solutions of these equations are

$$b_{W_n}=\sum_{m=1}^{4} A_{nm}C_m e^{(i/\hbar)(E_0+\hbar\lambda_m)t}, \qquad (n=1,\,2,\,3,\,4), \quad (36)$$

where the λ_m are the roots of the equation

$$\left| i\left(\lambda-\frac{W_m}{\hbar}\right)\delta_{mn}-\underset{n\neq m}{\frac{\omega H(W_m|M_\eta|W_n)}{W_n-W_m}}\right|=0 \quad (37)$$

and the A_{nm} are to be determined by substituting (36) back into (34). These expressions are too lengthy to be set down explicitly. The C_m are the four arbitrary constants of integration which must be determined by the normalization and the initial conditions. Let us suppose that initially ($t=0$) the atom is in a state characterized by the energy W_k so that initially $|b_{W_k}|^2=1$ and all the others are zero. Then at any other time, t, later we shall have

$$b_{W_n}=\frac{1}{\Delta}\sum_{m=1}^{4} A_{nm}A^{km}e^{(i/\hbar)(E_0+\hbar\lambda_m)t}, \quad (38)$$

where Δ is the determinant of the matrix $((A_{nm}))$ and A^{km} is the cofactor of the element A_{km}. The quantities $|b_{W_n}|^2$ give the probabilities of transition from the initial state.

The authors wish to express their appreciation to Professor I. I. Rabi for suggesting this problem and for invaluable advice and to Professors G. Breit and W. Pauli for interesting and helpful discussions. One of us (L. M.) would also like to thank Mr. Julian Schwinger of the Columbia University physics seminar for interesting and helpful discussions on various phases of this problem.

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Sound Absorption and Velocity in Mixtures

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The effects of (a) collision excitation probabilities dependent on the internal energy specification of the impinging molecules; (b) transitions in both colliding members; (c) triple and higher order collisions; (d) viscosity and conduction, are considered with reference to sound propagation. A comparative study is made of the generalized Kneser-Ruttgers method and the writer's method of investigation. It is shown that the two are developments of the same physical theory and may be looked upon as a thermodynamic and a kinetic theory transcript respectively. In particular, ω_i (a parameter, dependent on the frequency, which determines the degree to which equilibrium conditions are attained) plays a central rôle, implicitly, in the former method as well as in the latter. The kinetic theory transport equation interpretation of the use of C_∞ instead of $3k/2$ is noted. It is shown that for impurity contamination, the Kneser special assumptions and formulae fall out as consequences of the general mixture theory if certain approximations are valid. The triple collision hypothesis for H, O, O_2 mixtures is discussed and alternative explanations are suggested. The main contributions of this paper from the experimenter's viewpoint are the formulae for absorption and velocity in mixtures, derived by the two methods referred to above, in convenient form for application.

The first objective of this paper is the exhibition of a conveniently applied expression for sound absorption in mixtures of gases. The extensive experimental[1] work inaugurated on impurities in gases and gas mixtures emphasizes the timeliness of the calculations presented here. In the first paper on supersonics[2]

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[1] Three techniques have been followed in the experimental work. The first utilizes the piezoelectric oscillator in the way devised by G. W. Pierce, Proc. Am. Acad. Arts and Sci. **60**, 271 (1925). The second employs the acoustic interferometer invented and developed by J. C. Hubbard, Phys. Rev. **38**, 1011 (1931); **41**, 523 (1932). The third is concerned with absorption measurements by means of reverberation times. It is not restricted to any particular frequency region and owes its exploitation to V. O. Knudsen, J. A. S. A. **3**, 126 (1931).

[2] D. G. Bourgin, Nature **122**, 133 (1928); Phil. Mag. **7**, 821 (1929); Phys. Rev. **34**, 521 (1929); J. A. S. A. **5**, 108 (1932); Phys. Rev. **42**, 721 (1932); designated as I, II, III, IV, V respectively. In the interest of historical completeness, the work of Jeans' *Kinetic Theory of Gases* and K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928), may be mentioned. Both these investigations are on the pre-quantum theory model and the last named is, in fact, really a continuous fluid theory entirely macroscopic in perspective. Cf. I for discussion of the relation of this highly original theory to the writer's.

published by the writer, there is given a theory of sound absorption in mixtures, and later communications[3] simplify some of the findings. This research is, in a sense, a culmination of the previous work as regards simplifications and nomenclature on the one hand and certain natural generalizations on the other. For the case of impurities in a single gas, the empirical postulate of Kneser[4] expressed in the notation of this paper $k_{12} \sim aB + bB^2$ and the contingent formulae are shown to be logical consequences of a sub-case under the general theory.

The quantum theory of sound propagation making use of the concept of lags in adjustment of internal energy states was originally proposed and developed in its present form by the writer.[2] While the physical basis of the theory has undergone little improvement, there has, however, been real advance in the presentation of the formulae in a manner more amenable to the needs of the experimenter and in the application of the theory to specific gases.[5] As an alternative to the writer's method for developing the physical consequences of the theory, modification of a method used by Einstein[6] for investigating dissociating gases may be employed. This choice is to some extent a matter of individual preference as pointed out by Richards.[7] The impression that there is greater complexity in the writer's method is, in his opinion, unfounded as the sequel will show, and due possibly to a lack of realization that the original developments of I are completely general for n states, and accordingly slightly more formidable in appearance than a treatment for two states with which comparison is ordinarily made. The second objective of this paper is to discuss the two methods comparatively, and it is shown that the methods are almost completely equivalent.[8] This purpose is carried out in part by developing both the writer's and the Kneser-Ruttgers modification of Einstein's method (hereafter abbreviated to K.R. method)[9] for the mixture formula, and also by the discussion in the appendix. This appendix contains material whose introduction would impede the direct derivation of the main formulae of the paper.

In order to make this paper self-contained, the physical theory will be briefly reviewed. Consider a gas A maintained at temperature T_0. Under the influence of collisions some kinetic energy is taken up by the internal states of the atoms or molecules of A, but this is exactly balanced on the average by the internal energy given back. If the temperature be raised by the small amount δT, the increment in the number of molecules in the excited state i, after the passage of sufficient time, is, of course, $(\partial A_i/\partial T)|_{T=T_0}\delta T$ where A_i represents the number of i state molecules in unit volume, and is given mathematically by the Maxwell-Boltzmann formula. Since kinetic theory considerations are central in this paper it is more desirable to use K, the kinetic energy per molecule determined from the mean square of the velocity, rather than T, so that the increment may also be written $(\partial A_i/\partial K)|_{K=K_0}\delta K$. However if too short a time interval is taken, this new equilibrium value for state i is not attained. We may take account,

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[3] Reference 2, II, V.

[4] H. O. Kneser, V. O. Knudsen, Ann. d. Physik **21**, 682 (1935) and other papers of their own to which the authors refer.

[5] The penetrating papers of Richards, and Richards and Reid (scattered through the 1933 and 1934 issues of the Journal of Chemical Physics) contain an excellently balanced analysis of the application of theory to experiment and should not be overlooked by students endeavoring to orient themselves in this field. Though written from the viewpoint of the Einstein method, the authors have evidently a thorough understanding of the writer's method as well. Special mention ought be made of H. O. Kneser's work in interpreting his own and others' experimental work, for it has gone far in making this field significant, cf. reference 4. The papers already mentioned and those in reference 6 contain more adequate bibliographies. In the forefront of important contributors whom the reader may consult for other phases of supersonic work, one lists W. P. Pielemeyer, Phys. Rev. **36**, 1006 (1930); **41**, 833 (1932); A. Eucken and R. Becker, Zeits. f. physik. Chemie **B20**, 467 (1933); P. S. H. Henry, Proc. Camb. Phil. Soc. **28**, 249–255 (1931–32).

[6] The first presentation by H. O. Kneser contained inconsistencies which fortunately "balanced" out. The correct application was made by Ruttgers. A. Einstein, Sitz.-Ber. Berlin Acad. 380, 1920. H. O. Knese, Ann. d. Physik **5**, 761 (1931); Ruttgers, Ann. d. Physik **5**, 350 (1933).

[7] There is a difference in result in the sense that $\mathbf{C}_\infty$ replaces $3k/2$, but this is not an essential distinction. Cf. appendix, section (B).

[8] The criticism of the Kneser theory in paragraph 1 of IV, reference 2, implied that a microscopic state separation had to be imposed for completeness. When this is done, one obtains the theory described here as the K.R. method which is shown to be essentially equivalent to the writer's formulation. The extension of the original Kneser-Ruttgers work to more than two states was made by Richards, who, in fact, remarked the similarity to the three state calculation made by the writer in IV.

[9] The material on the K.R. method may be omitted by the reader without sacrificing the completeness of the derivations of the new results of this paper. Cf. reference 27.

mathematically, of such a condition by multiplying by a parameter ω_i whose value is determined by this time interval. Evidently $|\omega_i| \leqslant 1$.

If sound waves are propagated in the gas, the mean kinetic energy in any small region is an approximately harmonic function of the time. Hence the time interval referred to above, which is available for adjustment of the internal states to the external translational energy fluctuation, is evidently determined by the period or more conveniently the frequency of the kinetic energy oscillations. Furthermore, since the energy quanta in the excited states have a finite mean life they are not, on the average, immediately restored to the gas as translational energy; that is to say a phase lag must subsist in the relationship between external and internal energy changes. It is then clear that the parameters ω_i must be functions of ν involving phase lags. Now quite without any mathematics it seems clear that when the period of the sound wave is nearly the same as that of the mean life of the energy quantum of some state, an influence on the sound propagation may be expected. The degree of this influence is dependent on the amounts of internal energy exchanged at this particular 'mean life' rate. Roughly then the effect should be proportional to $(\partial A_i/\partial K)\epsilon_i$ where ϵ_i is the energy associated with the ith excited state. This will perhaps be clearer if we recall that the Laplace value for the velocity of sound depends on the ratio of the specific heats which in turn involves a sum over i of terms of just the form $(\partial A_i/\partial K)\epsilon_i$. In this connection it may be remarked that the Laplace formula may be maintained formally if, because of the dependence of the internal state populations on ω_i, one introduces 'effective' specific heats dependent on ν.

