The Effect of Certain Column Variables on Thermal Diffusion

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or

$$\beta_{\text{spec}}^* = -6.8/2.1(3.14)^{\frac{1}{2}} = -1.8 \text{ ev}$$

if we assume $d = 1.5$.

This gives for δ the respective values -2.3 and -2.7 ev. The first choice gives the closest resemblance between benzene and borazole and

gives at the same time what is probably a reasonable value for δ.[2]

It can be seen from the formulas for $E_2 - E_1$ that the main reason for the higher frequency of the borazole spectrum as compared with benzene is the appearance of the parameter d in the formula for borazole.

The Effect of Certain Column Variables on Thermal Diffusion

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Tests have been made on two thermal diffusion columns with different annular spacing. The results indicate that the dependence of the separation on temperature and annular spacing predicted by Furry, Jones, and Onsager holds. The dependence on pressure is slightly different than was predicted. The possibility that the index of repulsive force may depend on the pressure is pointed out.

NOMENCLATURE

C_v = specific heat at constant volume
D_{12} = coefficient of ordinary diffusion
D_T = coefficient of thermal diffusion
g = gravitational constant
L = column length
p = pressure in atmospheres
q = separation factor $(X_1{}^T X_2{}^B / X_2{}^T X_1{}^B)$
T = absolute temperature, °K
$\bar{T}$ = arithmetic average temperature, °K
ΔT = temperature difference between hot and cold walls
v_1, v_2 = convection velocity of species 1, 2
X_1, X_2 = mole fraction of species 1, 2 in feed
$X_1{}^T, X_2{}^T$ = mole fraction of species 1, 2 in top reservoir
$X_1{}^B, X_2{}^B$ = mole fraction of species 1, 2 in b.t.m. reservoir
w = one half of annular spacing
α = thermal diffusion ratio = (D_T/D_{12})
δ, ϵ = empirical constants
η = viscosity
λ = thermal conductivity
ρ = density
ν = index of repulsive force in $F = -(K_{12}/r^\nu)$

INTRODUCTION

THERMAL diffusion—the transport of molecules caused by a temperature gradient, was predicted theoretically by Enskog[1] in 1911

and independently by Chapman[2] in 1916. Its existence was confirmed experimentally by Chapman and Dootson[3] in 1917. With the development of the thermal diffusion column with hot wire by Clusius and Dickel[4] and the refinement to a concentric tube column by Brewer and Bramley,[5] it became a practical process for isotope separation.

Furry, Jones, and Onsager[6] and later Furry and Jones[7] have presented an extensive analysis of the theory of the column. This paper reviews their results briefly and compares the predicted effect of certain column variables on the separation with experiment.

THEORY

Furry, Jones, and Onsager[6] use the defining equation:

$$X_1 X_2 (v_1 - v_2) = -D_{12} \operatorname{grad} X_1 + D_T \operatorname{grad} \ln T, \quad (1a)$$

[1] D. Enskog, Physik. Zeits. **12**, 56, 533 (1911).
[2] S. Chapman, Phil. Trans. **216A**, 279 (1916).
[3] S. Chapman and F. W. Dootson, Phil. Mag. **38**, 248 (1917).
[4] K. Clusius and G. Dickel, Naturwiss. **26**, 546 (1938).
[5] A. K. Brewer and A. Bramley, Phys. Rev. **55**, 590(A) (1939).
[6] W. H. Furry, R. C. Jones, and L. Onsager, Phys. Rev. **55**, 1083 (1939).
[7] W. H. Furry and R. C. Jones, Rev. Mod. Phys. **18**, 219 (1946).

or

$$X_1X_2(v_1-v_2)$$
$$=D_{12}(-\text{grad}X_1+X_1X_2\alpha \text{ grad ln}T), \quad (1')$$

for the thermal diffusion coefficient, D_T, and thermal diffusion ratio, α. Applying the Navier Stokes Law for viscous flow to a simplified hydrodynamical model of the column, a general differential equation is obtained expressing the flux of one component in terms of the molecular properties of the gas and the constants of the column.

