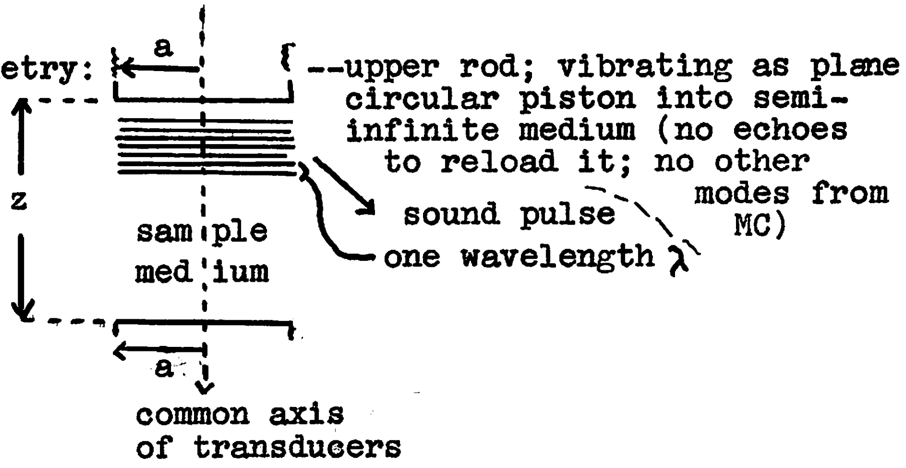
Diffraction Corrections

Much of this section is a rewrite or condensation of extensive information in notebook 5090: 48 ff. We give little text, so the presentation is somewhat rough, to keep its size down.

Geometry:



Sound pattern depends upon a/λ, z/λ, or a/λ, z. In our system a is fixed, λ ranges over 4 discrete values corresponding to the 4 frequencies, and z varies continuously from ≃ 0.6a to 7a. Compute average sound pressure on the lower rod face $\langle P\rangle_{av}$:

$$\langle P(z)\rangle_{av} = \int_0^a \frac{dr\,2\pi r P(z,r)}{\pi a^2}$$, implicit function of a/λ

$P(z,r) = i\omega\rho_0\varphi(z,r)$, φ =velocity potential

$$\varphi(z,r) = v_0 a\int_0^\infty e^{-\mu z} J_0(sr)J_1(sa)\,\frac{ds}{\mu}$$

J_n =Bessel function of order n
v_0 =sound velocity in medium
μ $=(s^2-k^2)^{\frac{1}{2}}$
k =propagation constant $=2\pi/\lambda$

From A. O. Williams, Jr., J. Acous. Soc. Am. 23,1(1951), omitting many steps:

$$\langle \Psi(z) \rangle_{av} = \frac{2\mathfrak{P}_o}{a}\int_0^{\infty} ds u^{-1} e^{-sz} \frac{J_1^2(sa)}{sa}$$

and using integral representations of the Bessel functions

$$= \frac{4\mathfrak{P}_o}{\pi i k}\int_0^{\pi/2} d\theta \sin^2\theta \left[e^{-ikz} - e^{-ik(z^2+4a^2\cos^2\theta)^{\frac{1}{2}}}\right],$$

which reduces to Bass' final expression for $\langle P(z) \rangle_{av}$ by multiplying by $i\omega\rho_o$. Our interest is in the ratio $\underline{R}$ of $\langle P(z) \rangle_{av}$ to the perfect plane wave pressure $\langle P_o(z) \rangle_{av} = \rho \mathfrak{P}_o \omega e^{-ikz}/k$,

$$R = 1 - \frac{4}{\pi}\int_0^{\pi} e^{-ik\left[(z^2+4a^2\cos^2\theta)^{\frac{1}{2}}-z\right]} \sin^2\theta d\theta$$

$$\equiv 1 - I.$$

$\underline{I}$ has no closed form. Williams expands the integrand in powers of $\cos\theta$, changes variables, and gets an analytic form good for $(4ka)/(z/a)^5 \ll 2\pi$ and $(ka^4)/z^3 \ll 1$. We want to treat $z/a \gtrsim 0.6$ and $ka \approx 230\text{-}700$, while Williams' expression does not converge at the lower range of z/a.

Bass changes variables:

$$\zeta = \frac{k}{2}\left[(z^2+4a^2)^{\frac{1}{2}}-z\right]$$

$$= \left[(z^2+4a^2\cos^2\theta)^{\frac{1}{2}}-z\right] / \left[(z^2+4a^2)^{\frac{1}{2}}-z\right]$$

$$I \rightarrow \frac{2}{\pi}\int_0^1 \left[1-\alpha(1-2u)\right]\left[\frac{1+\alpha u}{1+\alpha u-\alpha}\right]^{\frac{1}{2}}\left[\frac{1-u}{u}\right]^{\frac{1}{2}} e^{-2i\zeta u} du,$$

where for compactness $\alpha = (\zeta/ka)^2$.