Evidently the fidelity of reproduction in the internal states of the kinetic energy variation and accordingly the values of the ω_i and the 'mean lives' depend on the ease with which external and internal energies are exchanged in collision. One therefore introduces transition probability factors. A natural notation is k_{ij}^{σ}. The subscripts indicate that a molecule originally in state i goes to state j because of the collision. The superscript σ marks the fact that the colliding molecule under whose influence the transition was accomplished was in state σ. Later double transitions will be considered—the early part of this paper considers only single transitions so that the second molecule remains in state σ though its translational energy may, of course, be affected. The units for k_{ij}^{σ} are so chosen that the number of collision-inspired transitions from state i to state j in unit time and volume is given by $A_iA_\sigma k_{ij}^{\sigma}$.

Among the important questions of modern physics and chemistry are those associated with collision processes. A satisfactory quantum theoretic treatment of individual atomic and molecular collisions does not exist as yet because of the complexity both of the physical situation and the analysis. However statistical information may be obtained from the interpretations of sound data afforded by the lag theory of sound just sketched. This required information is embodied in the values of the collision transition probabilities k_{ij}^{σ}. Explicit connections between these transition probabilities and the experimentally determinable magnitudes such as the absorption, velocity, specific heat, etc., of the gases involved, are important ends of this paper and others in this field. From this point of view it would seem essential to consider collisions between molecules of different types in order to gain an idea of the factors influencing the effectiveness of collision, that is to say, a theory of sound propagation in *mixtures* is demanded.

The main ideas of the theory of sound for a single gas may be carried over in their entirety to the case of a mixture of gas A and gas B. As a measure of economy A and B will also stand for the number of molecules of each gas in unit volume. Two sets of parameters must now be used, namely ω_{A_i} and ω_{B_r}. For collisions in which A type molecules change their state, the small letters[10] k_{ij}^{σ} and g_{ij}^{σ} will be used. The first has already been defined. The second refers to collisions between an A type molecule in state i and a B molecule in state σ, thus $A_iB_\sigma g_{ij}^{\sigma}$ gives the number of molecules of gas A, originally in

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[10] The notation used in previous papers is slightly different, i.e., $\mathrm{f}_{ij} \equiv k_{ij}^{i}$ and the average value $f_{ij} \equiv \Sigma_\sigma(A_\sigma k_{ij}^{\sigma}/A - A_i)$, $\sigma \neq i$. The new notation lends itself to clearer exposition. Cf. appendix, section (A), for indication of equivalence of results. For i, $j = 1$, 2 there is really no difference in notations.

state i, which change to state j in unit time and volume because of AB collisions. The capitals $K_{rs}{}^{\sigma}$ and $G_{rs}{}^{\sigma}$ are used for transitions of the molecules of gas B. The first refers to the case that the colliding molecules are B_r and B_σ respectively, and the second that they are B_r and A_σ. In general i and j will be used as scripts for any of the n states of gas A molecules and r and s will be used similarly for gas B. However σ is used indiscriminately for reasons of convenience since it will usually be associated with a summation sign. This dual usage will cause no confusion because the symbols to which σ is attached already differentiate between the two gases.

The various transition factors[11] are not independent for the principle of detailed balancing requires that

$$A_ik_{ij}{}^{\sigma}=A_jk_{ji}{}^{\sigma}, \qquad A_ig_{ij}{}^{\sigma}=A_jg_{ji}{}^{\sigma},$$
$$B_rK_{rs}{}^{\sigma}=B_sK_{sr}{}^{\sigma}, \quad B_rG_{rs}{}^{\sigma}=B_sG_{sr}{}^{\sigma}. \tag{1}$$

The rate of change in i state populations contributed by double collisions is denoted by $D(A_i)$, the definition of $D(B_i)$ is similar

$$D(A_i)=-\Sigma_{\sigma,j}A_iA_\sigma k_{ij}{}^{\sigma}-A_jA_\sigma k_{ji}{}^{\sigma}+A_iB_\sigma g_{ij}{}^{\sigma}-A_jB_\sigma g_{ij}{}^{\sigma}. \tag{1a}$$

Evidently (cf. Eq. 1), $D(A_i)=0$ for equilibrium conditions. The effects of triple collisions as well as collisions in which both partners undergo transitions may be incorporated into these developments. The explicit modifications are given in the appendix (Eqs. 15 ff.).

The assumption of a lag in adjustment of the internal energy states may be expressed formally by writing for the change[12] in state i (or r) concentration of gas A (or B)

$$\delta A_i=(A_i/A)\delta A+\omega_{A_i}A^{\cdot}{}_i\delta K\,; \quad \delta B_r=(B_r/B)\delta B+\omega_{B_r}B^{\cdot}{}_r\delta K \tag{2a}$$

where $A^{\cdot}{}_i$, $B^{\cdot}{}_r$ stand for $\partial A_i/\partial K$ and $\partial B_r/\partial K$. For the developments of this paper the simplifying assumptions $\omega_{A_i}\equiv\omega_A$; $\omega_{B_r}\equiv\omega_B$ are made. The rate of change in occupants of state i due to passage of a sound wave[13] is denoted by ΔA_i (or ΔB_i).

$$\Delta A_i\equiv\delta D(A_i)=-\Sigma_{\sigma,\,j}\delta A_\sigma(A_ik_{ij}{}^{\sigma}-A_jk_{ji}{}^{\sigma})+\delta A_iA_\sigma k_{ij}{}^{\sigma}-\delta A_jA_\sigma k_{ji}{}^{\sigma}+\delta B_\sigma(A_ig_{ij}{}^{\sigma}-A_jg_{ji}{}^{\sigma})$$
$$+\delta A_iB_\sigma g_{ij}{}^{\sigma}-\delta A_jB_\sigma g_{ji}{}^{\sigma}+\delta g[\ ]+\delta k[\ ]. \tag{3a}$$

$\delta k[\ ]$, $\delta g[\ ]$ are generic notations for the totality of terms in the variations $\delta k_{ij}{}^{\sigma}$, $\delta k_{ji}{}^{\sigma}$ and $\delta g_{ij}{}^{\sigma}$, $\delta g_{ji}{}^{\sigma}$.

Since the relative number of molecules in the various states depends on temperature alone at equilibrium, merely increasing A or B by amounts δA or δB will not disturb the exact balance of internal and external energy collision exchanges; i.e., $\Delta A_i/\delta A$, $\Delta A_i/\delta B$ at constant K is 0. This is easily verified analytically for the substituion of $(\delta A/A)A_i$, for δA_i gives for the coefficient of δA in Eq. (3a), $D(A_i)/A$ or 0 at equilibrium; similarly for terms in δB. Thus only the second terms of Eq. (2a) play a role in ΔA_i or ΔB_r.

Next we notice that the coefficients of δA_σ and δB_σ are 0 by the principle of detailed balancing, Eq. (1). The transition probabilities are dependent solely on K. The terms $\delta k[\ ]$, $\delta g[\ ]$ might be difficult to calculate directly. Fortunately, however, they may be eliminated since $L_{\nu\to 0}\Delta A_i=L_{\omega_A\to 1}\Delta A_i=0$. We have, in fact,

$$0=L_{\nu\to 0}\Delta A_i=\Sigma_{j,\,\sigma}\delta k[\ ]+\delta g[\ ]+\delta K[A^{\cdot}{}_i(A_\sigma k_{ij}{}^{\sigma}+B^{\cdot}{}_\sigma g_{ij}{}^{\sigma})-A^{\cdot}{}_j(A_\sigma k_{ij}{}^{\sigma}+B_\sigma g_{ji}{}^{\sigma})]. \tag{3.1a}$$

We introduce the averaged probabilities[14]

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[11] If desired, the Einstein radiation transition probabilities may be added. Cf. I, reference 2.

[12] The δK is supposed so small that the distribution function is not appreciably modified.

[13] The equivalent notation in IV, reference 2, is $(\Delta)_T$ for D and $\Delta=\Delta(\Delta)_T$ for the present Δ and has caused readers some confusion. Authors employing the K.R. developments write d/dt and Δ for our D and δ respectively.

[14] The work would be more perspicuous, no doubt, if instead of the n state model with the one ω value a two state model ($i, j=1$ or 2) were used just as in the K.R. method in the succeeding paragraphs. The more general situation is taken in order to emphasize the fact that it is the ω and not the number of states that determines the behavior of the gas. The text treatment involves $\Sigma_j(R_{ij}-(N^{\cdot}{}_j/N^{\cdot}{}_i)R_{ji})$ independent of i, i.e., $\Sigma_jR_{ij}(\boldsymbol{\varepsilon}_i-\epsilon_j/\boldsymbol{\varepsilon}-\epsilon_j)$, where $\boldsymbol{\varepsilon}$ is the average energy. If $B\equiv 0$ the pure gas equations with $\omega_i\equiv\omega$ are obtained. The general case $\omega_i\not\equiv\omega$ is taken up in I, and IV of reference 2. Cf. also appendix.

$$R_{ij}=\Sigma_\sigma A_\sigma k_{ij}{}^\sigma/A\,;\quad P_{ij}=\Sigma_\sigma B_\sigma g_{ij}{}^\sigma/B\,;\quad A_iR_{ij}=A_jR_{ji},\quad \text{etc.};$$
$$S_{rs}=\Sigma_\sigma B_\sigma K_{rs}{}^\sigma/B\,;\quad Q_{rs}=\Sigma_\sigma A_\sigma G_{rs}{}^\sigma/A. \tag{3.2a}$$

Accordingly,[15]

$$\Delta A_i/\delta K=-(\omega_A-1)\Sigma_jA(A^\cdot{}_iR_{ij}-A^\cdot{}_jR_{ji})+B(A^\cdot{}_iP_{ij}-A^\cdot{}_jP_{ji}),$$
$$\Delta B_r/\delta K=-(\omega_B-1)\Sigma_jB(B^\cdot{}_rS_{rs}-B^\cdot{}_sS_{sr})+A(B^\cdot{}_rQ_{rs}-B^\cdot{}_sQ_{sr}). \tag{4a}$$

These are key equations[16] in our development of the theory.