To solve this equation it is necessary to know the temperature dependence of the molecular properties and, therefore, to select a satisfactory molecular model. One of the simplest models giving approximately satisfactory results is the point source of repulsive force model,

$$F=(-K_{12}/r^\nu). \quad (2)$$

For this model Chapman and Cowling[8] give the following relationships for the gas coefficients:

$$\eta=\Omega(T, m, \nu)=\Omega'T^{(\nu+3)/2(\nu-1)}, \quad (3a)$$

$$D_{12}=\psi(T, m, x, \nu, p)=\psi'\frac{T^{(3\nu+1)/2(\nu-1)}}{P}, \quad (3b)$$

$$\lambda=\gamma(\nu)\eta C_v, \quad (3c)$$

$$\alpha=\varphi(\nu, m, x)(\nu-5/\nu-1), \quad (3d)$$

$$D_T=X_1X_2\alpha D. \quad (3e)$$

It should be pointed out that more accurate molecular models indicate that α depends on the temperature.

The general equation cannot be solved, but if one ignores vertical diffusion the equation simplifies and can be solved using (3a)–(3d). A correction for vertical diffusion can then be appended to the solution. The solution is particularly simple if one considers that the temperature dependence of D_{12}, η, and λ is that of Maxwellian molecules ($\nu=5$). For many gases this simplification adds little inaccuracy.

One then obtains for the separation factor

[8] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (The Cambridge University Press, New York, 1939).

$q=(X_1^TX_2^B/X_2^TX_1^B)$ the relationship

$$\ln q=\frac{63L\alpha D_{12}\eta f(\Delta T/\bar{T})}{2\omega^4\rho g}$$
$$\times\left[\frac{1}{1+5670(D_{12}\eta\bar{T}/\omega^3g\rho\Delta T)^2}\right]. \quad (4)$$

The factor in the brackets is the correction for vertical diffusion.

The quantity $f(\Delta T/T)$ is essentially equal to one for $(\Delta T/T)\leqslant 0.50$.

Solving Eq. (4) for the thermal diffusion coefficient one obtains

$$D_T=\frac{2}{63}\frac{X_1X_2\omega^4\rho g \ln q}{L\eta}$$
$$\times\left[1+5670\left(\frac{D_{12}\eta\bar{T}}{\rho g\omega^4\Delta T}\right)^2\right]. \quad (5)$$

It is the purpose of this paper to consider the effect of certain column variables on the separation and to compare predicted values with experiment.

Assuming the Maxwellian temperature dependence of D_{12}, and η, α independent of temperature, and the ideal gas law, one obtains for (4)

$$\ln q=\frac{C_1\bar{T}^4}{\omega^4P^2}\left[\frac{1}{1+(C_2\bar{T}^{10}/P^4\omega^6)}\right], \quad (4')$$

where C_1 and C_2 are independent of T, p, and W. Equation (4') can be maximized with respect to p, T, or W at constant values of the other two variables. Figure 1 shows $\ln q$ plotted against pressure, with temperature and W as parameters. For this case the following values were assumed for the different variables:

$$L=250 \text{ cm}$$
$$D_{12}=0.1\times10^{-5}T^2$$
$$\eta=0.3\times10^{-4}T$$
$$\rho=0.488(T/P)$$
$$\alpha=0.012$$

Different values for these functions would merely shift the curves without changing the qualitative relations discussed below.

From this diagram it is convenient to study variations of $\ln q$ with (1) p and T at constant W, (2) p and W at constant T, (3) T and W at constant p.
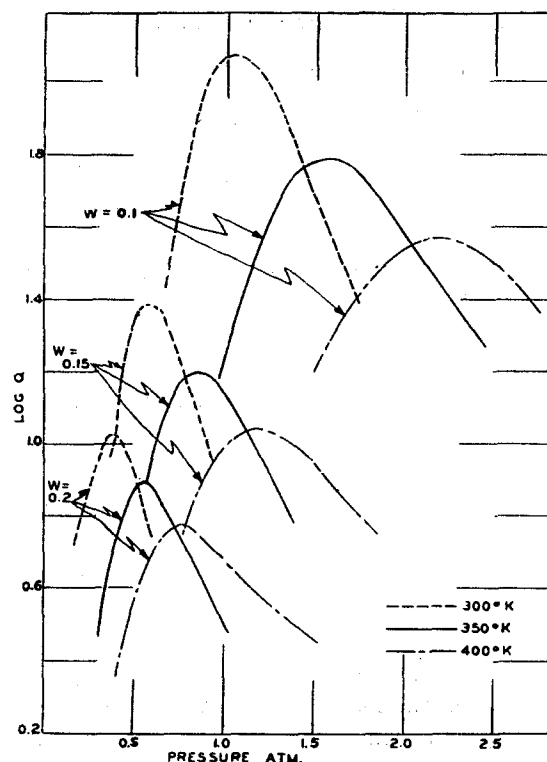
FIG. 1. Effect of temperature, pressure, and annular spacing on separation factor q.

