

RELAXATION EFFECTS AND THE HEAT TRANSFER IN A CHEMICALLY REACTING GAS MIXTURE WITH INERT DILUENTS

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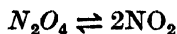
ABSTRACT. The authors' recent analysis of thermal conductivity of reacting gas mixtures, for detecting the effect of chemical reaction upon the binary diffusion coefficients between the unlike components of the mixture, has been extended to reacting gases diluted with inert gases. Existing thermal conductivity data of the reacting $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system diluted with helium and argon have been analysed. The results show that the theory of heat transport in reacting gases is still inadequate to account for the relaxation of chemical energy in diluted reacting gas systems.

INTRODUCTION

It has long been known that the heat transport in a reacting gas mixture may be augmented by the flow of molecular enthalpies along a diffusion current across the system. The composition of the gas mixture, which is determined by the equilibrium relationships at the ambient temperature, varies across the system due to the temperature gradient and thus mass-gradients are set up which cause the diffusional flow of the reacting species. If the system is in local chemical equilibrium, these mass gradients can be determined directly from the boundary conditions.

It is, however, only for very fast reactions that the condition of local chemical equilibrium is satisfied. At low reaction rates, effects of relaxation of chemical energy come into play and the simple relation between the temperature gradient and the mass gradients breaks down, with a consequent decrease in the mass gradients from the equilibrium value. Hence the analytic expression for the reactive thermal conductivity (Butler *et al*, 1957, Brokaw, 1960) which applies for the condition of local equilibrium has to be corrected for relaxation effects for systems with low or intermediate reaction rates. The most comprehensive treatment of the thermal conductivity of reacting mixtures with intermediate reaction rates has been given by Brokaw (1961), who introduced the relaxation correction in terms of the boundary conditions of the system and showed that the effective thermal conductivity may depend on the apparatus geometry and scale.

The reacting system which has been most widely studied is the dissociating nitrogen tetroxide gas :



For a reaction of this type, the ‘chemical’ thermal conductivity is given by

$$\lambda_R = \frac{pD_{12}}{RT} \left(\frac{\Delta H^2}{RT^2} \right) \frac{x_1 x_2}{(1+x_1)^2} \quad \dots \quad (1)$$

where the indices 1 and 2 refer to the components N_2O_4 and NO_2 respectively, D_{12} is the binary diffusion coefficient, ΔH is the heat of reaction and x_1 and x_2 are the respective mole-fractions. It was shown by the authors in two recent publications (Rai Dastidar *et al.*, 1966, 1967) henceforth referred to as I and II that, as an effect of the chemical reaction, the binary diffusion coefficient D_{12} was somewhat lowered from the value obtained from the classical Chapman-Enskog theory. As a result, the chemical thermal conductivity defined in eqn. (1) should be revised to the form

$$(\lambda_R)_{eff} = \frac{(pD_{12})_{eff}}{RT} \left(\frac{\Delta H^2}{RT^2} \right) \frac{x_1 x_2}{(1+x_1)^2} \quad (2)$$

where $(D_{12})_{eff}$ is the ‘‘effective’’ diffusion coefficient between components 1 and 2 in the reaction. As $(D_{12})_{eff} < D_{12}$, $(\lambda_R)_{eff}$ must be smaller than λ_R , which corresponds to the local chemical equilibrium condition in the system. It was shown in ref. II that, when the thermal conductivity values were (i) free of, or (ii) corrected for, relaxation effects,

$$(\lambda_R)_{eff} = \lambda_{expt1} - \lambda_f \quad (2')$$

where λ_f is the ‘‘frozen’’ conductivity of the mixture in the absence of the reaction. Also, it follows that the experimental thermal conductivity should necessarily be smaller than the equilibrium value $\lambda_e = (\lambda_f + \lambda_R)$.

In a series of measurements, Coffin (1959) has determined the thermal conductivity of the reacting system $N_2O_4 \rightleftharpoons 2NO_2$ diluted with inert gases. It has been shown by Mark Cher (1962) that the probability of a collision of an N_2O_4 molecule with another molecule reacting in the dissociation or activation of the N_2O_4 molecule is governed by a ‘‘collision efficiency’’ of the other molecule, the efficiency of an N_2O_4 molecule being unity. Consequently, in a reacting gas diluted with some inert gas the speed of reaction may considerably go down, and it would be of interest to observe the effect of this lowering of reaction rate upon the influence of the chemical reaction upon the diffusion coefficient.