Now, integrals $\underline{I}_n = \int_0^1 du e^{-2i\zeta u} u^n \left(\frac{1-u}{u}\right)^{\frac{1}{2}}$ can be expressed in terms of a few Bessel functions, as by identifying the integral with a confluent hypergeometric function

(M. Abramowitz and I. Stegun, Handbook of Mathematical Functions, N.B.S., Washington, D.C., 1964 ; p. 505). Also Bass implies

$$I_o = \frac{\pi}{2}\left[J_0(\zeta)+iJ_1(\zeta)\right]e^{-i\zeta}.$$

Using $I_n = \frac{i}{2}\frac{d}{d\zeta}I_{n-1}$ and the J_n recursion relations to reduce all Bessel functions to J_o, J_1, we find

$$I_1 = \frac{i\pi}{4\zeta} J_1 e^{-i\zeta} \text{ (argument of J implicitly } \zeta\text{)}$$

$$I_2 = \frac{i\pi}{8\zeta^2} e^{-i\zeta}\left[\zeta J_o-(2+i\zeta)J_1\right]$$

$$I_3 = \frac{\pi}{16\zeta^3} e^{-i\zeta}\left[(3\zeta+2i\zeta^2)J_o-(6+4i\zeta-2\zeta^2)J_1\right]$$

$$I_4 = \frac{i\pi}{32\zeta^4} e^{-i\zeta}\left[(-12\zeta-9i\zeta^2+4\zeta^3)J_o+(24+18i\zeta-11\zeta^2-4i\zeta^3)J_1\right].$$

We still have to expand the factor in the integrand

$$f(u) = \left[\frac{1+\alpha u}{1+\alpha u-\alpha}\right]^{\frac{1}{2}}$$

in polynomial form. Bass expands about u = 0, but this won't converge for small z/a (large α). Instead we expanded about $u = \frac{1}{2}$ arbitrarily and gathered powers of u. Terms to u^3 adequately represented f(u) in the important range $z/a \gtrsim 0.5$ for u in the range 0,1:

$$f(u) \simeq \sum_{n=0}^{3} \frac{f^{(n)}(\frac{1}{2})}{n!}(u-\tfrac{1}{2})^n$$

$$= A' + B'u + C'u^2 + D'u^3.$$

Total integrand:

$$g(u) = \left[1+\alpha(1-2u)\right] f(u) \simeq \sum_{n=0}^{4} c_n u^n$$

and

$$I = \frac{2}{\pi}\int_0^1 du\, g(u)\left(\frac{1-u}{u}\right)^{\frac{1}{2}} e^{-2i\zeta u}$$

$$\simeq \frac{2}{\pi}\sum_{n=0}^{4} c_n \int_0^1 du\; u^n\left(\frac{1-u}{u}\right)^{\frac{1}{2}} e^{-2i\zeta u}$$

$$= \frac{2}{\pi}\sum_{n=0}^{4} c_n I_n \ .$$

Gathering terms in ζ^n:

$$R = 1-I$$

$$= 1-2e^{-i\zeta}\Big[\frac{J_0}{3}\Big(-i\frac{3}{8}c_4+\Big\{\frac{9}{32}c_4+\frac{3}{16}c_3\Big\}\zeta+\frac{i}{8}\Big\{c_4+c_3+c_2\Big\}\zeta^2$$

$$+ \frac{c_0}{2}\ {}^{3}\Big)$$

$$+\frac{J_1}{4}\Big(i\frac{3}{4}c_4-\Big\{\frac{9}{16}c_4+\frac{3}{8}c_3\Big\}\zeta-\frac{i}{32}\Big\{11c_4+8c_3$$

$$+8c_2\Big\}\zeta^2+\frac{1}{8}\Big\{c_4+c_3+c_2+2c_1\Big\}\zeta^3+\frac{1}{2}c_0\zeta^4\Big)\Big]$$

where

$c_0 = (1-\alpha)A'$ / $c_1 = 2\alpha A'+(1-\alpha)B'$ / $c_2 = 2\alpha B'+(1-\alpha)C'$

$c_3 = 2\alpha C'+(1-\alpha)D'$ / $c_4 = 2\alpha D'$

and

$A' = A - \frac{1}{2}B + \frac{1}{4}C - D/8$ $\qquad$ $B' = B - C + \frac{3}{4}D$

$C' = C - \frac{3}{2}D$ $\qquad$ $D' = D$

and

$A = b/c$ $\qquad$ $B = -\alpha^2/2bc^3$ $\qquad$ $C = \dfrac{\alpha^3(4+\alpha)}{8b^3c^5}$

$$D = \frac{\alpha^4(4+2\alpha+\alpha^2)}{8b^5c^7}$$

and

$\kappa = \zeta^2/(ka)^2$; $\zeta = \frac{k}{2}\left[(z^2+4a^2)^{\frac{1}{2}}-z\right]$; z,k,a are given in the dimensions of the problem.