The first category corresponds to the problem of establishing optimum operating conditions in an existing column. The second or third would be involved in design considerations where the temperature or pressure were fixed within narrow limits by external circumstances.

At constant W one can always improve the separation by decreasing the temperature and pressure approximately in such a manner that $(C_2 \bar{T}^{10})/(W^6 p^4)$ always equals one.

At constant temperature the separation can always be improved by increasing p and decreasing W, subject to a similar limitation.

Likewise, at constant pressure the separation can be improved by decreasing $\bar{T}$ and W as above.

The possibility of improving the separation by adjusting the above variables is subject to further limitations, as pointed out by Furry and Jones,[7] because of remixing due to asymmetry, remixing due to turbulence, and unduly long separation times.

The possibility of asymmetry in construction, which would cause remixing currents, increases with decreasing W and therefore limits the feasibility of moving indefinitely in this direction.

The Reynolds number, which is a measure of turbulence, is defined by Onsager and Watson[9] as proportional to $(W^3 p^2 \Delta T / \bar{T}^5)$. This limits the possibility of large pressure increases except at very small values of W, very high temperature, or very low values of ΔT. These factors are subject to further limitations discussed below.

The relaxation time is roughly proportional to $(\bar{T}^{10} L)/(W^7 p^5 (\Delta T)^2)$. This imposes a limitation on the feasibility of decreasing W, p, or $\Delta \bar{T}$ indefinitely, or of operating at very high temperature. It also limits the practical length of a column. These problems, including the practicality of multi-stage and continuous operation are discussed in detail by Furry and Jones.[7]

The following sections present the results of experiments performed on two single-stage batch columns connected to reservoirs on each end, to test certain of the relationships described above.

TABLE I. Constant pressure data $p = 1.118$ atmos.

Column I Run No.	Av. Temp.°K	Feed	Percent CO$_2$ Top	B.t.m.	ln$q$
1	382	54.41	57.72	48.38	0.376
1	382	54.41	57.59	48.85	0.352
2	362	54.22	56.91	49.11	0.314
2	362	54.22	55.98	48.52	0.299
3	334	58.34	57.83	50.86	0.281
3	334	58.34	57.44	50.66	0.273
4	379	57.07	59.48	49.40	0.408
4	379	57.07	59.65	49.56	0.409
5	356	56.89	58.10	49.73	0.337
5	356	56.85	56.90	49.60	0.295
6	311	55.47	56.38	51.54	0.195
6	311	55.47	55.77	50.94	0.194
7	334	57.57	59.76	53.95	0.237
7	334	57.57	59.66	53.79	0.237
8	357	53.50	56.67	49.38	0.293
8	357	53.50	56.41	49.09	0.294
9	398	52.68	57.45	48.10	0.376
9	398	52.68	57.20	48.96	0.376

Column II					
10	405	58.22	77.73	36.29	1.813
10	405	58.22	79.44	35.06	1.968
11	379	55.29	74.29	35.55	1.576
11	376	55.30	73.51	36.46	1.304
12	355	55.83	68.94	37.64	1.317
12	353	55.84	68.82	37.17	1.320

[9] L. Onsager and W. W. Watson, Phys. Rev. **56**, 474 (1939).

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Experiments were performed on two concentric tube columns each 244 cm long and connected to 200-cc reservoirs at each end. Column I had an annular spacing of 0.456 cm ($W=0.228$) and column II an annular spacing of 0.308 cm ($W=0.154$ cm).

The outside wall was cooled by circulating cooling water through a jacket. The water was maintained at $16.5\pm1°C$ and never gained over $1°C$ in passing through the column. The inner wall was heated by radiant energy from a hot wire passed up the inside tube and held in place by ceramic spaghetti and spacers. The inside tube was sealed off and evacuated to eliminate convection currents.