THEORETICAL

In his paper Coffin published the thermal conductivity measurements of diluted $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ system at three temperatures, with three different concentrations of the diluent for each temperature. The diluents used were Helium and Argon. The strength of the diluent was given in terms of the "atom fraction" a , defined as

$$a = \frac{p_3}{2p_1 + p_2 + p_3} \quad (3)$$

where the p 's are partial pressures and the indices 1, 2 and 3 refer to N_2O_4 , NO_2 and the diluent respectively. The molefraction x_3 of the diluent is of course given by

$$\frac{p_3}{p_1 + p_2 + p_3} = \frac{p_3}{P} \quad (4)$$

For such a ternary mixture with one inert component, the reactive conductivity is given by

$$\lambda_R = \frac{1}{RT} \left(\frac{\Delta H^2}{RT^2} \right) \left[\frac{(x_2 + 2x_1)^2}{PD_{12}x_1x_2} + \frac{x_3}{PD_{13}x_1} + \frac{4x_3}{PD_{23}x_2} \right]^{-1} \quad (5)$$

where x 's are the molefractions. The "frozen" conductivity λ_f can be calculated according to Hirschfelder-Eucken formula (Hirschfelder *et al*, 1954; Hirschfelder, 1957) for thermal conductivity of mixtures of polyatomic gases.

The molefractions x_1 , x_2 and x_3 can be calculated from the experimental "atom fraction" a as follows. Eqn. (3) can be re-written as

$$a = \frac{P - p_1 - p_2}{P + p_1} \quad (6)$$

Again, the equilibrium constant $K_p = \frac{p_2^2}{p_1}$; substituting this expression for K_p

in eqn. (6) it can be shown that

$$\begin{aligned} p_2 &= \frac{1}{2(1+a)} \left[\{K_p^2 + 4PK_p(1-a^2)\}^{\frac{1}{2}} - K_p \right] \\ p_1 &= p_2^2 / K_p \\ p_3 &= P - p_1 - p_2 \end{aligned} \quad (7)$$

The mole fractions are now directly obtained by dividing the partial pressures by the total pressure P . The equilibrium constant K_p for the dissociation $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ has been given (Bodenstein *et al*, 1922).

Values of the mole fractions thus calculated are given in table 1. The theoretical values of λ_f , λ_R and $\lambda_e(=\lambda_f+\lambda_R)$ along with the experimental conductivity values are given in Table II. For the calculation the Lennard-Jones (12 : 6) potential was used, the force constants for N_2O_4 and NO_2 being previously given by the authors (Barua *et al*, 1965). The usual combination rules (Hirschfelder *et al*, 1954) were used. The λ_e -values originally calculated by Coffin who used an older set of force constants given by Brokaw (1958), are also included in Table 2.

In order to analyse the effect of chemical reaction upon the diffusion coefficient, it was necessary to ensure that the experimental values were free from relaxation effects. For the nitrogen tetroxide dissociation, these effects are negligible towards pressures .5 atm and higher (Rai Dastidar *et al*, 1967), but for lower pressures the relaxation effects are quite significant and have to be taken account of. Since, however, the present theory (Brokaw, 1961) of heat transport in reacting gases is not immediately applicable here owing to the presence of diluents we confine ourselves to the analysis of data at the three highest pressures for each diluent concentration at each temperature : namely, 1 atm, 0.7 atm and 0.5 atm, where the relaxation effects should be minimum. For a ternary mixture eqn. (5) can be rewritten, in analogy with eqn. (2), as

$$(\lambda_R)_{eff} = \frac{1}{RT} \left(\frac{\Delta H^2}{RT^2} \right) \left[\frac{(x_2+2x_1)^2}{P(D_{12})_{eff}x_1x_2} + \frac{x_3}{P(D_{13})_{eff}x_1} + \frac{4x_3}{P(D_{23})_{eff}x_2} \right] \quad (8)$$

At each pressure, we have three experimental quantities $(\lambda_R)_{eff}$ corresponding to the three atom fractions of the diluent, and hence the three effective diffusion coefficients $(D_{12})_{eff}$, $(D_{13})_{eff}$ and $(D_{23})_{eff}$ can be obtained by solving three simultaneous equations. Calculated values of the ratio D/D_{eff} thus obtained are given in table 3.