The complex response ratio R is converted to an effective db loss Q,

$$|R| = e^{-Q/8.686} \rightarrow Q = 8.686 \ln|R| .$$

Q was computed for my system for a = 12.7 mm. (fixed), for four frequencies f = 4.5, 7.5, 10.5, and 13.5 MHz. (for 4 values of propagation constant k, that is), and in turn for a grid of heights z (hence for ζ or κ) from about 8 to 66 mm. in steps of 2 mm. (and later out to 80 mm.). Several sound velocities were tried without changing the results noticeably, so we settled on a standard β of 1570 m./sec. The FORTRAN computer program to do the work is listed in the pages stapled in notebook 5090: 52. Its input consists of: the number of classes of velocity (and absorption--explained later), and labels; number of frequencies and the f_i; a and β; the grid of z_i; absorption κ; and print option parameters. It is extensively commented and easy to use. Our results in Table IV check with Bass' for larger z/a. The apparent loss factor Q was monotonic for all f in my range of z, even at very low z. This verifies that diffraction is not the cause of signal oscillation with micrometer height, and reinforces the judgment that mode conversion is the real cause.

Bass notes that non-zero absorption α can be accommodated in the formalism by making the propagation constant *k* complex, $\underline{k} = 2\pi/\lambda - i\alpha$ (distinguish absorption α from $\alpha = \zeta^2/(ka)^2$). The goal here is to show that *Q* from diffraction is additive to absorption losses for all practical purposes:

$$Q(\alpha,z) \simeq Q_0(z) + \alpha z$$

$$Q(\alpha,z) = Q_1(z) + \alpha z,$$

that is, that $\underline{Q}_1 \simeq \underline{Q}_0$. We wrote new routines to compute the Bessel functions of complex argument ζ. Rather than rewrite in complex arithmetic the computing center routines which are more general than we need, we noticed that ζ is large enough even at z/a as small as 0.5 (Reζ ranges from 35.4 to 503 in our work) to use asymptotic expansions (Abramowitz and Stegun, p. 364):

$$J_0(z) \simeq \left(\tfrac{2}{\pi}\right)^{\frac{1}{2}} z^{-\frac{1}{2}} \left\{ \left(1 - \frac{9}{128z^2} + \frac{3675}{32768z^4}\right)\cos(z - \tfrac{1}{4}\pi) + \left(-\frac{1}{8z} + \frac{75}{1024z^3}\right)\sin(z - \tfrac{1}{4}\pi) \right\}$$

$$J_1(z) \simeq \left(\tfrac{2}{\pi}\right)^{\frac{1}{2}} z^{-\frac{1}{2}} \left\{ \left(1 + \frac{15}{128z^2} - \frac{14175}{32768z^4}\right)\cos(z - \tfrac{3}{4}\pi) + \left(\frac{3}{8z} - \frac{105}{1024z^3}\right)\sin(z - \tfrac{3}{4}\pi) \right\}$$

These expansions are used with standard complex double precision sin and cos routines, CDSIN, CDCOS.

Since cos z, sin z can be written as $\frac{1}{2}(e^{iz}+e^{-iz})$, $\frac{1}{2i}(e^{iz}-e^{-iz})$, the form of $e^{-i\zeta} J_0(\zeta)$ in the expression for *R* (hence $|\underline{R}|$, *Q*) can be seen as dominated by the lead term $e^{-i\zeta} e^{i\zeta} = 1$ for any complex *z*, if its imaginary part is small. Thus corrections from nonadditivity of diffraction and true absorption require Im $\underline{k} = \alpha$ to approach the order of magnitude of Re $\underline{k} = 2\pi/\lambda$, which never occurs in our experiments. We proceeded with the calculations and obtained results $\underline{Q_1(z)}$ indistinguishable from $\underline{Q_0(z)}$ (additions to notebook $\underline{5090}$: 52). They are not reported in Table IV.

