corresponding states applies to the Joule–Thomson effect in mixtures as well as in pure gases. Also with the limits of this constancy, Eq. (1) holds, and consequently the hypothetical critical temperature as a linear function of composition is a useful working hypothesis.

Our thanks are due to the Wisconsin Alumni Research Foundation whose generous assistance enabled full time to be devoted to these problems.

The helium used here and in other work was supplied by the Bureau of Mines of the United States Government. We thank them for their help which made this extensive work with helium possible.

In this as in some other problems grants from the Rumford Fund of the American Academy of Arts and Sciences have been very helpful.

Much of the reduction of the experimental data and the preparation of many of the curves was carried out by Mr. L. Joos, whose assistance is gratefully acknowledged.

Summary

This article presents: (a) data and curves for the variation of the Joule–Thomson coefficient, μ, as a function of pressure (1–200 atm.), of temperature (−100 to 250°C.) and of composition, for four mixtures of helium and nitrogen. These are obtained from: (b) experimental data and curves for the isenthalps of these mixtures; (c) data for the inversion curves ($\mu = 0$); (d) a general picture of the isenthalpic curves; (e) an application of the theorem of corresponding states to the Joule–Thomson effect.

MADISON, WIS.

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