DISCUSSION OF RESULTS

At present no theory is available which takes into account the effects of relaxation in a chemically reacting gas mixture when an inert diluent is present. However, to make the analysis possible we have confined our analysis to comparatively higher ranges of pressure where relaxation effects are likely to be small or absent. On this assumption the system can now be treated as in local chemical equilibrium.

From table 2 it may be seen that λ_e -values obtained by using the new set of force constants for N_2O_4 and NO_2 are always higher than λ_{opt} -values whereas those obtained by using the old set of force constants are sometimes lower than λ_{opt} -values. The results obtained with the new set of force constants are more reasonable as, due to the relaxation effects the experimental thermal conductivity should be lower than the calculated value for local chemical equilibrium.

The computed D/D_{eff} values for the N_2O_4 - NO_2 pair, N_2O_4 -diluent pair and the NO_2 -diluent pair of molecules are shown in columns 4, 5 and 6 of table 3 respectively. It was shown in ref. II that in order to assess the retarding influence of chemical reaction on diffusion from thermal conductivity measurements it is essential to eliminate completely the relaxation effects. The trend of rise in D_{12}/D_{12}^{eff} with the fall of pressure and with increase of diluent concentration indicates that the relaxation effects are still present at the pressures for which calculations have been made. However, at such pressures analysis of undiluted $N_2O_4 \rightleftharpoons 2NO_2$ system had not shown any relaxation effect in ref. II. This most probably points to a retardation of the reaction rate caused by the presence of the diluents. Since the analysis shows clearly the presence of relaxation effects the actual values of the ratios of the diffusion coefficients are without any physical significance. A part of the apparently irregular values of D/D_{eff} ratio may also be due to experimental uncertainties.

TABLE I
Molefractions of N_2O_4 , NO_2 and diluents in the diluted N_2O_4 - NO_2 system

Diluent Gas	T ($^{\circ}K$)	α	P (atm)	x_1	x_2	x_3
Helium	300	.1682	1.00	.47373	.27839	.24788
			.70	.43812	.31999	.24189
			.50	.40170	.36254	.23577
..	300	.3766	1.00	.29364	.21918	.48718
			.70	.27028	.25133	.47839
			.50	.24654	.28402	.46945
..	300	.6267	1.00	.13734	.14989	.71277
			.70	.12458	.17064	.70478
			.50	.11187	.19132	.69681
..	320	.1682	1.00	.31226	.46702	.22072
			.70	.26875	.51785	.21340
			.50	.22845	.56493	.20662
..	320	.3766	1.00	.18895	.36329	.44776
			.70	.16136	.40127	.43737
			.50	.13610	.43604	.42786
..	320	.6267	1.00	.08219	.23960	.67821
			.70	.06862	.26167	.66970
			.50	.05661	.28122	.66218
..	350	.1682	1.00	.11177	.70123	.18700
			.70	.08529	.73216	.18255
			.50	.06494	.75593	.17912

Values of the mole fractions thus calculated are given in table 1. The theoretical values of λ_f , λ_R and $\lambda_e (= \lambda_f + \lambda_R)$ along with the experimental conductivity values are given in Table II. For the calculation the Lennard-Jones (12 : 6) potential was used, the force constants for N_2O_4 and NO_2 being previously given by the authors (Barua *et al*, 1965). The usual combination rules (Hirschfelder *et al*, 1954) were used. The λ_e -values originally calculated by Coffin who used an older set of force constants given by Brokaw (1958), are also included in Table 2.

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			.50	.11187	.19132	.69681
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			.50	.13610	.43604	.42786
"	320	.6267	1.00	.08219	.23960	.67821
			.70	.06862	.26167	.66970
			.50	.05661	.28122	.66218
"	350	.1682	1.00	.11177	.70123	.18700
			.70	.08529	.73216	.18255
			.50	.06494	.75593	.17912

Table I (Contd.)