By making use of the equations of the kinetic theory of gases it is possible to obtain another expression for $\Delta A_i/\delta K$, $(\Delta B_r/\delta K)$. Thus one may solve for ω_A and ω_B, and substitute these values in Eq. (4a) to give $\Delta A_i/\delta K$; $\Delta B_r/\delta K$ directly in terms of the R's and P's, etc. The kinetic theory equations required may be looked upon as being modifications of the transport equation.

The first is

$$\frac{\partial}{\partial t}\left\{\begin{matrix}A\\ B\end{matrix}\right.=-\frac{\partial}{\partial x}\begin{matrix}A\\ B\end{matrix}\quad v. \tag{4.1a}$$

v is the mass motion velocity.

Next, according to the equipartition principle, A and B molecules have equal translational energies. Since their mass motions are also equal, there is no collision term and we may write, with $N=A+B$,

$$\frac{\partial}{\partial t}(m_AA+m_BB)v=-\frac{\partial}{\partial x}\left(\frac{2}{3}NK\right), \tag{4.2a}$$

$$\frac{\partial}{\partial t}NK=-\frac{\partial}{\partial x}\left(\frac{5}{3}NKv\right)+\Delta K, \tag{4.3a}$$

$$\frac{\partial}{\partial t}\left\{\begin{matrix}A_i\\ B_r.\end{matrix}\right.=-\frac{\partial}{\partial x}\left\{\begin{matrix}A_i\\ B_r.\end{matrix}\right.v+\Delta\begin{matrix}A_i\\ B_r.\end{matrix}. \tag{4.4a}$$

ΔK is the translational energy change due to collision. These equations have already been given in (I) and (II) (cf., however, the correction given in footnote 2 of (III)). For the rest we set

$$\delta N=|\delta N|e^{i(\nu t-x/\lambda)}\,;\quad \delta K=|\delta K|e^{i(\nu t-x/\lambda)},\quad \text{etc.} \tag{4.5}$$

and neglect products involving two variationals. *Note ν is 2π times the frequency while λ is $1/2\pi$ times the wave-length.*

Eqs. (4.1a) and (4.4a) are therefore

$$j\nu\delta A=jA\,\delta v/\lambda, \tag{4.11a}$$
$$j\nu\delta A_i=jA_i\delta v/\lambda+\Delta A_i, \tag{4.41a}$$

whence

$$\Delta A_i=j\nu[\delta A_i-A_i\delta A/A]\quad =j\nu\omega_AA^\cdot{}_i\delta K. \tag{4.411a}$$

On equating this value for ΔA_i to that given in Eq. (4a), there results

$$\delta Kj\nu\omega_AA^\cdot{}_i=-(\omega_A-1)\delta K\Sigma_jAA^\cdot{}_i[R_{ij}=(A^\cdot{}_j/A^\cdot{}_i)R_{ji}]+BA^\cdot{}_i[P_{ij}-(A^\cdot{}_j/A^\cdot{}_i)P_{ji}].$$

Accordingly

$$\omega_A=\frac{1}{1+j\nu/\Sigma_jA(R_{ij}-(A^\cdot{}_j/A^\cdot{}_i)R_{ji})+B(P_{ij}-(A^\cdot{}_j/A^\cdot{}_i)P_{ji})} \tag{5a}$$

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[15] For the single gas $F(\omega)$ in Kneser's notation is our ω, cf. Eq. (18) of reference 6. In Ruttger's paper his Eq. 23 is effectively $\omega_1N^\cdot{}_1\delta K=-\Delta N_1$. Cf. Eq. (5a). Ruttgers goes through several steps to obtain his Eq. (24) which is our Eq. (2a). Of course these equations already occur in I, reference 2.

[16] Since all developments of the theory by the writer use Eq. (4a) as a basic equation, it may be accepted by the reader not interested in detail as a sort of postulate along with the kinetic theory equations (Eq. 4.1a, 4.4a).

and therefore,

$$\Delta A_i = \frac{j\nu A^{\cdot}_i \delta K}{1 + j\nu/A\Sigma_j[(R_{ij} - (A^{\cdot}_j/A^{\cdot}_i)R_{ji}) + B(P_{ij} - (A^{\cdot}_j/A^{\cdot}_i)P_{ji})]}.$$

Similarly

$$\Delta B_r = \frac{j\nu B^{\cdot}_r \delta K}{1 + j\nu/B\Sigma_s[s_{rs} - (B^{\cdot}_s/B^{\cdot}_r)s_{sr} + A(Q_{rs} - (B^{\cdot}_s/B^{\cdot}_r)Q_{sr})]}. \tag{5.1a}$$

Since ΔK is the negative of the internal energy change due to collisions, it may be written down immediately as $\Delta K = -\Sigma_i \Delta A_i \epsilon_i^A + \Sigma_r \Delta B_r \epsilon_r^B$, with ϵ_i^A the ith energy state value for gas A.

The succeeding six paragraphs indicate the K.R. approach to essentially the formulae already derived. To facilitate comparison with the K.R. method, let us introduce the auxiliary notation $a_i = UA_i$ and $a = UA$, i.e., a_i and a are the number of molecules in the volume U, while A_i and A are the concentrations or number in unit volume. We remark now that in the developments of the theory one may either maintain the volume fixed while permitting the molecule count a to change, or associate different volumes with a fixed molecule count a. The equivalence is immediate from $a = UA$, i.e.,

$$(\delta a/a)_U = -(\delta U/U)_a. \tag{6}$$

The first viewpoint with $U \equiv 1$ and fixed (so that $a_i \equiv A_i$, $a \equiv A$) is used in the writer's developments; the second is followed in the K.R. argument. Consider ΔA_i. It has been demonstrated that δA and δB drop out of Eq. (3a) which means that all the results obtained must be consistent with A and B being held constant.[17] Since U is considered fixed on the writer's viewpoint, this is the same as saying that a and b may be taken fixed. For later comparison with Eq. (3b) it is desirable to write ΔA_i with U introduced explicitly. From what has just been said it is evident that

$$\Delta A_i \equiv \Delta(a_i/U)\,|_{U,\,a,\,b} \equiv (1/U)\Delta a_i\,|_{a,\,b}. \tag{6.1}$$

If the K.R. viewpoint of variable U be adopted the notation ΔA_i might be expected to mean $a_i\Delta(1/U) + \Delta a_i/U$. We proceed to show in conformity with the result Eq. (6.1) that, using the K.R. method, again only the second term enters.

For the K.R. method[18] Eq. (1a) is written down as before

$$\begin{aligned} &D(A_1) = (1/U)D(a_1) = A_1^2 k_{12}^1 + A_1 A_2 k_{12}^2 - A_2^2 k_{21}^2 - A_2 A_1 k_{21}^1 + A_1(B_1 g_{12}^1 + B_2 g_{12}^2) - A_2(\cdots), \\ &D(A_2) = (1/U)D(a_1) = \cdots, \quad D(B_1) = \cdots, \end{aligned} \tag{1b}$$

where i, j of Eq. (1a) are restricted to the values 1, 2.

The variations may of course be carried out precisely as in the writer's method, but to maintain parallelism with the usual forms of development, one writes

$$\left(\frac{A_2}{A_1}\right) = \frac{k_{21}^\sigma}{k_{12}^\sigma} = \frac{g_{21}^\sigma}{g_{12}^\sigma} = e^{-(\epsilon_2^A - \epsilon_1^A)/kT} = \mu_A\,; \quad A_1 = \frac{A}{1+\mu_A}\,;$$

$$\left(\frac{B_2}{B_1}\right) = \frac{K_{21}^\sigma}{K_{12}^\sigma} = \frac{G_{21}^\sigma}{G_{12}^\sigma} = e^{-(\epsilon_2^B - \epsilon_1^B)/kT} = \mu_B\,; \quad B_1 = \frac{B}{1+\mu_B}.$$

Then

$$(\Delta A_i) = -[\{\Sigma^2_{\sigma=1} A_\sigma k_{21}^\sigma + \Sigma^2_{\rho=1} B_\rho g_{21}^\rho\}[\delta(\mu_A A_1) - \delta A_2] + (\mu_A A_1 - A_2)\delta\Sigma_\sigma A_\sigma k_{21}^\sigma + \Sigma^2_{\rho=1} B_\rho g_{21}^\rho], \tag{3b}$$

referring to Eq. (1a) or (1b). The last block of terms vanishes because of Eq. (1). It would be more in keeping with the spirit of a K.R. method development to express A_i in terms of a_i/U and then factor out the U term, and vary only a_i. This would give for the right side above

$$-\{\Sigma^2_{\sigma=1} a_\sigma k_{21}^\sigma + \Sigma^2_{\rho=1} b_\rho g_{21}^\rho\}[\delta(\mu_A a_1) - \delta a_2]U + 0. \tag{3.1b}$$

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[17] The fact that ΔA was proved independent of δA is immediate confirmation.

[18] In the K.R. work only the first collision change is taken into account in the single gas case. However the generalization is simple to make, and is, besides, of small effect probably because of the relative fewness of A_2A_2 collisions; cf. Richards, references 5, 8.