The inside wall temperatures were measured by means of thermocouples inserted in the inside tube from each end and held in place by spring steel rings. The whole thermocouple, except for the head which was protected by the ring, was insulated to prevent exposure to radiation.
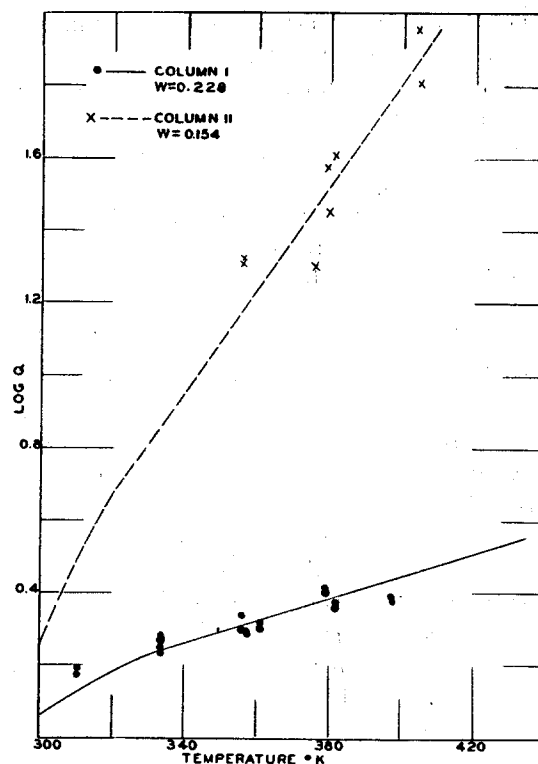
On the average, the top and bottom tempera-

TABLE II. Constant temperature data $T=380°K$.

Column II Run No.	Pressure (Atmos.)	Feed	Percent CO_2 Top	B.t.m.	ln$q$
1	1.116	56.15	74.61	37.03	1.610
2	0.836	55.02	72.80	36.92	1.520
2	0.845	55.02	72.42	37.34	1.483
3	0.625	51.02	64.98	38.95	1.068
3	0.631	51.02	64.48	38.24	1.076
4	0.397	50.07	56.48	43.47	0.523
4	0.390	50.07	55.68	42.36	0.536
5	0.998	53.21	70.95	34.81	1.521
6	0.682	51.47	65.50	36.97	1.175
6	0.686	51.47	65.24	36.13	1.199
7	1.410	55.16	67.23	40.20	1.112
7	1.395	55.16	67.43	39.51	1.154
8	0.510	51.30	62.39	42.84	0.795
8	0.510	51.30	62.79	42.37	0.831
9	0.744	53.63	67.34	34.64	1.359
9	0.744	53.63	66.69	34.71	1.326
10	1.593	57.44	67.87	42.96	1.032
10	1.590	57.44	67.66	43.08	0.994
11	1.248	56.48	71.03	40.08	1.299
11	1.247	56.48	71.70	40.12	1.330
12	0.312	55.14	56.24	48.75	0.301
12	0.309	55.14	56.21	49.13	0.285
13	1.805	49.58	62.97	41.99	0.854
13	1.805	49.58	63.01	42.40	0.839
14	1.153	53.49	68.97	36.01	1.374
14	1.143	53.49	68.91	35.14	1.409
15	1.082	53.49	69.59	34.67	1.462
15	1.082	53.49	69.51	34.96	1.445
16	0.924	53.49	69.66	34.21	1.485
17	0.433	51.08	58.56	43.31	0.615
17	0.439	51.08	58.40	41.67	0.676

FIG. 2. Comparison of experimental and predicted separation factor as a function of temperature and annular spacing.

ture differed by $6°C$ with a maximum difference of $12°C$. It is felt that this difference represents errors in thermocouple readings due to exposure to radiation rather than actual differences in wall temperature.

The gases used were carbon dioxide obtained from the Ohio Chemical Company and 99.9 percent propane obtained from the Matheson Company. The method of purification and analysis followed closely that described by Wall and Leaf,[10] making use of a Zeiss portable interferometer for analyses, with purified propane being the reference gas.