Diluent Gas	T ($^{\circ}K$)	a	P (atm)	x_1	x_2	x_3
Helium	350	.3766	1.00	.06485	.53113	.40102
			.70	.04914	.55575	.39511
			.50	.03721	.57218	.39061
"	350	.6267	1.00	.02512	.33244	.64244
			.70	.01871	.34287	.63842
			.50	.01397	.35058	.63545
Argon	300	.1820	1.00	.45997	.27432	.26571
			.70	.42531	.31528	.25941
			.50	.38988	.35717	.25296
"	300	.3768	1.00	.29349	.21912	.48739
			.70	.27014	.25127	.47859
			.50	.24641	.28395	.46965
"	300	.6152	1.00	.14341	.15317	.70342
			.70	.13023	.17446	.69532
			.50	.11707	.19571	.68722
"	320	.1820	1.00	.30290	.45997	.23713
			.70	.26061	.50996	.22943
			.50	.22147	.55623	.22231
"	320	.3768	1.00	.18885	.36319	.44796
			.70	.16127	.40116	.43757
			.50	.13602	.43592	.42805
"	320	.6152	1.00	.08626	.24547	.66827
			.70	.07212	.26829	.65958
			.50	.05960	.28854	.65186
"	350	.1820	1.00	.10824	.69006	.20170
			.70	.08257	.72040	.19703
			.50	.06286	.74370	.19344
"	350	.3768	1.00	.06481	.53397	.40122
			.70	.04911	.55558	.39531
			.50	.03718	.57200	.39081
"	350	.6152	1.00	.02657	.34180	.63154
			.70	.01981	.35281	.62738
			.50	.01480	.36080	.62431

TABLE 2

Thermal conductivities (experimental and theoretical) of the diluted N_2O_4 - NO_2 system in cal .cm⁻¹ sec⁻¹ deg⁻¹ units

Diluent Gas	T (°K)	α	P (atm)	$\lambda_f \times 10^5$	$\lambda_R \times 10^5$	$\lambda_e \times 10^5$	$\lambda_{expt.} \times 10^5$	$\lambda_e(\text{old}) \times 10^5$	$(\lambda_R)_{eff} \times 10^5$
Helium	300	.1682	1.00	5.56	26.01	31.57	31.2	29.56	25.64
			.70	5.41	29.05	34.47	33.6	32.39	28.19
			.50	5.26	31.79	37.05	35.5	34.94	30.24
"	300	.3766	1.00	9.89	27.14	37.02	36.4	34.65	26.51
			.70	9.68	29.76	39.44	38.2	37.06	28.52
			.50	9.47	31.92	41.39	39.1	39.05	29.63
"	300	.6267	1.00	17.00	26.27	43.27	39.9	40.82	22.90
			.70	16.74	27.89	44.63	41.8	42.24	25.06
			.50	16.48	28.88	45.36	41.2	43.08	24.72
"	320	.1682	1.00	7.21	34.03	41.24	38.1	37.55	30.89
			.70	7.21	34.77	41.98	38.8	38.33	31.59
			.50	7.21	34.43	41.64	37.8	38.12	30.59
"	320	.3766	1.00	11.42	32.30	43.72	40.4	39.93	28.98
			.70	11.35	32.02	43.36	39.4	39.69	28.05
			.50	11.28	30.74	42.02	37.4	38.54	26.12
"	320	.6267	1.00	18.43	26.48	44.90	40.2	41.42	21.77
			.70	18.28	24.91	43.19	38.0	39.88	19.72
			.50	18.15	22.72	40.87	35.6	37.76	17.45
"	350	.1682	1.00	7.89	23.31	31.20	28.6	28.57	20.71
			.70	7.89	19.51	27.39	24.8	25.10	16.91
			.50	7.88	15.94	23.82	21.2	21.82	13.32
"	350	.3766	1.00	11.97	18.72	30.69	27.8	28.02	15.83
			.70	11.92	15.23	27.15	24.3	24.76	12.38
			.50	11.88	12.17	24.05	21.6	21.89	9.72
"	350	.6267	1.00	19.10	11.66	30.76	27.7	28.15	8.60
			.70	19.02	9.10	28.12	25.4	25.68	6.38
			.50	18.97	7.03	26.00	23.7	23.69	4.73
Argon	300	.1820	1.00	4.01	22.62	26.63	25.0	24.30	20.99
			.70	4.05	25.26	29.31	26.4	26.80	22.35
			.50	4.08	27.64	31.72	29.0	29.07	24.92
"	300	.3768	1.00	4.17	19.57	23.74	22.4	21.89	18.23
			.70	4.19	21.51	25.70	23.6	23.76	19.41
			.50	4.22	23.12	27.34	24.7	25.33	20.48
"	300	.6152	1.00	4.27	14.25	18.52	16.0	17.36	11.73
			.70	4.28	15.20	19.49	16.6	18.31	12.32
			.50	4.30	15.82	20.12	16.7	18.95	12.40
"	300	.1820	1.00	4.60	29.57	34.17	31.0	31.35	26.40
			.70	4.65	30.21	34.86	30.9	32.08	26.25
			.50	4.69	29.91	34.60	30.2	31.93	25.51

TABLE 2 (Contd.)