The equivalence with Eq. (3b) follows from

$$\delta(\mu_A A_1) - \delta A_2 - (1/U)\{\delta(\mu_A a_1) - \delta a_2\} = -(\delta U/U)\{\mu_A a_1 - a_2\} = 0.$$

The vanishing of the term on the right is the precise analogue of the disappearance of the δA term on the writer's method from Eq. (3a), as is obvious on writing $(\delta A/UA) = (\delta B/UB)$ for $-(\delta U/U^2)$. It appears from this last remark that though the δ symbol implies variation of A or U, the true value of ΔA_i (Eq. 3b) is also obtained if δ be considered as a partial variation at constant volume, cf. Eq. (6.1). Thus we are again justified in writing $\Delta(A_i) \equiv (1/U)\Delta a_i|_{a,\, b \text{ fixed}}$. Also,

$$\delta\mu_A = \delta A_2/A_1 = (A^{\cdot}_2/A_1 - (A^{\cdot}_1/A_1)\mu_A)\delta K, \quad A^{\cdot}_2 = -A^{\cdot}_1;$$

$$\therefore \quad \delta(\mu_A A_1) - \delta A_2 = A_1 \delta\mu_A + (A/A_1)\delta A_1 = -A^{\cdot}_1(A/A_1)\delta K + (A/A_1)\delta A_1. \tag{2b}$$

We assume now that D and δ are commutative, i.e., $\Delta A_i \equiv \delta D(A_i) \equiv (D\delta A_i)_{U=1}$. Evidently $D(f)$ is a time rate so that if all variations are harmonic in time, i.e., $\delta f = |\delta f| e^{j\nu t}$, then

$$D(\delta A_i)_{U=1} \equiv \Delta A_i = j\nu(\delta A_i)_{U=1}. \tag{5b}$$

This equation is the analogue of Eqs. (4.11) and (5a). Solving Eqs. (3b) and (5b) simultaneously one obtains the value of $(1/A^{\cdot}_1)(\delta A_i/\delta K)_{U=1}$ (which is called ω_A in the writer's work) and $\Delta A_i/\delta K$. Evidently the results are exactly Eqs. (5a) and (5.1a) again. The writers who employ the K.R. development would however write the results in terms of the a's instead of the A since later the U variations are considered basic

$$\Delta a_1 = -\Delta a_2 = j\nu a^{\cdot}_1 \delta K/[1 + j\nu/(a/U)(R_{12} + R_{21}) + (b/U)(P_{12} + P_{21})]. \tag{5.1b}$$

The other equations introduced in the K.R. method are

$$\rho_A V = A m_A, \quad \rho_B U = B m_B, \tag{4.1b}$$

$$pU = nkT, \quad \text{the equation of state}^{19} \tag{4b}$$

and the equation for adiabatic change[20]

$$(aC_{A\infty} + bC_{B\infty})\delta T + (\epsilon_2{}^A - \epsilon_1{}^A)\Delta a_1 + (\epsilon_2{}^B - \epsilon_1{}^B)\Delta b_1 + p\delta U = 0, \tag{4.3b}$$

$$V^2 = \delta p/\delta\rho, \quad \text{where } V \text{ is the velocity of sound.} \tag{4.2b}$$

$C_{A\infty}$ is the effective specific heat per mol. at constant volume of gas A when the sound frequency is "very high." The meaning of this last condition as well as the distinction between $3k/2$ and $C_{A\infty}$ or $C_{B\infty}$ is taken up in appendix E.

These equations, too, when expressed in variational forms are exactly equivalent to the set (4a–4.4a) used by the writer. In particular the central equation (4.3b) is the thermodynamic statement of Eq. (4.3a). As verification Eq. (4.3a) goes to

$$(N\delta K + K\delta N)j\nu = (j/\lambda)(5NKv/3) + \Delta K. \tag{6.2}$$

Making use of Eq. (4.11a), this is

$$(N\delta K - \tfrac{2}{3}K\delta N)j\nu = \Delta K. \tag{6.3}$$

Recalling $\delta N/N = -\delta U/U$, this is

$$N\delta K + \tfrac{2}{3}KN(\delta U/U) = \Delta K = -(\Delta A_1(\epsilon_2{}^A - \epsilon_1{}^A) + \Delta B_1(\epsilon_2{}^B - \epsilon_1{}^B)). \tag{64}$$

The equation of state is $pU = nkT$, with $n = NU$, and it may either be taken from the set (4b) or from kinetic theory. Hence

$$(3kn\delta T/2) + p\delta U - (\Delta K)U = 0 \quad \text{if} \quad K = 3kT/2. \tag{6.5}$$

This is Eq. (4.3b) with $aC_{A\infty} + bC_{B\infty} = 3kn/2$. Cf. appendix D for removal of this restriction.

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[19] The results may be generalized by using other relations between p, T, U or N, K, m for the equation of state—the effect is on the coefficient p/ρ (or K/m). Cf. Richards for use of the van der Waals equation.

[20] $C_{A\infty}$, $C_{B\infty}$ is the "effective" frequency free term for the range up to the last absorption band.

From Eqs. (4.1a) and (4.3a), in conjunction with Eq. (4.5), one has immediately for $\delta N/\delta K$,

$$\delta N/\delta K=(\Delta K-j\nu N)/(j\nu K-j(5/3)(KV/\lambda)), \tag{7a}$$

where $V=\lambda\nu$ is the velocity of sound. An expression for $\delta N/\delta K$ is also obtained from Eqs. (4.1a) and (4.2a), whence on elimination and substitution of the equipartition value $K=3kT/2$ there results

$$V^2=\frac{kT}{\mathbf{m}}\left[\frac{-Nk(5/2)j\nu+(3/2)k(\Delta K/\Delta T)}{-Nk(3/2)j\nu\;+3k/2(\Delta K/\Delta T)}\right] \tag{8a}$$

with $\mathbf{m}$, the mean mass,[21] i.e. $=(Am_A+Bm_B)/N$. Furthermore, one remarks that

$$A^{\cdot}{}_1\epsilon_1{}^A+A^{\cdot}{}_2\epsilon_2{}^A=A^{\cdot}{}_1(\epsilon_1{}^A-\epsilon_2{}^A)=\frac{d}{dT}(A_1\epsilon^{\cdot}{}_1{}^A+A_2\epsilon_2{}^A)\frac{dT}{dK}=AC_A/(3k/2)\,;$$

where C_A is the ordinary internal specific heat per molecule of gas A similarly for C_B. They may be considered measured at 0 frequency. The end result[22] is

$$V^2=\frac{kT}{\mathbf{m}}\left[1+k\Big/\left(\frac{3}{2}k+\frac{1}{N}\left\{\frac{AC_A}{1+j\nu/A\Gamma_{11}+B\Gamma_{12}}+\frac{BC_B}{1+j\nu/A\Gamma_{21}+B\Gamma_{22}}\right\}\right)\right], \tag{8.1a}$$

$$\Gamma_{11}=R_{12}+R_{21}\,;\quad \Gamma_{22}=S_{12}+S_{21}\,;\quad \Gamma_{12}=P_{12}+P_{21}\,;\quad \Gamma_{21}=Q_{12}+Q_{21}.$$

Now $kT/m\equiv p/\rho$ and this will be the factor used hereafter, cf. reference 19.

In accordance with the general principle of replacement of δN by δU in going from the writer's to the K.R. calculation, we first combine Eqs. (4b) to (4.2b) to get $\delta U/\delta T$, whence substituting the value of $\delta U/\delta T$ from Eqs. (4.3b) and (5.1b) we have

$$V^2=\frac{p}{\rho}\left[1+k\Big/\left(\frac{AC_{A\infty}+BC_{B\infty}}{N}+\frac{1}{N}\left\{\frac{AC_A}{1+j\nu/A\Gamma_{11}+B\Gamma_{12}}+\frac{BC_B}{1+j\nu/A\Gamma}\right\}\right)\right]. \tag{8.1b}$$

Except for the occurrence of $(AC_{A\infty}+BC_{B\infty})/N$, henceforth written $\mathbf{C}_\infty$, in the place of $3k/2$ the final equation (Eq. (8.1a) and Eq. (8.1b)) deduced by either method is the same (and has been given before by the writer for specialized k_{ij}).

The calculation of main interest for the purpose of this paper is the absorption. The sound wave may be represented as $e^{-x/\lambda \sin\phi}e^{j(\nu t-x/\lambda\cos\phi)}$. Since ϕ is small for nearly all practical cases

$$\cos\phi/\cos 2\phi\sim 1$$
$$\mu=2\sin\phi\sim\tan 2\phi.$$

This approximation[23] gives the absorption formula a considerable advantage in simplicity over the strictly rigorous results, i.e.,

$$\mu=\text{absorption coefficient per wave-length}\div 2\pi=\nu D(\mathfrak{C}_p-\mathfrak{C}_v)/(\mathfrak{C}_p\mathfrak{C}_v+\nu^2D^2)=2\nu kD/\mathfrak{C}_p\mathfrak{C}_v+\nu^2D^2. \tag{9}$$

The notation of V is adhered to here, namely

$V^2=V_0{}^2e^{2i\phi}$, $V_0{}^2$ is the real part of V^2, cf. Eqs. (8.1).

$\mathfrak{C}_V={}_\infty+\dfrac{1}{N}\left[\dfrac{AC_A}{1+\nu^2/\Sigma_A{}^2}+\dfrac{BC_B}{1+\nu^2/\Sigma_B{}^2}\right]=$ "effective" specific heat per mol. at constant volume,

$\mathfrak{C}_p=\mathfrak{C}_V+k=$ "effective" specific heat per mol. at constant pressure,

$\Sigma_A=A\Gamma_{11}+B\Gamma_{12}\,;\quad \Sigma_B=B\Gamma_{22}+A\Gamma_{21}$ (Cf. Eq. (8.1a) and Eq. (10.3)),

$$D=\frac{1}{N}\left\{\frac{AC_A}{\Sigma_A(1+\nu^2/\Sigma_A{}^2)}+\frac{BC_B}{\Sigma_B(1+\nu^2/\Sigma_B{}^2)}\right\},$$

$\mathbf{C}=\mathbf{C}_i+\mathbf{C}_\infty\,;\quad \mathbf{C}_i=(AC_A+BC_B)/N.$

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[21] $\mathbf{m}$ replaces the slightly awkward notation (cf. reference 2 of III). N/S used in V and earlier.

[22] Called Eq. (2.1) in V, reference 2.

[23] The factor 2 takes care of the fact that intensities and not amplitudes are being compared.

