The Effect of Pressure on the Thermal Diffusion Ratio

H. G. Drickamer and J. R. Hofto

TABLE III. Comparison with data given by Fox and Hipple for isobutane.

Mass of ion	Slope in percent/°C	
		F–H
41	+0.4	+0.75
43	+0.4	+0.6
57	+0.3	+0.5

Stevenson, in a private communication, reports a closer correspondence between data taken on another Westinghouse instrument and these data.

Several general conclusions may be drawn from the data.

(1) The heavier the molecule, the greater the dependence of both relative abundances and sensitivity on temperature.
(2) Branched molecules show greater coefficients than their corresponding straight chain isomers.
(3) Olefins and diolefins show smaller temperature coefficients than their corresponding saturated compounds.

A final conclusion is that in view of the considerable magnitudes of many of the temperature coefficients, accurate analytical work requires some form of temperature control of the ion source.

* In a separate experiment, it was demonstrated that the gas entering the ion source came into thermal equilibrium with the walls of the source before ionization.
[1] R. E. Fox and J. A. Hipple, J. Chem. Phys. **15**, 208 (1947).
[2] D. P. Stevenson, J. Chem. Phys. **17**, 101 (1949).
[3] N. D. Coggeshall, J. Chem. Phys. **12**, 19 (1944).
[4] H. W. Washburn and C. E. Berry, Phys. Rev. **70**, 559 (1946).

The Effect of Pressure on the Thermal Diffusion Ratio

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ACCORDING to the theory of Enskog and Chapman[1] the thermal diffusion ratio should be independent of pressure at ordinary pressures. Experimental evidence is scanty and somewhat contradictory. Grew[2] shows data at two pressures for CO_2-H_2 which indicate the α is independent of pressure. Data obtained for the system $CO_2-C_3H_8$ in a column at pressures from 0.3 to 1.8 atmos.[3] indicate that either α varies with pressure for this system or that the theory of the column must be modified. This situation is being investigated exhaustively in this laboratory. As a preliminary step, runs were made over a series of pressures from 0.5 to 2.0 atmos. in the system argon-neon. The two-bulb set-up previously described[4] was used. The gases were analyzed in a thermal conductivity apparatus.[5]

The system was chosen because the molecules were spherically symmetrical and the system would be far above the critical temperature, offering the simplest possible place to start. The results are shown in Table I and Fig. 1. Some difficulty was experienced
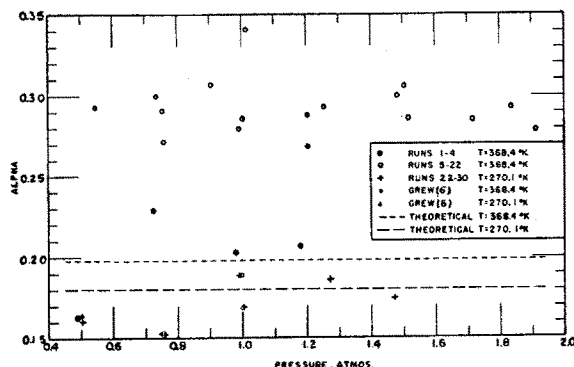

FIG. 1.

TABLE I. Thermal diffusion data.