Table I. Sample of Raw Ultrasonic Data

Order of data explained in text; formats given in program listing

```
  0.1238 34.66  4.51DATA 2/25/70 BY VPG; THIS RUN STARTS TRADIN OF BETA AT 4.5 M
HZ ONLY, NEW WAY; 5 DB READING IN 3RD RUN IS W/ POOR LIQ. CONTACT
 3
 6
29.00 37.93 47.25 55.95 64.85 74.08   .    .    .    .    .    .    .
 6
29.10 38.37 47.30 56.35 66.38 75.00   .    .    .    .    .    .    .
 6
29.00 38.09 47.72 57.18 66.22 75.57   .    .    .    .    .    .    .
 1
 5  5.000-06
70.00 60.00 50.00 40.00 30.00
09.00 07.72 06.44 05.16 03.89   .    .    .    .    .    .    .    .
  0.1238 34.66  7.52DATA 2/25/70 BY VPG; LAST 7.5 MHZ BETA; SIGNAL UNSTEADY, ESP
. BETWEEN 1,2 DB. IN 1ST RUN
 2
10
29.00 34.84 41.45 46.00 50.81 55.59 60.46 64.52 69.26 73.70    .    .    .
10
31.17 36.25 40.87 46.30 51.52 56.32 60.80 65.29 70.40 75.00    .    .    .
 1
 5  5.000-06
70.00 60.00 50.00 40.00 30.00
09.09 07.81 06.54 05.26 04.00   .    .    .    .    .    .    .    .
  0.1238 34.66 10.53DATA 2/25/70 BY VPG

 2
13
29.00 31.79 34.48 37.20 39.97 43.83 45.50 48.00 51.06 53.68 56.28 58.88 62.01
13
31.53 34.36 36.81 39.76 42.76 45.58 48.39 51.13 54.11 56.70 59.65 62.43 65.00
 0
  0.1238 34.66 13.53DATA 2/25/70 BY VPG; SIGNAL BOUNCE  AT 5-6 DB 1ST RUN, 4-3 D
B IN 2ND RUN ; RETUNED FOR 2ND RUN
 2
13
29.00 30.98 32.92 34.87 35.76 37.58 39.84 41.34 43.16 45.06 47.25 49.07 51.04
13
29.90 32.08 33.85 36.12 37.62 39.63 41.60 43.56 45.32 47.42 49.34 51.12 53.00
 0
  0.1238 33.46 13.53DATA 2/25/70 BY VPG;

 2
13
29.00 30.99 32.86 34.77 36.77 38.62 40.49 42.43 44.26 46.15 48.11 49.99 51.92
13
30.94 33.02 34.78 36.49 38.42 40.31 42.25 44.16 46.16 48.14 50.11 52.06 54.00
 0
  0.1238 33.46 10.54DATA 2/25/70 BY VPG;

 2
13
29.00 31.93 34.67 37.21 40.34 43.07 46.30 49.15 51.99 54.94 57.73 60.51 63.48
13
30.44 33.26 36.19 38.84 41.74 44.62 47.55 50.58 53.34 56.34 59.10 61.84 65.00
 0
  0.1238 33.46  7.54DATA 2/25/70 BY VPG; 9 DB IN 3RD RUN UNUSUAL
```

```
 3
 10
29.00 34.03 38.90 43.84 48.78 54.02 58.78 63.40 68.06 72.97   .     .     .
 10
29.58 34.51 39.79 45.16 50.58 55.58 60.75 65.70 70.37 75.00   .     .     .
 10
29.00 34.08 39.64 44.65 49.71 54.33 59.66 64.41 69.24 71.39   .     .     .
 0
 0.1238 33.46  4.52DATA 2/25/70 BY VPG

 3
 5
29.00 39.08 48.17 57.38 67.23   .     .     .     .     .     .     .     .
 5  1
36.45 46.10 55.67 64.90 74.00   .     .     .     .     .     .     .     .
 5
29.00 39.39 48.78 58.05 67.53   .     .     .     .     .     .     .     .
 1
 5  5.00D-06
70.00 60.00 50.00 40.00 30.00
09.00 07.72 06.44 05.16 03.88   .     .     .     .     .     .     .     .
 0.1238 32.66  4.52DATA 2/25/70 BY VPG; POOR T(ENCL.) CONTROL

 5
 5
29.00 39.07 49.37 59.61 69.56   .     .     .     .     .     .     .     .
 5
31.39 41.97 51.67 61.40 71.00   .     .     .     .     .     .     .     .
 5
29.00 39.53 49.58 58.45 67.74   .     .     .     .     .     .     .     .
 5
31.35 40.56 51.52 60.58 70.00   .     .     .     .     .     .     .     .
 5
29.00 38.82 47.85 57.70 67.62   .     .     .     .     .     .     .     .
 1
 5  5.00D-06
70.00 60.00 50.00 40.00 30.00
08.00 06.71 05.43 04.16 02.88   .     .     .     .     .     .     .     .
 0.1238 32.66  7.54DATA 2/25/70 BY VPG; POOR T(ENCL.) CONTROL

 2
 10
29.00 34.12 39.34 44.45 49.54 54.67 60.92 64.56 69.60 74.91   .     .     .
 9  1
34.13 39.16 44.21 49.36 54.64 59.71 65.43 70.54 75.00   .     .     .     .
 0
 0.1238 32.66 10.54DATA 2/25/70 BY VPG; POOR T(ENCL.) CONTROL; BATH TEMP. READJ
. TO CORRECT DRIFT
 2
 13
29.00 32.07 34.65 37.75 40.70 43.56 46.35 49.56 52.43 55.39 58.33 61.12 64.24
 13
30.56 33.39 36.71 39.51 42.35 45.44 48.40 51.41 54.55 57.53 60.43 63.46 66.00
 0
 0.1238 32.66 13.54DATA 2/25/70 BY VPG; POOR T(ENCL.) CONTROL

 2
 13
29.00 30.70 32.51 34.38 36.24 37.95 39.82 41.63 43.59 45.58 47.55 49.47 51.30
 13
30.42 32.36 34.12 36.04 37.90 39.70 41.67 43.46 45.35 47.31 49.15 51.10 53.00
```

Table II. Sample of Initial Computed Absorptions, Velocities

Format: the headings over the columns of results are explained below. The run conditions X, T, f listed in the first three columns identify the total set of α and β data following. Absorption data come first, then α-averaging in the same format. The velocity data are of slightly different format; most noticeably, the velocity value is printed in floating point rather than integer format.