Fortunately, the rather forbidding expression in Eq. (9) may be simplified by removing factors of $(1+\nu^2/\Sigma_A{}^2)(1+\nu^2/\Sigma_B{}^2)$ from numerator and denominator. Thus

$$\mu=\left\{\frac{\dfrac{\nu k}{N}\left\{\dfrac{AC_A}{\Sigma_A}\left(1+\dfrac{\nu^2}{\Sigma_B{}^2}\right)+\dfrac{BC_B}{\Sigma_B}\left(1+\dfrac{\nu^2}{\Sigma_A{}^2}\right)\right\}}{\mathbf{C}_\infty(\mathbf{C}_\infty+k)\left[1+\dfrac{\nu^2}{\Sigma_A{}^2}\right]\left[1+\dfrac{\nu^2}{\Sigma_B{}^2}\right]+(2\mathbf{C}_\infty+k)\mathbf{C}_i+\dfrac{\nu^2}{N}\left\{\dfrac{AC_A}{\Sigma_B{}^2}+\dfrac{BC_B}{\Sigma_A{}^2}\right\}(2\mathbf{C}_\infty+k)+\mathbf{C}_i{}^2+\dfrac{\nu^2}{N}\left\{\dfrac{AC_A}{\Sigma_B}+\dfrac{BC_B}{\Sigma_A}\right\}}\right.$$

$$=\frac{\left\{\dfrac{\nu k}{N}\left[\dfrac{AC_A}{\Sigma_A}\left(1+\dfrac{\nu^2}{\Sigma_B{}^2}\right)+\dfrac{BC_B}{\Sigma_B}\left(1+\dfrac{\nu^2}{\Sigma_A{}^2}\right)\right]\right\}}{\begin{array}{l}(\mathbf{C}+k)\mathbf{C}+\nu^2\left\{\dfrac{1}{\Sigma_A{}^2}\left(\mathbf{C}_\infty+\dfrac{BC_B}{N}+k\right)\left(\mathbf{C}_\infty+\dfrac{B}{N}C_B\right)\right.\\ \qquad\left.+\dfrac{1}{\Sigma_B{}^2}\left(\mathbf{C}_\infty+\dfrac{AC_A}{N}+k\right)\left(\mathbf{C}_\infty+\dfrac{AC_A}{N}\right)+\dfrac{2ABC_AC_B}{N^2\Sigma_A\Sigma_B}\right\}+\nu^2(\mathbf{C}_\infty+k)\mathbf{C}_\infty.\end{array}} \tag{9.1}$$

Very often the following approximations are permissible:

$$BC_B/N\mathbf{C}_\infty,\quad AC_A/N\mathbf{C}_\infty\ll 1. \tag{9.2}$$

This allows us to write the denominator as nearly

$$(\mathbf{C}_\infty+k)\mathbf{C}_\infty[(\Sigma_A{}^2+\nu^2)(\Sigma_B{}^2+\nu^2)/(\Sigma_A\Sigma_B)^2].$$

The approximate expression for μ is now

$$\mu=\frac{\nu k}{N}\left[\frac{AC_A\Sigma_A}{(\mathbf{C}_\infty+k)\mathbf{C}_\infty(\Sigma_A{}^2+\nu^2)}+\frac{BC_B\Sigma_B}{(\mathbf{C}_\infty+k)\mathbf{C}_\infty(\Sigma_B{}^2+\nu^2)}\right]. \tag{9.3}$$

This is sufficiently near to being a sum of effects due to each gas separately to make the result easy to comprehend physically.[24]

So far all the work done on supersonics has assumed pair collisions to be the only significant ones. It is, however, easy to extend the result to triple and higher order collisions and indeed the formulae maintain their appearance, except that the $\left\{\begin{matrix} k_{ij} & \cdots & G_{rs} \\ R_{ij} & & Q_{rs}\end{matrix}\right.$ assigned to n body collisions have an $n-1$ degree factor in the gas concentrations; i.e., A^pB^q, $p+q=n-1$ rather than the normal first degree term in A or B. The general triple collision is, of course,

$$A_iB_jB_K\rightarrow A_\sigma B_\tau B_\gamma. \tag{10}$$

This sort of collision is omitted just now because its inclusion complicates the expressions for ω_A and ω_B. Cf. Appendix, section C.

Consider the case

$$A_1B_rB_s\rightarrow A_2B_rB_s \tag{10.1}$$

with the transition probability $k_{12}{}^{rs}$ in the forward direction and $k_{21}{}^{rs}$ in the reverse. Evidently the contribution to ΔA_1 is

$$(\Sigma_{r,\,s}B_rB_sk_{12}{}^{rs})\delta A_1-(\Sigma_{r,\,s}B_rB_sk_{21}{}^{rs})\delta A_2. \tag{10.2}$$

On comparing with Eqs. (3a) and (3.2a) it is plain that it is only necessary to add the terms

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[24] The appearance of Eq. (9.3) suggests that the parameter $Z=\nu/N$ will rid the result of pressure dependence *provided* Σ_A and Σ_B depend only linearly on A and B. Cf. Richards for a single gas.

$\Sigma_{r,\,s}B_rB_sk_{12}{}^{rs}/B^2$ and $\Sigma_{r,\,s}B_rB_sk_{21}{}^{rs}/B^2$ to P_{12} and P_{21} in Eq. (3.2a) in order to include this triple collision[25] effect. Since for the two state gas model $\dot{A}_1=-\dot{A}_2$ there results[26]

$$\begin{aligned} B\Gamma_{12}&=B(P_{12}+P_{21})+\Sigma_{r,\,s}B_rB_sk_{21}{}^{rs}\\ &=B\left(\frac{1+\mu_A}{1+U_B}\right)\left[(g_{21}{}^1+\mu_Bg_{21}{}^2)+\frac{B}{1+U_B}(k_{21}{}^{11}+\mu_Bk_{21}{}^{12}+\mu_B{}^2k_{21}{}^{22})\right]. \end{aligned} \tag{10.3}$$

Of course similar terms may be added for A. In this way Σ_A and Σ_B may be considered made up of terms in A, B, A^2, $B^2\cdots A^n, B^n$ depending on the order of collisions assumed important.[27]

By making the arbitrary assumption that $k_{12}{}^1$ was proportional to B (and, in the case of H_2O in O_2, to B^2 also) Kneser has been able to get agreement with experiment for impurity contamination.[28] To understand why such a proposal works and what the deeper relation is with collision probabilities we shall derive the impurity contamination case as a special instance of the mixture formulae. We may start either with the definition of ω_A and ω_B, Eq. (5a); or with Eq. (9.3). The Kneser 'normal' situation arises when $B((1+\mu_A)/(1+\mu_B))(g_{21}{}^1+\mu_Bg_{21})$ dominates all other terms in Σ_A and Σ_B. For generality the derivation is given with the weaker assumption $AC_A\Sigma_A\gg\Sigma_BBC_B$, then

$$\omega_B\sim1,\quad \omega_A\sim1/(1+j\nu/\Sigma_A).$$

The result for the absorption is, therefore,

$$\mu=\frac{(\nu k/N)(AC_A\Sigma_A)}{(\mathbf{C}_\infty+k)(\mathbf{C}_\infty)[\nu^2+(1+C_AA/N(\mathbf{C}_\infty+k))(1+AC_A/N\mathbf{C}_\infty)\Sigma_A{}^2]}. \tag{9.4}$$

If, *furthermore*, $AC_A\ll C_{\infty A}N$ (cf. Eq. (9.2)) there results

$$\mu=\frac{(\nu k/N)(AC_A\Sigma_A)}{\mathbf{C}_\infty(\mathbf{C}_\infty+k)(\nu^2+\Sigma_A{}^2)}. \tag{9.5}$$

Kneser's 'normal' case is given by suppressing the A and B^2 terms in Σ_A (cf. Eq. (10.3)). The formula proposed for H_2O in O_2 merely suppresses the A term,[29] leaving $B\Gamma_{12}$ alone. It is, however, to be noticed that $\mathbf{C}_\infty$ in Eq. (9.5) is the mean specific heat. Written out in detail

$$N^2\mathbf{C}_\infty(\mathbf{C}_\infty+k)=B^2(C_{A_\infty}-C_{B_\infty})^2+NB(C_{B_\infty}-C_{A_\infty})(k+2C_{A_\infty})+N^2C_{A_\infty}(C_{A_\infty}+k). \tag{9.6}$$

For the case of $B\sim H_2O$ and $A\sim O_2$ for instance, using the values $C_{A_\infty}=5k/2$, $C_{B_\infty}=1k/2$ the variation of $\mathbf{C}_\infty(C_\infty+k)$ is only about 0.005 in the range from 0 to 1 percent H_2O.[30] A similar remark holds generally for experiments at low frequencies. At higher frequencies the maximum shifts in the direction of increasing B and the variation of the Eq. (9.6) term can no longer be neglected unless C_{A_∞} and C_{B_∞} are equal.

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[25] The derivation on the K.R. method is equally easy.

[26] Unless there is special reason to assume the associated k factor large, the terms with μ_A, μ_B, $\mu_B{}^2$ may probably be dropped.

[27] The experimenter interested only in an applicable result of this investigation is referred to Eqs. (9.1), (9.3), (9.4), (9.5), (11.1), (12), and (12.1). For convenience of reference, using $K_{21}{}^{2jK}$ as the "reaction rate" for $B_2A_jA_K\rightarrow B_1A_jA_K$,

$$\begin{aligned} \Sigma_A&=A(k_{21}{}^1+\mu_Ak_{21}{}^2)+B\left(\frac{1+\mu_A}{1+\mu_B}(g_{21}{}^1+\mu_Bg_{21}{}^2)\right)+B^2\frac{(1+\mu_A)}{(1+\mu_B)^2}\{k_{21}{}^{211}+\mu_Bk_{21}{}^{212}+\mu_B{}^2k_{21}{}^{222}\}\\ &+\\ \Sigma_B&=B(K_{21}{}^1+\mu_BK_{21}{}^2)+A\left(\frac{1+\mu_B}{1+\mu_A}\right)\{G_{21}{}^1+\mu_AG_{21}{}^2\}+A^2\frac{(1+\mu_B)}{(1+\mu_A)^2}\{K_{21}{}^{211}+\mu_AK_{21}{}^{212}+\mu_A{}^2K_{21}{}^{222}\}. \end{aligned}$$

[28] Of course this is only a special type of behavior of impurities. (For other possibilities cf. remarks on the classification of mixtures.) However, this special case seems the one of greatest practical interest at this time.

[29] Kneser, Knudsen, reference 4, p. 691.

[30] The anomalous appearance of Knudsen's $\mu\sim\log B$ curves for H_2O at low frequencies is not explained by this and may credibly be due to the B^2 term. The double transition collisions ought perhaps be looked into. Cf. Eq. (15.5).