The two columns were operated over a range of average temperature of $311°K–405°K$ at 1.118 atmospheres pressure. The average temperature was considered to be the arithmetic average of the hot and cold wall temperatures. Then column II was operated at pressures from 0.309–1.805 atmospheres with a constant average temperature of $380°K$.

[10] F. T. Wall and B. Leaf, J. Phys. Chem. 46, 820 (1942).

The feed analysis was maintained substantially constant at 55 percent carbon dioxide throughout. The experimental results are presented in Tables I and II.

Runs were continued until samples indicated no further change in analyses. In general, the first sample was not taken until at least four times the approximate relaxation time, as discussed by Furry and Jones,[7] had elapsed.

COMPARISON OF THEORY AND EXPERIMENT

The first constant pressure runs on column I indicated that the best value of v for the point source of repulsive force model was 6.15. Using this value and the equations of Chapman and Cowling,[8] Chapters 9 and 10, to predict α and D, and the data of Trautz and Kurz[11] for the viscosity of carbon dioxide-propane mixtures, values of $\ln q$ were calculated from Eq. (4). In Fig. 2 these values are compared with the experimental values of $\ln q$ taken from Table II. The agreement obtained for the two columns indi-

FIG. 3. Comparison of experimental and predicted effect of pressure on the separation factor.

[11] M. Trautz and F. Kurz, Ann. d. Physik 9, 981 (1931).

cates definitely that the dependence of $\ln q$ on W is correctly predicted by Eq. (4). Also, the equation appears to predict the correct dependence of $\ln q$ on the temperature over the temperature range covered. It should be pointed out that since the cold wall temperature was fixed, it was not possible to vary the average temperature, $\bar{T}$, independently of ΔT.

Seventeen runs were made at different pressures using column II. Since these data were the last obtained, after operating and analytical techniques had been perfected, it is felt that these runs are the most reliable ones.

Evaluating the constants in Eq. (4) from data in the literature or in the case of α and D_{12} from theory (using the 6.15 point source model) one obtains an equation for $\ln q$

$$\ln q = \frac{2.60}{P^2}\left[\frac{1}{1+(0.495/P^4)}\right]. \quad (6)$$

Figure 3 compares experimental values of $\ln q$ with those predicted from Eq. (6). It can be seen that the general shape of the two curves is the same, but that the agreement is quantitative only in the pressure region around 1.2 atmospheres where the value of $v = 6.15$ was first established from experiment. Further, it can be seen that no adjustment of the non-pressure dependent variables will bring the curves into agreement.

Possible reasons for the discrepancy include: (1) Some consistent experimental error. (2) The lack of spherical symmetry of the molecules, whereas the equations are derived for spherically symmetrical molecules. (3) The use of the inverse power model and of the Maxwellian model for D_{12}, η, and λ. (4) The method of solution of the differential equation for diffusion used by Furry, Jones, and Onsager,[6] first ignoring vertical diffusion and then appending a correction for it. (5) The possibility that v and, therefore, α may depend on the pressure. Considering these in order, no source of consistent error in the experimental work was discovered.