Absorption

X = mole fraction lutidine; T = temperature (C.); f = frequency (MHz.)

N = for individual runs : no. of db readings = N_{kn}
for averaging : no. of runs = N_k

$\alpha = \alpha/f^2$, in 10^{-17} Np. cm.$^{-1}$ sec.^{2}; σ^{α} = error bound in percent $(100*\sigma^{\alpha}/\alpha)$; $\chi^2 = (\chi^2/(N-F))^{\frac{1}{2}}$, N, F as in text

I = for individual runs : which point deleted by 3-d test
for average of runs : which run deleted (never occurs)

C is an indicator of type of fit done; $C = C_A C_N$

C_A= blank : linear fit or straight averaging
Q : nonlinear fit (individual runs only)

C_N= blank : initial fit, all data points used
\- : result of 3-d test; point denoted by I above has been deleted

REMARKS : under individual runs, two types occur, and only for runs with 3-d test deletions. 'Preferred' means this is the best deletion, giving lowest χ^2; 'taken auto'ly (ok)' means this is the latest deletion and was automatically chosen by the original program for averaging--but it was not the best one; this is rectified by hand later, as explained in the text.

under averages, the straight average with no deletions is the only one occurring. It is followed by the value of the average error rescale parameter P for the N_k runs in the particular average.

Velocity : exact analog of headings. Only one run is made; no averaging is done, just 3-d testing; no error rescale is computed.

X	T	F	N	C	α	σ^{α}	I	χ^2	REMARKS
0.1238	34.66	4.51	6		585	2.03	0	0.36	
					-585	2.03	1	0.01	TAKEN AUTO'LY (OK)
				Q	574	0.75	0	0.36	G=-0.07 EG=0.19
				Q	-569	0.75	5	0.24	PREFERRED
			6		571	2.03	0	0.33	
					-574	2.22	5	0.13	PREFERRED
				Q	564	0.74	0	0.36	G=-0.05 EG=0.20
				Q	-570	0.77	5	0.14	PREFERRED
			6		563	2.03	0	0.39	
					-563	2.03	7	0.14	TAKEN AUTO'LY (OK)
				Q	547	0.70	0	0.31	G=-0.11 EG=0.19
				Q	-547	0.63	2	0.25	PREFERRED
				Q	-544	0.70	5	0.32	TAKEN AUTO'LY (OK)
			3		573	1.21	0	0.93	AVG. ESCALE=0.32
			5		1563.5	0.25	0	0.53	
					-1560.0	0.35	5	0.13	TAKEN AUTO'LY (OK)
0.1238	34.66	7.52	10		402	0.94	0	2.50	
					-415	1.10	1	1.86	PREFERRED
				Q	347	0.31	0	1.21	G=-0.22 EG=0.06
				Q	-348	0.29	3	0.79	PREFERRED
				Q	-339	0.40	10	1.11	TAKEN AUTO'LY (OK)
			10		406	0.94	0	1.03	
					-406	0.94	5	1.11	TAKEN AUTO'LY (OK)
				Q	384	0.42	0	0.68	G=-0.09 EG=0.04
				Q	-382	0.42	8	0.56	PREFERRED
				Q	-381	0.56	10	0.69	TAKEN AUTO'LY (OK)
			2		409	0.71	0	0.0	AVG. ESCALE=1.50
			5		1569.4	0.25	0	0.76	
					-1564.8	0.35	5	0.34	TAKEN AUTO'LY (OK)
0.1238	34.66	10.53	13		376	0.66	0	1.61	
					-376	0.66	6	0.46	PREFERRED
			13		365	0.66	0	0.67	
					-364	0.73	13	0.50	PREFERRED
			2		370	0.49	0	0.0	AVG. ESCALE=0.48
0.1238	34.66	13.53	13		347	0.65	0	2.08	
					-347	0.65	6	0.53	TAKEN AUTO'LY (OK)
				Q	366	0.86	0	1.97	G= 0.05 EG=0.03
				Q	-368	0.80	4	1.55	PREFERRED
				Q	-365	0.88	12	2.05	TAKEN AUTO'LY (OK)
			13		326	0.65	0	0.91	
					-325	0.67	4	0.63	PREFERRED
				Q	319	0.72	0	0.85	G=-0.02 EG=0.02
				Q	-318	0.69	5	0.81	PREFERRED
				Q	-317	0.76	9	0.85	TAKEN AUTO'LY (OK)
			2		335	0.47	0	0.0	AVG. ESCALE=1.54
0.1238	33.46	13.53	13		328	0.65	0	0.35	
					-328	0.65	6	0.85	TAKEN AUTO'LY (OK)
			13		327	0.65	0	0.73	
					-327	0.65	4	0.25	TAKEN AUTO'LY (OK)
			2		327	0.46	0	0.0	AVG. ESCALE=0.57