The explanation for the triple collision effect as advanced by Kneser and Knudsen is that a reaction of the form $2H_2O+O_2 \rightleftarrows 2H_2O_2$ takes place and hence these are very efficient triple collisions. However, apart from objections based on chemical considerations, a rough computation shows that this efficiency must be unreasonably high even under favorable interpretations. If W represents the fraction of the total number of the triple collisions of Kneser-Knudsen type actually effective for absorption and a prime (here and below) indicates an excited molecule and Z_{33}, Z_3, Z_2 stand for the number of collisions of type $H_2O+H_2O+O_2'$, $O_2'+O_2+O_2$, $O_2'+O_2$ respectively then Kneser and Knudsen[29] have shown that $W \sim B\Gamma_{12}/Z_{33}$. Their experiments give $B\Gamma_{12} \sim 5\cdot 10^8(B/N)^2$. In order to throw in relief the relation of other physical collision processes that may be postulated to account for the experimental data we shall write $Z_{33} \sim (B/N)^2 Z_3 = (B/N)^2(Z_3/Z_2)Z_2$. With the values $Z_2 \sim 4\cdot 10^9$ and $Z_3/Z_2 \sim 10^{-3}$ at normal pressure and a temperature of 20°C there results $W \sim 10^2$. Granting that this impossible result may be ascribed to the grossness of the collision number estimates, there remains the indication that practically every $H_2O+H_2O+O_2'$ collision would have to involve an O_2' internal energy change effective in absorption. This is extremely unlikely and casts doubt on the suggestion that these are the important collisions.

The Kneser-Knudsen results may be explained in another way, however,—namely one involving an increase in the effective number (rather than the efficiency) of the collisions. Specifically we may assume loosely-bound complexes of the sort AB, $(O_2\cdot H_2O)$ or alternatively BB $(H_2O\cdot H_2O)$ in the mixture. The known strong field of O_2 and other arguments of a qualitative nature lends some support to the first of these conjectures. For the AB union there are two types of binary collisions of importance: (a) $A'B+AB$, and (b) $A'B+B$. If r is the fraction of B molecules occurring as components of the complex AB, the collision frequency for case (b) is $\sim 2r(1-r)(B/N)^2Z_2$ and for (a) is less accurately $\sim r^2(B/N)^2Z_2$. The assumptions, (justifiable in such a rough preliminary survey), made here, are that $r \ll 1$, that the ratio of vibrating O_2 molecules is unaffected by association and, for (b), that if all excited O_2 molecules were associated the collision frequency for $H_2O\cdot O_2'+O_2$ would be closely that for $O_2'+O_2$. For (a) it is assumed that the collision number is the same, considering now *all* O_2 molecules associated, as for pure O_2. Comparison with the expression for Z_{33} occurring on the Kneser-Knudsen hypothesis (treated supra) indicates that for $r>5\cdot 10^{-4}$ for (b) and $r>10^{-\frac{3}{2}}$ for the (a) collisions, the postulated association would increase the collision frequency and thus give a more plausible (smaller) W value. Of course, if both (a) and (b) collisions are of comparable efficiency, the collision frequency increase is still greater.

The ingenious suggestion of the H_2O polymerization is due to Professor H. M. Mott-Smith, and may be treated in similar fashion, though it is apparently not so plausible as the first type of association. The writer owes much to the staff of the Department of Physical Chemistry of this university for clarifying discussion of the H_2O polymerization possibility and the chemical aspects of the Kneser-Knudsen peroxide reaction hypothesis. A test of $O_2\cdot H_2O$ (or even $H_2O\cdot H_2O$) association seems in order—either by sound methods, pressure isotherms, or light absorption spectra of O_2 under various concentrations of H_2O as impurity (or *vice versa*). Since the (a) type collisions depend on the squared concentration of O_2, this supposition might be checked by using a high N_2 atmosphere with O_2 and H_2O present in variable amounts in a sound mixture experiment.

Eq. (9.3) (in special cases the more exact Eq. (9.1) may be necessary) suggests a classification of mixtures[31] dependent on the relative size of the terms in Σ_A and Σ_B. The detailed investigation is entirely like that just given (cf. Eq. (9.5)) for the impurity contamination type.

The velocity[32] in the mixture is

$$V^2=(kT/\mathbf{m})(1+R\mathfrak{C}_V/(\mathfrak{C}_V{}^2+\nu^2D^2)). \tag{11}$$

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[31] There is obviously a difference in type between the $\mu \sim \log \nu$ and the $\mu \sim \log B$ curves. The first set are expected to give rise to two maxima of the same general shape.

[32] Strictly speaking, the true (velocity)^2 is $V_0{}^2 \cos^2 \phi$, Eq. (11), whereas what we are calculating is $V^2 \cos 2\phi$, but the difference is negligible.

A common factor of $[(1+\nu^2/\Sigma_A{}^2)(1+\nu^2/\Sigma_B{}^2)]^{-1}$ in numerator and denominator cancels and there results[33]

$$V^2=\frac{p}{\varrho}\left\{1+\frac{k(\mathbf{C}+\nu^2\{C_{\mathrm{I}}/\Sigma_B{}^2+C_{\mathrm{II}}/\Sigma_A{}^2\}+\nu^4\mathbf{C}_\infty/(\Sigma_A\Sigma_B)^2)}{\mathbf{C}^2+\nu^2\{(C_{\mathrm{II}}/\Sigma_A)^2+(C_{\mathrm{I}}/\Sigma_B)^2+2(C_AC_B/\Sigma_A\Sigma_B)\}+\nu^4(C_\infty/\Sigma_A\Sigma_B)^2}\right\}, \tag{11.1}$$

where

$$C_{\mathrm{I}}=\mathbf{C}_\infty+(AC_A/N),\quad C_{\mathrm{II}}=\mathbf{C}_\infty+(BC_B/N). \tag{11.1}$$

The point of inflection of least abscissa[34] for the $V^2\sim\log\nu$ curve with B fixed is approximately

$$\nu_i=[\mathbf{C}/\{(C_{\mathrm{I}}/\Sigma_B)+(C_{\mathrm{II}}/C_A)\}\{1-\mathbf{C}\mathbf{C}_\infty/\Sigma_A\Sigma_B(C_{\mathrm{I}}/\Sigma_B+C_{\mathrm{II}}/\Sigma_A)^2+\cdots\}]. \tag{12}$$

For the impurity contamination case the results are written using Σ_A for compactness though, as before, the A term is supposed to be of minor importance.

$$V^2=\frac{p}{\varrho}\left\{1+\frac{k[(\mathbf{C}_\infty+AC_A/N)+\nu^2\mathbf{C}_\infty/\Sigma_A{}^2]}{(\mathbf{C}_\infty+AC_A/N)^2+(\nu^2/\Sigma_A{}^2)\mathbf{C}_\infty{}^2}\right\},\quad \nu_0\sim(\mathbf{C}/\mathbf{C}_\infty)\Sigma_A. \tag{12.1}$$

Appendix

(A) Previous papers of the writer used the notation $\mathbf{f}_{ij}=k_{ij}{}^i$ and $f_{ij}=\Sigma_\sigma{}'N_\sigma k_{ij}{}^\sigma/(N-N_i)$, $\sigma\neq i$. This separation was more one of form rather than fact for the derivation given neglected terms in $\partial f_{ij}/\partial N_\sigma$ and is valid only when $\mathbf{f}_{ij}=f_{ij}$.[35] Since the results are all stated in terms of the symbols[36] R_{ij}, we have only to use the correct generalized form of R_{ij} as given in the text to have accurate interpretations in all cases,[37] i.e.,

$$R_{ij}=\Sigma_\sigma N_\sigma k_{ij}{}^\sigma/N=(N_i\mathbf{f}_{ij}+(N-N_i)f_{ij})/N \tag{13}$$

rather than the value

$$R_{ij}{}'=(2N_i(\mathbf{f}_{ij}-f_{ij})+Nf_{ij})/N \tag{13.1}$$

used in earlier papers.

Although this result for R_{ij} has already been established in a simple manner in the text (cf. Eq. (3.2a)), in the interest of continuity with the notation in previous papers, we shall now show that the addition of $\partial f_{ij}/\partial N$ terms does indeed bring the earlier expression (Eq. (13.1)) into conformity with Eq. (13).

Reference to I and IV shows that f_{ij} occurs in $D(N_i)$ with the coefficient $N_i(N-N_i)$. The new terms in the coefficient of δN_i, because of inclusion of $\partial f/\partial N_\sigma$ terms, are

$$(\partial f_{ij}/\partial N_i)(N-N_i)N_i-(\partial f_{ji}/\partial N_i)(N-N_j)N_j. \tag{13.2}$$

Evidently

$$\begin{aligned}\frac{\partial f_{ij}}{\partial N_i}&=\frac{1}{N-N_i}f_{ij},\\ \frac{\partial f_{ji}}{\partial N_j}&=\frac{1}{N-N_j}f_{ji}{}^i=\frac{N_i}{N_j}\frac{1}{(N-N_j)}f_{ij}{}^i=\frac{N_i}{N_j}\frac{1}{(N-N_j)}\mathbf{f}_{ij}.\end{aligned} \tag{13.3}$$

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[33] The general equation of velocity in mixtures was given in the author's early papers, reference 2, I, II, V—the one given here is simpler because of algebraic reductions and also a superior nomenclature, besides including triple collision effects in the Γ's.

[34] Cf. appendix for remarks about the inflection point calculations.

[35] A similar assumption is made in Richards' paper, J. Chem. Phys. **1**, 863 (1933). Kneser's and Ruttgers' work uses a single type of collision as being significant so that the differentiation does not arise there. M. Rose, J. Chem. Phys. **2**, 260 (1934), mentions this point.

[36] It is assumed that the notation and ideas are fairly familiar to the reader either from say 1, IV of reference 2, or from reading the first section of this paper.