The second possibility can only be tested by the use of spherically symmetrical molecules, such as the rare gases. There appears, however, to be no *a priori* reason why the lack of spherical symmetry should affect the pressure dependence at these low pressures.
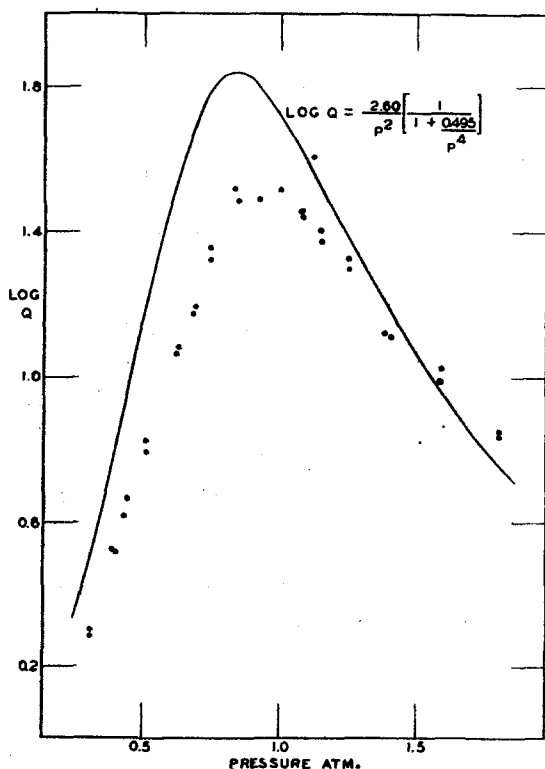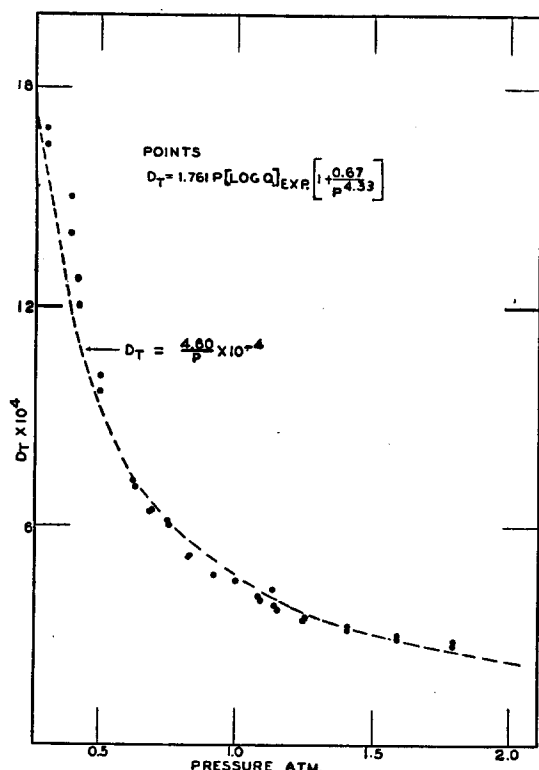
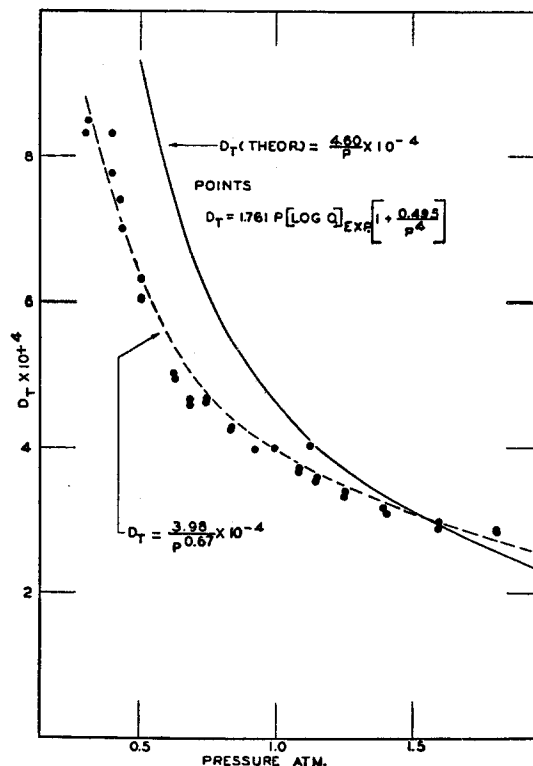FIG. 4. Comparison of theoretical values of D_T with those predicted from empirical Eq. (8).

FIG. 5. Comparison of values of D_T predicted from Eq. (5) with values obtained from Eq. (13) when V is taken to be a function of pressure.

Third, the inverse power model is known to be somewhat crude. However, the more refined models so far studied do not predict any different pressure dependence for the gas coefficients.