Run No.	Pressure atmos.	Time hr.	$T_H °K$	$T_C °K$	$\%Ne_H$	$\%Ne_C$	Alpha
1	1.179	21.5	474	293	49.5	47.0	0.207
2	0.981	5.5	466	290	49.9	47.5	0.203
3	0.725	10.0	466	291	50.1	47.4	0.229
4	0.489	7.2	473	290	49.6	47.6	0.163
5	0.547	16.8	476	291	50.7	47.1	0.293
6	0.757	15.0	468	288	53.2	49.9	0.272
7	1.012	8.3	476	291	54.0	49.8	0.341
8	1.202	10.4	478	292	54.2	50.9	0.269
9	1.518	10.3	476	292	53.4	49.9	0.286
10	1.717	11.1	468	290	53.6	50.2	0.285
11	1.912	10.3	481	287	53.2	49.6	0.279
12	1.503	11.3	478	291	53.4	49.6	0.306
13	0.990	10.4	479	291	53.0	49.5	0.280
14	0.752	11.2	471	287	52.7	49.1	0.291
15	1.839	22.0	476	291	52.1	48.5	0.293
16	1.462	10.3	477	292	51.7	48.0	0.300
17	1.201	11.2	473	291	51.7	48.2	0.288
18	0.904	10.6	484	291	50.3	46.4	0.307
19	0.698	12.6	474	291	51.8	46.3	0.452
20	1.256	20.8	479	293	51.7	48.1	0.293
21	1.005	9.3	483	292	52.1	48.5	0.286
22	0.733	12.7	479	293	51.7	48.0	0.300
23	0.990	5.8	382	198	50.6	47.5	0.189
24	0.751	5.8	379	197	50.7	48.2	0.153
25	0.504	5.5	378	196	50.4	47.7	0.164
26	1.471	6.0	377	198	50.5	47.7	0.175
27	1.272	6.2	375	209	50.7	48.1	0.186
28	1.002	4.8	374	202	50.3	47.7	0.169
29	0.758	4.9	378	197	50.7	48.2	0.153
30	0.503	6.9	386	197	50.4	47.7	0.161

with the analyses at low densities. The theoretical lines were calculated using the Lennard-Jones model as previously described.[4] It can be seen that runs 1–4 and 22–30 agree well with the theory and with the data of Grew.[6] It is believed that a slight amount of air was present in the system for runs 5–22. It can be said that at low pressures and at temperatures well above the critical there is no effect of pressure on α. At lower temperatures some increase of α with pressure is possible. Measurements are now being made in a column at pressures up to 100 atmos. and in the neighborhood of the critical point.

[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1939).
[2] K. E. Grew, Nature **156**, 267 (1945).
[3] Drickamer, O'Brien, Brese, and Ockert, J. Chem. Phys. **16**, 122 (1948).
[4] Drickamer, Downey, and Pierce, J. Chem. Phys. **17**, 408 (1949).
[5] P. E. Palmer and E. R. Weaver, Tech. Pap. Bur. Stand. **18**, No. 29, 35–100 (1924).
[6] K. E. Grew, Proc. Roy. Soc. (London) **189**, 402 (1947).

The Near Ultraviolet Absorption Spectra of the Diazines

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ULTRAVIOLET absorption spectra of pyridazine[1] and pyrazine[1] vapors have been obtained for use in a "semi-empirical" evaluation of the C—N and N—N bond integrals and for additional data on nitrogen-containing compounds isoelectronic with benzene. Replacement .of CH groups in benzene by the more electronegative N atoms causes marked changes in the near ultraviolet spectrum. Pyridazine, pyrazine, and pyrimidine[2] have two medium to strong absorption transitions in the near ultraviolet—a diffuse system near 2500A and a sharp system at longer wavelengths. The diffuse system is composed of a series of broad bands with rather wide spacings, while the sharp system is built up of line-like bands. These sharp bands form short progressions with spacings (332–398, 474–485, 532–585, 936–968, 957–1014 cm⁻¹)

TABLE I. Near ultraviolet absorption by diazine solutions.

System		Pyridazine*		Pyrazine**		Pyri-midine†
		Hexane	Water	Cyclohexane	Water	Water
Sharp	λ_0	~3700A	~3400A	~3330A	~3230A	~2950A
	λ_{max}	3400A	2990A	3270A	3000A	~2700A
	ϵ_{max}	~400	~355	1018	780	~400
Diffuse	λ_0	~2680A	~2600A	~2800A	~2800A	~2580A
	λ_{max}	2480A	2450A	2600A	2600A	2405A
	ϵ_{max}	~690	~1200	6350	6580	~2350

* R. C. Evans and F. Y. Wiselogle, J. Am. Chem. Soc. **67**, 60 (1945).
** This investigation.
† F. M. Uber and R. Winters, J. Am. Chem. Soc. **63**, 137 (1941).

similar to those of pyridine[3] and the monosubstituted benzenes.[4] The O—O transitions are the strongest lines in the sharp systems and occur at 26,656 cm^{-1} (3750A) for pyridazine, at 30,879 cm^{-1} (3238A) for pyrazine, and at 31,079 (3217A) for pyrimidine.