X	T	F	N	C α	σ^{α}	I	χ^2	REMARKS
0.1238	33.46	10.54	13	356	0.66	0	0.59	
				-356	0.67	4	0.46	PREFERRED
			13	357	0.66	0	0.35	
				-357	0.66	4	0.46	TAKEN AUTO'LY (OK)
			2	356	0.47	0	0.0	AVG. ESCALE=0.41
0.1238	33.46	7.54	10	403	0.94	0	0.63	
				-403	0.94	4	0.46	TAKEN AUTO'LY (OK)
			10	385	0.94	0	0.98	
				-381	1.09	10	0.73	PREFERRED
			10	402	0.94	0	2.29	
				-391	1.08	10	0.80	PREFERRED
			3	392	0.59	0	2.73	AVG. ESCALE=0.72
0.1238	33.46	4.52	5	550	2.68	0	0.43	
				-561	3.78	1	0.17	PREFERRED
			5	558	2.66	0	0.47	
				-569	3.75	1	0.32	PREFERRED
			5	544	2.68	0	0.65	
				-561	3.77	1	0.16	PREFERRED
			3	563	2.17	0	0.21	AVG. ESCALE=0.23
			5	1561.1	0.25	0	0.19	
				-1560.0	0.35	5	0.13	TAKEN AUTO'LY (OK)
0.1238	32.66	4.52	5	510	2.69	0	0.32	
				-503	3.82	5	0.08	PREFERRED
			5	528	2.68	0	0.61	
				-542	3.78	1	0.30	PREFERRED
				-516	3.81	5	0.43	TAKEN AUTO'LY (OK)
			5	539	2.68	0	0.99	
				-562	3.77	1	0.65	PREFERRED
			5	535	2.68	0	0.82	
				-535	2.68	1	0.17	TAKEN AUTO'LY (OK)
			5	542	2.68	0	0.26	
				-540	2.85	2	0.16	PREFERRED
			5	531	1.46	0	1.14	AVG. ESCALE=0.51
			5	1564.0	0.25	0	0.77	
				-1568.8	0.35	1	0.34	TAKEN AUTO'LY (OK)
0.1238	32.66	7.54	10	385	0.94	0	1.09	
				-387	0.96	7	0.46	PREFERRED
			9	381	1.08	0	0.58	
				-378	1.28	9	0.41	PREFERRED
			2	383	0.77	0	0.0	AVG. ESCALE=0.43
0.1238	32.66	10.54	13	350	0.66	0	0.42	
				-350	0.66	7	0.41	TAKEN AUTO'LY (OK)
			13	344	0.66	0	0.76	
				-342	0.73	13	0.48	PREFERRED
			2	345	0.49	0	0.0	AVG. ESCALE=0.45
0.1238	32.66	13.54	13	335	0.65	0	0.83	
			13	333	0.65	0	0.31	
			2	334	0.46	0	0.0	AVG. ESCALE=0.63

Table III. Final Computed Absorptions[a], After Data Purging[b]; With Error Bounds (σ^{α}_{Xf}, in percent), and Chi-Square Confidence Functions (χ^2_X) on Errors

α_{ex}/f^2, 10^{-17} Np. cm.$^{-1}$ sec.^{2}

(or, σ^{α}_{Xf}, %)

X(lutidine)	f(MHz.) = T(C.)	4.5	7.5	10.5	13.5	α_{cl}/f^2 (χ^2_X)
0.9901	32.65	---	65	72	74	9
	33.47	---	69	76	73	9
	34.66	---	69	73	74	9
		(---)	(7.8)	(2.4)	(1.6)	(0.37)
0.427	32.68	82	91	86	87	22
	33.48	82	83	83	86	22
	34.68	94	84	84	88	21
		(5.6)	(4.7)	(1.7)	(1.5)	(0.75)
0.3823	32.66	98	108	104	107	22
	33.45	103	106	99	106	21
	34.66	107	106	102	104	21
		(5.8)	(3.7)	(1.2)	(1.1)	(0.49)
0.3042	32.66	155	152	146	137	24
	33.46	144	142	143	140	24
	34.66	152	145	141	139	23
		(2.7)	(2.7)	(0.7)	(0.7)	(1.20)
0.2132	32.64	240	222	210	208	23
	33.46	236	226	222	212	22
	34.66	247	234	218	208	21
		(2.6)	(1.4)	(0.5)	(0.8)	(0.44)
0.1772	32.64	319	292	266	252	22
	33.46	324	294	270	254	21
	34.66	340	295	271	256	20
		(1.2)	(1.5)	(0.5)	(0.7)	(0.54)
0.1238	32.66	488	373	327	315	19
	33.46	514	381	337	309	19
	34.66	526	400	352	317	18
		(1.6)	(1.0)	(0.5)	(0.7)	(1.00)