The fourth possibility is not so easily disposed of. The fact that Eq. (4) predicts the correct temperature and W dependence for $\ln q$ indicates that its form is correct. If one considers an empirical equation of the form:

$$\ln q = \frac{2.60}{P^2}\left[\frac{1}{1+(\delta/P^\epsilon)}\right], \tag{7}$$

values of δ and ϵ can be obtained from experimental values of $\ln q$, and Eq. (7) becomes

$$\ln q = \frac{2.60}{P^2}\left[\frac{1}{1+(0.67/P^{4.33})}\right]. \tag{7'}$$

Equation (5) for D_T, calculated from experimental data, is then modified

$$[D_T]_{\text{exper.}} = 1.761$$
$$\times 10^{-4}P\left[1+\frac{0.67}{p^{4.33}}\right][\ln q]_{\text{exper.}}. \tag{8}$$

Using the relations of Chapman and Cowling,[8] one obtains the equation

$$D_T = (4.60\times 10^{-4})/p, \tag{9}$$

with the 6.15 inverse power model. Figure 4 compares values of D_T predicted from Eq. (9) with those calculated from Eq. (8). Since the 6.15 model was used in obtaining α for Eq. (7') the agreement is to be expected.

The fifth possibility has no direct theoretical basis. If the inverse power model were really adequate, ν would be independent of temperature and pressure. However, in comparing viscosity data with theory it is found that ν must be considered a function of temperature to obtain agreement between theory and experiment. There is evidence from viscosity investigations at elevated pressures that ν may increase with pressure. Chapman and Cowling[8] point out that the solid elastic spherical model ($\nu = \infty$) gives a better fit for nitrogen at high pressures than at atmospheric pressure where $\nu = 8.8$. The data of

Comings, Egly, and Mayland[12] indicate that for numerous gases the temperature dependence of the viscosity decreases with increasing pressure even at relatively low pressures in the neighborhood of 10–20 atmospheres.

The temperature dependence of the viscosity is given by

$$\eta_2/\eta_1 = (T_2/T_1)^S, \qquad (10)$$

where

$$S = \tfrac{1}{2} + (2/\nu+1). \qquad (11)$$

So a decreasing value of S corresponds to an increasing value of ν and, thus, to a "hardening" of the molecular model with increasing pressure. If ν were only slightly pressure dependent, the value of S would not vary noticeably with pressure at ordinary pressures, but α, which is very sensitive to changes in ν, might vary appreciably.

If one substitutes Eq. (3d) for α in Eq. (4), considering $\varphi(\nu)$ as a constant to be evaluated at a pressure where the theoretical and experimental values of $\ln q$ coincide, one obtains as an approximate equation for ν over the pressure

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[12] E. W. Comings, R. S. Egly and J. C. Mayland, University of Illinois Exper. Stat. Bull. 354 (1944).

range covered:

$$\nu = \frac{5 - 0.206p^{0.333}}{1 - 0.206p^{0.333}}. \qquad (12)$$

Using this value in the theoretical equations one obtains approximately

$$D_T = \frac{3.98 \times 10^{-4}}{p^{0.67}}. \qquad (13)$$

The values of D_T predicted from this equation agree closely with those calculated from experiment by Eq. (5), which becomes

$$D_T = 1.761p[1 + (0.495/p4)] \\ \times (\ln q)_{exper.} \times 10^{-4}. \qquad (14)$$

This agreement is shown in Fig. 5.

Considerably more experimental work would be necessary before one could put much reliance in Eq. (12) for ν and use it to extrapolate to higher pressures or to other systems. If such a relationship is really general it would provide an incentive for operating thermal diffusion columns at slightly elevated pressure.

The C—H Bond Energy in Toluene and Xylenes

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(Received October 15, 1947)

The pyrolysis of toluene and the xylenes was investigated by a new technique, which made it possible to study these reactions for degree of decomposition ranging from 0.01 percent up to a few percent. It was shown that these reactions are homogeneous, unimolecular reactions. It was found that the weakest bond in these molecules is the C—H bond in the methyl group. The bond energy of that C—H bond was found to be 77.5 kcal. for toluene and meta-xylene, 75 kcal. for para-xylene and 74 kcal. for ortho-xylene. These data indicate that the resonance energy of the benzyl radical is 24.5 kcal. and that the hyper-conjugation in para-xylene decreases the C—H bond energy in the methyl group of this molecule by 2.5–3 kcal.

A RECENT investigation of the pyrolysis of benzyl iodide by C. Horrex[1] and the author revealed the great stability of the benzyl radical. This work gave rise to the suspicion that the resonance energy of the benzyl radical

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[1] This will shortly be published elsewhere.

is much higher than was previously thought and the present study was started in the hope of further clarifying this point. It was decided to investigate the pyrolysis of toluene, and in particular the nature of the first step of its decomposition.