Both the band systems apparently correspond to "allowed" transitions by virtue of their intensities. The transition involved for the sharp system must be to a state with dimensions similar to those of the ground state because of the line-like character of the bands and the lack of long progressions. Yet the vibrational frequencies in this excited state seem comparable to those in the $^1B_{2u}$ benzene state (considering substituted benzenes). Assuming sp^2 hybridization for the valence electrons of both carbon and nitrogen atoms in the molecular plane, and considering only the π-electrons being mobile, as in benzene, transitions from the ground state to the lowest two excited singlet states are allowed for the diazines. This picture of the electronic levels is being investigated by a semi-empirical molecular orbital treatment.

Spectra of these compounds in solution are functions of the solvent and are displaced slightly from the vapor phase values. Values for λ_0 (long wave-length edge of the band), λ_{max}, and ϵ_{max} are given in Table I.

A detailed account of the observed bands and their assignments, and the results of investigations of possible electronic states involved, will be published in future papers.

[1] The authors wish to thank Dr. R. C. Evans for the sample of pyridazine and Mr. J. F. Bruesch for the sample of pyrazine.
[2] F. M. Uber, J. Chem. Phys. **9**, 777 (1941).
[3] H. Sponer and H. Stücklen, J. Chem. Phys. **14**, 101 (1946).
[4] R. C. Hirt and J. P. Howe, J. Chem. Phys. **16**, 480 (1948).

Raman Spectra of Certain Phosphoric Acids and Their Salts

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IN continuing the work indicated in a recent Letter to the Editor,[1] the following lines in Table I were found and their depolarization factors determined.

TABLE I.

HPO₃		NaPO₃		KH₂PO₂		NaH₂PO₂	
$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ
373	0.76	303	0.62	470	0.96	465	0.85
513	0.96	387	0.73	589	0.36	592	0.37
723	---*	662	0.15	784	0.56	784	0.52
897	0.07	1100	0.28	928	0.86	930	0.82
1073	0.14	1155	0.13	1046	0.20	1047	0.28
1179	0.33	1249	1.00	1087	0.97	1090	0.70
				1162	0.73	1157	0.78
				2356	0.37	2359	0.37

K₄P₂O₇		K₂H₂P₂O₇		Na₂H₂P₂O₇		K₂Na₂P₂O₇	
$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ
339	0.70	314	0.63	318	0.51	344	0.55
532	0.88	469	0.72	475	0.69	511	0.81
722	0.25	711	0.35	728	0.27	709	0.27
1027	0.15	952	0.34	956	0.18	1027	0.16
1118	0.67	1087	0.21	1103	0.22	1112	0.48
		1175	0.68				

H₃PO₄		KH₂PO₄		K₂HPO₄		K₃PO₄**		NaH₂PO₄	
$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ	$\Delta\nu$	ρ
366	0.64	379	0.39	394	0.79	420	0.58	383	0.87
508	0.74	514	0.52	537	0.89	573	0.71	511	0.87
918	0.18	753	---*	865	0.08	704	---*	886	0.08
1058	0.40	880	0.07	976	0.09	936	0.19	1062	0.14
		1069	0.10						
		1196	---*	1081	0.62	1014	0.58		

* The symbol --- indicates the lines were too faint for depolarization measurements.
** Repeated investigations do not show the very faint line 2385 which was reported earlier.

It is to be noted that some discrepancies between the values of the depolarization factors for similar salts are present. These are being investigated more closely and will be reported in a later paper.

[1] P. Hoffmann and T. J. Hanwick, "Raman spectra of certain phosphoric acids and their salts," J. Chem. Phys. **16**, 1163 (1948).