[37] Unfortunately, careless proofreading overlooked the omission of two whole phrases in the derivation of ΔN_i in IV and may possibly account for some difficulty in reading Richards has alluded to. However, I, reference 2, contains virtually the same derivation. In Eqs. (1.07), (1.08) all terms are of course inside the differentiating operators. Another error of obvious type is the omission of summation signs at the top of page 724. The correct statement is, of course, that $\Sigma_i(\Delta K_i)=N\Sigma_iN^{\cdot}{}_iA_i\epsilon_i\delta K$. A number of correspondents have inquired about the proof that $\Sigma_i(A_i-\Sigma_js_j)\Delta K_i=S\Sigma_iN^{\cdot}{}_i\epsilon_i\delta K$. The direct verification is tedious. The truth of the relationship is patent on realizing that for vanishing frequencies there is perfect adjustment. With $L_{\nu\to0}(\omega_i-1/j\nu)=(A_i-\Sigma_js_j)/S$ there follows

$$\begin{aligned}L_{\nu\to0}\Sigma_i(\Delta K_i)\frac{\omega_i-1}{j\nu}&=\Sigma_i(A_i-\Sigma_js_j)\Delta K_i\\&=-\Delta K=C_i\delta K=\Sigma_iN^{\cdot}{}_i\epsilon_i\delta K.\qquad\text{Q.E.D.}\end{aligned}$$

As errata in V may be mentioned the omission of squares from the $N_1\Gamma_{11}+N_2\Gamma_{12}$ and $N_1\Gamma_{21}+N_2\Gamma_{22}$ terms in the definition of $\mathfrak{C}_\nu$. Also the definition of D omits the factors $(1+\nu^2/\Sigma^2{}_A)^{-1}$; $(1+\nu^2/\Sigma^2{}_B)^{-1}$ in the coefficients of AC_A/Σ_A and BC_B/Σ_B. These two inadvertencies do not affect Eq. (7.2) of that paper.

Therefore

$$NR_{ij}'-N_i\mathbf{f}_{ij}+N_if_{ij}=N_i\mathbf{f}_{ij}+(N-N_i)f_{ij}=NR_{ij}. \tag{13.4}$$

(B) The text treatment has established that except possibly for C_∞ in place of $3k/2$ the K.R. and the writer's methods lead to similar results. The text work has, however, restricted itself to a single ω characterizing each gas, but the equivalence of the methods is obviously not dependent on this simplification. As an exercise in point we may derive the result for a single gas

$$\Delta A_i=-(\omega_i-1)A\Sigma_j\{(A^{\cdot}_iR_{ij})-(A^{\cdot}_jR_{ji})(\omega_j-1)\} \tag{14}$$

used in I and IV, by the K.R. method. The calculation will, incidentally, enable the reader to see at once how multiple collision transitions fit in. If, then,

$$\mu_2=A_2/A_1\cdots;\qquad \mu_i=A_i/A_1;\qquad A_i=\mu_iA/1+\mu_2+\mu_3+\cdots\mu_n \tag{14.1}$$

we may write

$$\begin{aligned}D(a_1)/U&=-[(A_1\mu_2-A_2)\Sigma_\sigma A_\sigma f_{21}{}^\sigma+(A_1\mu_3-A_3)\Sigma A_\sigma f_{31}{}^\sigma+\cdots(A_1\mu_i-A_i)\Sigma f_{i1}{}^\sigma A_\sigma+\cdots\\&=0 \text{ at equilibrium,}\end{aligned} \tag{14.2}$$

$$D(a_i)/U=\cdots$$

$$\Delta a_1/U=-A\{(\delta(A_1\mu_2)-\delta A_2)R_{21}+(\delta(A_1\mu_3)-\delta A_3)R_{31}+\cdots(\delta(A_1\mu_i)-\delta A_i)R_{i1}+\cdots \tag{14.3}$$

It is easy to see that

$$\delta\mu_i=(A^{\cdot}_i/A_1-(A^{\cdot}_1/A_1)\mu_i)\delta K. \tag{14.5}$$

On substituting these values in Eq. (14.2) and adopting the notation $\delta A_i/\delta K=\omega_i=\delta a_i/U\delta K$ one arrives at Eq. (14) for $i=1$. In exactly the same way, the general case ($i=2, 3, \cdots n$) may be determined so that in all cases Eq. (14) is reproduced. On specializing the range i, j as 1, 2, 3, there results the case treated in IV, etc., thus verifying that the results of that paper may be arrived at by the K.R. method.

(C) The collisions treated so far have been restricted to change in only one of the colliding molecules.[38] More general collisions may be introduced into the theory at the expense of complicating the resulting formulae. Consider for instance the collision taking A_iA_j into A_kA_h respectively. The transition probabilities are written $f^{ij}{}_{ik,\,jh}$ and $f^{kh}{}_{ki,\,hj}$. The contribution of these collisions[39] to ΔA_i is

$$-A_kf^{kh}{}_{ki,\,hj}\left[\delta\left(\frac{A_iA_j}{A_k}\frac{\mu_k\mu_h}{\mu_i\mu_j}\right)-\delta A_h\right]\cdot \tag{15}$$

This may be shown easily enough to reduce to

$$-A_kA_hf^{kh}{}_{ki,\,hj}\left\{\frac{A^{\cdot}_i}{A_i}(\omega_i-1)+\frac{A^{\cdot}_j}{A_j}(\omega_j-1)-\frac{A^{\cdot}_k}{A_k}(\omega_k-1)-\frac{A^{\cdot}_h}{A_h}(\omega_h-1)\right\}\cdot \tag{15.1}$$

Accordingly the term $A_kf^{kh}{}_{ki,\,hj}$ adds to the other terms of R_{ki}; $A_hf^{kh}{}_{ki,\,hj}$ adds to those of R_{hj} and the other two terms are easily seen to be parts of R_{ik} and R_{jk} for they are, respectively, A_k/A_i and A_h/A_j times the first named. Cf. Eq. (3.2a).

By analogy with the case of the mixture whose treatment immediately follows, one would expect as a modification in the three state pure gas model that, instead of getting a second degree denominator in $j\nu$ for ω_i ($i=1, 2, 3$), we should get a cubic. The writer has not tested this however.

We consider now the case of simultaneous transitions in the partners of a double collision. The *new* terms in $D(A_i)$ are

$$-(A_iB_jf^{ij}{}_{ik,\,jh}-A_kB_hf^{kh}{}_{ki,\,hj}). \tag{15.2}$$

On passing to ΔA_i these become

$$-(\delta A_iB_jf^{ij}{}_{ik,\,jh}+\delta B_jA_i)f^{ij}{}_{ik,\,jh}-(\delta A_kB_h+A_k\delta B_h)f^{kh}{}_{ki,\,hj}; \tag{15.3}$$

then with the argument leading to Eq. (4a) we have here for the *new* terms

$$\begin{aligned}\Delta A_i&=-(\omega_A-1)\Sigma_{k,\,j,\,h}(A^{\cdot}_iB_jf^{ij}{}_{ik,\,jh}-A^{\cdot}_kB_hf^{kh}{}_{ki,\,hj})-(\omega_B-1)\Sigma_{k,\,j,\,h}(A_iB^{\cdot}_jf^{ij}{}_{ik,\,jh}-A_kB^{\cdot}_hf^{kh}{}_{ki,\,hj}),\\ \Delta B_j&=\cdots.\end{aligned} \tag{15.4}$$

Evidently the solution for ω_A, ω_B is the ratio of a linear to a quadratic polynomial in $j\nu$. Thus the expressions for the absorption and velocity will *not* be of the simple type given in the text. The complex velocity of sound may be written down at once as may also the expression for $\mathfrak{C}_v$, $\mathfrak{C}_n$, D after which the deduction of the expression for μ and $|V|$ is a matter of straightforward reduction. The algebra involved in manipulating the resulting expressions appears to be so

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[38] The redistribution of internal energies in an excited molecule has not yet been explicitly recognized in the equations.

[39] To balance the use of the K.R. method here, the double transitions in mixtures, treated next, is discussed by the writer's method.

heavy that a complete discussion will not be attempted in this paper. Perhaps the most important double transition to be expected is that written as $(A_1B_2)\rightarrow(A_2B_1)$. The formulae will be expressed for this case

$$\omega_A=\frac{j\nu S_1+l}{(j\nu)^2+j\nu m+l},\qquad \omega_B=\frac{j\nu S_2+l}{j\nu m+(l-\nu^2)},$$

$$V^2=\frac{p}{\rho}\left[\frac{\mathfrak{C}_v+k-j\nu D}{\mathfrak{C}_v-j\nu D}\right]=\left(\frac{p}{\rho}\left[1+\frac{j\nu k}{j\nu \mathbf{C}_\infty+(1/N)\{\omega_A A C_A+\omega_B B C_B\}}\right]\right), \tag{15.5}$$

$$\mathfrak{C}_v=\mathbf{C}_\infty+\frac{1}{N}\left\{AC_A\Big/\left(1+\nu^2\left\{\frac{\nu^2+m(m-S_1)-l}{\nu^2(mS_1-l)+l^2}\right\}\right)+BC_B\Big/\left(1+\nu^2\left\{\frac{\nu^2+m(m-S_2)-l}{\nu^2(mS_2-l)+l^2}\right\}\right)\right\},$$

$$D=\frac{1}{N}\left[\frac{AC_A(ml-S_1l+\nu^2S_1)}{l^2+\nu^2(m^2-2l)+\nu^4}+\frac{BC_B(ml-S_1l+\nu^2S_2)}{(l-\nu^2)^2+\nu^4}\right],$$

$$S_1=\Sigma_A+(A^{\cdot}{}_1B_1(1+\mu_A)f^{21}{}_{21,\,12}-A_1B^{\cdot}{}_1(1+\mu_B)f^{12}{}_{12,\,21})/A^{\cdot}{}_1,$$

$$S_2=\Sigma_B-(A^{\cdot}{}_1B_1(1+\mu_A)f^{21}{}_{21,\,12}-A_1B^{\cdot}{}_1(1+\mu_B)f^{12}{}_{12,\,21})/B^{\cdot}{}_1,$$

$$l=(\Sigma_A\Sigma_B)+(\Sigma_A)A_1(1+\mu_B)f^{12}{}_{12,\,21}+(\Sigma_B)B_1(1+\mu_A)f^{21}{}_{21,\,12},$$

$$m=\Sigma_A+\Sigma_B+A_1(1+\mu_B)f^{12}{}_{12,\,21}+B_1(1+\mu_A)f^{21}{}_{21,\,12}.$$