Diluent Gas	T (°K)	α	P (atm)	$\lambda_f \times 10^5$	$\lambda_R \times 10^5$	$\lambda_e \times 10^5$	$\lambda_{expt.} \times 10^5$	$\lambda_e(\text{old}) \times 10^5$	$(\lambda_R)_{eff} \times 10^5$
Argon	320	.3768	1.00	4.67	23.54	28.21	24.6	26.16	19.93
			.70	4.70	23.41	28.11	24.2	26.13	19.50
			.50	4.73	22.55	27.28	23.1	25.42	18.37
"	320	.6152	1.00	4.67	14.73	19.40	15.9	18.27	11.23
			.70	4.69	13.95	18.64	15.2	17.60	10.51
			.50	4.70	12.81	17.51	14.0	16.56	9.30
"	350	.1820	1.00	5.32	20.23	25.55	22.0	23.75	16.68
			.70	5.35	16.93	22.28	18.8	20.62	13.45
			.50	5.37	13.83	19.20	15.9	17.78	10.53
"	350	.3768	1.00	5.28	13.86	19.14	17.1	17.92	11.82
			.70	5.20	11.31	16.60	14.4	15.48	9.11
			.50	5.31	9.05	14.36	12.3	13.38	6.99
"	350	.6152	1.00	5.17	6.71	11.89	9.7	11.24	4.53
			.70	5.18	5.26	10.44	8.6	9.84	3.42
			.50	5.18	4.08	9.26	7.7	8.72	2.52

TABLE 3
Effective diffusion coefficient (D_{eff})

Diluent Gas	T (°K)	P (atm)	D_{12}	D_{13}	D_{23}
			$(D_{12})_{eff}$	$(D_{13})_{eff}$	$(D_{23})_{eff}$
Helium	300	1.00	1.0513	.5581	.6501
		.70	1.1264	.5883	.7291
		.50	1.4151	.0295	1.5083
	320	1.00	1.1329	.3175	.9189
		.70	1.2024	.6817	.7935
		.50	1.3108	2.0299	.2676
	350	1.00	1.1515	.8162	1.0744
		.70	1.2758	.9399	.5929
		.50	1.6366	1.2079	.8953
Argon	300	1.00	1.2960	.1633	.0068
		.70	1.6402	.1456	.1033
		.50	2.7712	.1444	.2331
	320	1.00	1.3277	.1470	.1440
		.70	1.7482	.1329	.1896
		.50	2.8214	.3038	.3407
	350	1.00	1.4160	.2044	.2559
		.70	1.7095	.2704	.1839
		.50	3.1007	.3040	.4805

This analysis brings out the inadequacy of the theory for heat conductivity chemically reacting gas mixtures when a diluent is present. In practical cases in general diluents are present. Consequently this aspect of the problem of heat transfer in chemically reacting gas mixture deserves attention both from the theoretical and the experimental points of view.

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REFERENCES

- Barua A. K. and Rai Dastidar T. K., 1965, *J. Chem. Phys.*, **43**, 4140.
Bodenstein, M. and Lindner, B., 1922, *Z. Physik. Chem.* **100**, 82.
Brokaw R. S., 1958, *NACA RM E57K19a*, Washington, D.C.
1960, *J. Chem. Phys.*, **32**, 1005.
1961, *J. Chem. Phys.*, **35**, 1569.
Butler J. N. and Brokaw, R. S., 1957, *J. Chem. Phys.*, **26**, 1636.
Cher, Mark, 1962, *J. Chem. Phys.* **37**, 2564.
Coffin K. P., 1959, *J. Chem. Phys.*, **31**, 1290.
Hirschfelder J. O., Curtiss C. F. and Bird R. B., 1954, *Molecular Theory of Gases and Liquids*, John Wiley, New York.
Hirschfelder J. O., 1957, *Sixth Symposium on Combustion*, Reinhold Publ. Corpn., New York. p. 351.
Rai Dastidar T. K., and Barua A. K., 1966, *Trans. Faraday Soc.*, **62**, 3131.
1967, *Proc. Phys. Soc.* **92**, 800