α_{ex}/f^2, 10^{-17} Np. cm.$^{-1}$ sec.^{2}

(or, σ^{α}_{Xf}, %)

X(lutidine)	f(MHz.) = T(C.)	4.5	7.5	10.5	13.5	α_{cl}/f^2 (χ^2_X)
0.0892	32.66	564	426	341	290	17
	33.48	594	459	350	301	16
	33.84	600	458	356	306	16
		(1.4)	(0.9)	(0.5)	(0.7)	1.12)
0.0722	32.66	515	445	339	267	15
	33.44	559	491	348	276	15
		(1.2)	(0.6)	(0.5)	(0.7)	(1.57)
0.0664	32.66	557	465	327	262	15
	33.45	613	498	358	285	15
		(1.2)	(0.6)	(0.5)	(0.7)	(0.66)
0.0614	32.64	486	430	304	238	14
	33.45	524	431	317	254	14
		(1.7)	(1.0)	(0.5)	(0.7)	(2.58)
0.0436	32.64	371	313	229	180	11
	33.46	406	340	241	185	11
	33.84	415	345	241	187	11
		(2.0)	(1.0)	(0.5)	(0.7)	(1.09)
0.0288	32.68	189	195	138	101	9
	33.42	202	210	141	107	9
	34.64	231	222	154	113	8
		(3.2)	(2.6)	(1.0)	(1.1)	0.65)
0.0000[c]	all	19	19	19	19	6

---

[a] quoted as α_{ex}/f^2, after subtracting α_{cl}/f^2 and the mode conversion correction

[b] see text on method of data-point deletion

[c] literature value, not our measurements

Final Computed Velocities, After Data Purging[a]

β, m. sec.$^{-1}$ (error bound σ_β=0.3%, all)

(values at f=4.5 MHz. and underlined values are most reliable)

X(lutidine)	f(MHz.) T(C.)	4.5	7.5	10.5	13.5
0.9901	32.65		1324.4	1336.2	1330.0
	33.47		1326.9	1324.6	1331.7
	34.66		1320.1	1324.3	1329.2
0.427	32.68	1478.6	1497.2	1495.5	1507.6
	33.48	1489.2	1498.8	1495.8	1502.6
	34.68	1489.1	1488.7	1493.9	1498.6
0.3823	32.66	1508.3	1507.8	1517.8	1520.9
	33.45	1504.2	1499.7	1508.3	1515.1
	34.66	1499.9	1500.4	1508.8	1514.0
0.3042	32.66	1540.0	1529.2	1534.2	1527.8
	33.46	1533.6	1532.9	1549.8	1527.9
	34.66	1522.4	1526.3	1527.8	1544.8
0.2132	32.64	1549.9	----	1559.7	1569.8
	33.46	1552.3	1555.0	1556.0	1574.1
	34.66	1553.3	1547.8	1548.8	1559.8
0.1772	32.64	1564.0	1566.7	1573.1	1592.1
	33.46	1567.6	1560.1	1569.1	1572.3
	34.66	1567.0	1556.9	1563.5	1581.1
0.1238	32.66	1568.8			
	33.46	1561.1			
	34.66	1560.0	1564.8		

4.5 MHz. only

X	T	β
0.0892	32.66	1558.8
	33.48	1559.9
	33.84	1554.9
0.0722	32.66	1567.0
	33.44	1560.6
0.0664	32.66	1565.8
	33.45	1566.3
0.0614	32.64	1565.2
0.0614	33.45	1562.2
0.0436	32.64	1561.6
	33.46	1556.7
	33.84	1557.8
0.0288	32.68	1562.2
	33.42	1562.7
	34.64	1560.0

(continued)

β, m. sec.$^{-1}$ (error bound σ_{β}=0.3%, all)

(values at f=4.5 MHz. and underlined
values are most reliable)

X(lutidine)	f(MHz.) T(C.)	4.5	13.5
0.0000	32.64	1516.8	1525.3
	34.66	1518.6	
benzene	32.65	1260.7	

---

^{a}see text on method of data-point deletion

Table IV. Diffraction Corrections $Q_o(a/\lambda, z/\lambda) = Q_o(z)$ for

Our System, a = 12.7 mm., β = 1570 m./sec.