(D) To complete the comparison of the K.R. and the writer's methods, it will now be shown how, by slight modification, the fundamental equations may be made to yield C_∞ in place of $3k/2$. It may be verified in fact that it is sufficient to replace the coefficients 2/3 and 5/3 in Eqs. (4.2a) and (4.3a) by k/C_∞ and $1+k/C_\infty$ respectively. These changes are given their interpretation by the assumption of an external energy no longer identical with the translational energy. We have now

$$\begin{aligned}K&=C_\infty T\\&=[C_\infty/3k/2](\tfrac{1}{2}m(\overline{u^2+v^2+w^2})),\end{aligned} \tag{16}$$

where u, v, w are the component velocities of the molecules.[40]

(E) By way of further elucidation of the interpretations given in IV, one remarks that, physically speaking, increasing the sound frequency has as net result complete ankylosis of all states eventually. However, if some states have a long mean life, the frequency at which ankylosis for them is practically total may very well leave the other states only slightly affected. (The relation $dK/dT=3k/2$ preserves the true physical model.) For computational purposes over this first range, one may consider the rest of the states absolutely, instead of merely relatively, unaffected. This amounts to having, instead of a single term of this independent nature (namely $3k/2$), the sum $3k/2+d/dT\Sigma_jA_j\epsilon_j=C_\infty$ where the summation includes only the short life states, thus giving a mathematically convenient, though physically fictional, representation.

(F) In view of the remarks just concluded in this appendix, as well as the comparative study made in the text, we may say that the K.R. and the writer's methods differ almost solely in the fact that the last uses the language of kinetic theory while the first uses that of thermodynamics and chemical reactions. We have shown that not only is there equivalence in the end result, namely the expression for the velocity of sound, but also in the separate steps and basic assumptions. It would seem to the writer that the kinetic theory formulation is more "natural" since the mechanism and processes involved are kinetic in nature. Furthermore the use of concentrations (i.e. A_i) rather than total populations (a_i) has on the one hand the advantage of clarity and on the other almost automatically excludes errors arising from manipulations[6] with U. From the practical viewpoint perhaps the most important difference is connected with the writer's *explicit* introduction of the ω_i. These not only give logical sequence to the steps of the argument, but are essential to the definition of the classes of states which act as *units* (i.e., ω_i is the same for these states)—that is to say, precision is given to statements such as "states . . . come in or drop out together."[41]

(G) Of course, finite amplitude, viscosity, conductivity,[42] etc., may affect the absorption and sound velocity to some degree. As a formal scheme the last two agencies may be incorporated approximately (as in II) by adding the term $s\partial^2v/\partial x^2$ to Eq. (4.2a) and $\vartheta\partial^2K/\partial x^2$ to Eq. (4.3a). ω_A and ω_B are unaffected. (Cf. Eq. (5a).) The method of the text yields directly

$$\begin{aligned}V^4\mathbf{m}(\omega_AAC_A+\omega_BBC_B+NC_\infty)+V^2\{&-j\nu(s(\omega_AAC_A+\omega_BBC_B+NC_\infty))+\mathbf{m}NC_\infty\vartheta\\&-\tfrac{2}{3}K[\omega_AAC_A+\omega_BBC_B+NC_\infty+k]\}+\tfrac{2}{3}j\nu KN\vartheta-s\vartheta NC_\infty\nu^2=0,\end{aligned} \tag{17}$$

from which the information of interest may be obtained, but the paper is already too long for consideration of the μ and $|V|$ expressions here.

(H) The remainder of this appendix is devoted to some comments on IV. If the physical ideas of IV be adhered to, the three states referred to there are the ground state $\epsilon_3=0$, the excited state ϵ_1 of appreciable occurrence and of long mean

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[40] The coefficient kT/m (of V^2) becomes $C_\infty T/m$ which is again p/ρ.

[41] Richards, reference 5.

[42] Cf. II, reference 2, and also Rocard, J. d. Physik **1** (1930).

life, and ϵ_2, the short life state (or, if the proper specific heat contribution of the internal energy states is to be maintained, a single equivalent state for all those of short life). It will be supposed then that ϵ_2 is closely $C_v-\epsilon_1$. With the $3k/2$ theory, the three state calculation is necessary. If the shorter lived of the two states is lumped with the translational energy, only a two state calculation is needed for fair approximation.[43]

We shall show now that whether or not this change be made in the final equations, i.e., C_∞ for $3k/2$, the term $\Sigma N^{\cdot}_i A_i\epsilon_i/\Sigma s_j$, which[44] is the component of interest in the main results of IV, always reduces, except for small correction terms, to C_i-C_1, i.e., the long lived $i=1$ state "drops out" of the internal specific heat. Under hypothesis A of that paper R_{21} and R_{31} are very small. Therefore

$$\Sigma_i{}^3\frac{N^{\cdot}_iA_i\epsilon_i}{\Sigma s_j}=\frac{\Sigma_iN^{\cdot}_i\Sigma_K(R_{iK}-(N^{\cdot}_K/N^{\cdot}_i)R_{Ki})\epsilon_i}{\frac{1}{2}\Sigma_j\Sigma_KR_{jK}}\sim\frac{s_1N^{\cdot}_1\epsilon_1}{s_2+s_3}+\frac{N^{\cdot}_2A_2\epsilon_2}{s_2+s_3}\,; \tag{18}$$

also

$$\frac{A_2}{s_2+s_3}\sim\left(s_2-\frac{N^{\cdot}_3}{N^{\cdot}_1}R_{32}\right)\bigg/R_{23}+R_{32}=\frac{R_{23}\epsilon_2}{(\epsilon_2-\boldsymbol{\varepsilon})R_{23}+R_{32}}, \tag{18.1}$$

where $\boldsymbol{\varepsilon}$ is the mean value of ϵ, i.e., $(\epsilon_1\mu_1+\epsilon_2\mu_2)/(1+\mu_1+\mu_2)$; $\mu_i=N_i/N_3$. Hence the further reduction

$$=\frac{\epsilon_2(1+\mu_1+\mu_2)}{(\epsilon_1\mu_1+\epsilon_2(1+\mu_1))(1+\mu_2)}\sim 1.$$

Thus to terms in μ_1 and $s_1/(s_2+s_3)$

$$\frac{\Sigma N^{\cdot}_iA_i\epsilon_i}{\Sigma s_j}\sim N^{\cdot}_2\epsilon_2=(d/dK)(N_1\epsilon_1+N_2\epsilon_2)-N^{\cdot}_1\epsilon_1=\frac{C_i-N^{\cdot}_1\epsilon_1}{3k/2}=\frac{C_j-C_1}{3k/2}\,.$$

It is manifest then that Eq. (2.092) of IV is a refinement of the grosser theory expressed by Eq. (2.021) and does, indeed, reduce to it when small correction terms are neglected.

If now the $3k/2$ be changed to C_∞ the results of IV may be considered as a second order approximation with *three types*[45] of *excited states*. We have then[46]

$$C_\infty=3k/2+(d/dT)N_3\epsilon_3,\qquad C_i=(d/dT)(N_1\epsilon_1+N_2\epsilon_2).$$

It is easy to see that the reduction of $\Sigma N^{\cdot}_iA_i\epsilon_i/\Sigma s_j$ is precisely the same as before (cf. Eq. (11.2)) to C_i-C_1.

The value of ν_0 in Eq. (2.10) of IV, as is obvious from the context, lacks a term. The value should be[47]

$$\nu_0\sim\frac{Ns_1(3k/2+C_i)}{\{3k/2+(\Sigma N^{\cdot}_iA_i\epsilon_i/\Sigma s_j)\}\left(1-\dfrac{s_1}{s_2+s_3}\left(\dfrac{3k/2+C_i}{3k/2+(\Sigma N^{\cdot}_iA_i\epsilon_i/\Sigma s_j)}\right)\right)}\,.$$

From the results stated in Eq. (18.2) above this we get

$$\nu_0\sim\frac{Ns_1C_v}{(C_v-C_1)\left(1-\dfrac{s_1}{s_2+s_3}\dfrac{C_v}{C_v-C_1}\right)}\,.$$

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[43] Of course the results of the $3k/2$, three state theory are not the same as those of the two state C_∞ theory, for in the latter case the lumped internal energy states are assumed absolutely free of frequency dependence whereas in the former the weak frequency modifications are included, but the concordance is much better than that between say a two and a three state $3k/2$ (or C_∞) formula. Cf. IV, reference 2, for discussion of mean life interpretations.

[44] $A_i=\Sigma_j(R_{ij}-(N^{\cdot}_j/N^{\cdot}_i)R_{ji})$; $s_j=\Sigma_KR_{jK}$.

[45] There is no necessity to assume that ϵ_3 has the lowest energy.

[46] This covers the case of one very short lived state and two others, both long lived but of different orders.

[47] The value of ν_0 given above has been obtained after extensive approximation. If Eq. (2.091) of IV, reference 2, be written

$$V^2=\frac{p}{\rho}\left\{1+\frac{a_2+a_1\nu^2+\nu^4}{b_2+b_1\nu^2+\nu^4}\right\}$$

the inflection point for the $V^2\sim\log\nu$ curve is determined as the root of a fourth degree equation in ν^2. Neglecting all but the last two terms there is obtained

$$\nu_0{}^2\sim\frac{\beta_2}{\beta_1(1-[4(\beta_2-\alpha_2)/\beta_1(\alpha_1-\beta_1(\alpha_2/\beta_2))])}\,.$$

This is further approximated as $(\beta_2/\beta_1)^{\frac{1}{2}}$. Throughout the parameter of smallness is s_1/s_2+s_3. In cases where this ratio is not excessively small, enough detail has been indicated to enable the reader to supply the next higher terms. The neglect of higher degree terms in the eighth degree equation for ν_0 is supported by the observation that for $\nu_0=(\beta_2/\beta_1)^{\frac{1}{2}}$ the ratio of the neglected terms to those retained involves powers of s_1/s_2+s_3.