(Parameters in parentheses are the more general reductions: a/λ is given next to f, z/λ next to Q itself)

z., mm. \ f, MHz. (a/λ)	Q_o in decibels			
	4.5(36.4)	7.5(60.7)	10.5(84.9)	13.5(109.2)
8	0.255 (22.9)	0.198	0.167	0.148
10	0.286 (28.7)	0.222	0.188	0.165
12	0.313 (34.4)	0.243	0.206	0.182
14	0.339 (40.1)	0.263	0.222	0.196
16	0.362 (45.8)	0.281	0.238	0.210
18	0.384 (51.6)	0.298	0.252	0.222
20	0.404 (57.3)	0.314	0.266	0.235
22	0.424 (63.1)	0.329	0.279	0.246
24	0.442 (68.8)	0.344	0.291	0.257
26	0.462 (74.5)	0.358	0.303	0.267
28	0.479 (80.2)	0.372	0.314	0.277
30	0.496 (86.0)	0.384	0.325	0.287
32	0.510 (91.7)	0.396	0.336	0.296
34	0.526 (97.4)	0.408	0.346	0.305
36	0.543 (103)	0.420	0.357	0.314
38	0.558 (109)	0.434	0.366	0.323
40	0.571 (115)	0.443	0.375	0.331
42	0.583 (120)	0.456	0.384	0.340
44	0.597 (126)	0.464	0.393	0.347
46	0.615 (132)	0.474	0.403	0.355
48	0.626 (138)	0.486 (229)	0.411	0.362
50	0.635 (143)	0.497 (239)	0.420	0.370
52	0.655 (149)	0.506 (248)	0.427	0.377
54	0.659 (155)	0.515 (258)	0.437	0.386
56	0.678 (160)	0.523 (268)	0.445	0.391
58	0.683 (166)	0.532 (277)	0.451 (388)	0.399
60	0.703 (172)	0.543 (287)	0.458 (401)	0.405
62	0.704 (178)	0.554 (296)	0.466 (415)	0.413 (533)
64	0.726 (183)	0.559 (306)	0.473 (420)	0.420 (550)
66	0.729 (189)	0.568 (315)	0.481 (441)	0.425 (568)
68	0.741 (195)	0.580 (325)	0.490 (455)	0.431 (585)
70	0.760 (201)	0.583 (334)	0.498 (468)	0.437 (602)
72	0.758 (206)	0.597 (344)	0.503 (482)	0.443 (619)
74	0.772 (212)	0.600 (354)	0.508 (495)	0.449 (636)
76	0.792 (218)	0.613 (363)	0.517 (508)	0.455 (654)
78	0.792 (224)	0.615 (373)	0.525 (522)	0.462 (671)
80	0.797 (229)	0.629 (382)	0.528 (535)	0.469 (688)

Appendix V. Details of Theoretical Interpretation of Ultrasonic Results.

Paper I developed and extended Fixman's theory for interpreting critical region sound absorption in molecular terms, beginning from a general framework of irreversible thermodynmaics. Paper II presented the ultrasonic results for our binary system, which gave clear indications of an additional absorption from thermal relaxation. It also outlined the two-part (critical + thermal) relaxation theory we developed thermodynamically to analyze our results quantitatively. Paper II finally presented our analysis, limited to the critical absorption only by fundamental theoretical obstacles. In this Appendix we give the details of our general theory and of the data interpretation, for the record as well as for any future work toward a useable total theory. First we give more details in Fixman's theory of critical absorption. Then we give details of the chemical/physical models for thermal relaxation and for solution thermodynamics. The thermodynamics could have been a unifying link between critical and thermal relaxation mechanisms, but it failed.

(A) Reduction of α_{CR}/f^2 to the molecular parameters h, l^2 or ζ, l^2:

--(1) Form of α_{CR}/f^2 from Fixman theory (equation numbers not of the form V.XX refer to our papers I or II, or to Fixman's paper on α, ref. 5 of paper I):

$$\alpha_{CR} = \frac{\omega(\gamma_0 - 1)}{2\beta C_p} \operatorname{Im} \Delta_M \qquad (I.38)$$

$$\Delta_M = \frac{\Delta}{n_1+n_2}, \quad \Delta = \text{heat capacity/unit vol.,}$$

$$n_i = \text{moles/unit vol.}$$

From (I.33) and (I.34):

$$\Delta = \frac{kh}{4\pi^2}\left(T_c \frac{\partial \kappa^2}{\partial T}\right)^2 I$$

$$I = \int \frac{dk\; k^4}{(k^2+\kappa^2)(i\omega + hk^2[k^2+\kappa^2])}$$

Change variables: $x = k/\kappa$, $d = \kappa^2 (h/\omega)^{\frac{1}{2}}$; (V.1)

$$I = \frac{\kappa^3}{\omega d^2} \int \frac{dx\; x^4}{(1+x^2)(-id^{-2}+x^2[1+x^2])}$$

$$= \frac{\omega^{-\frac{1}{4}}}{h^{3/4}} d^{-\frac{1}{2}} \int \sim\sim\sim \quad \equiv \frac{\omega^{-\frac{1}{4}}}{h^{3/4}} f(d) \qquad (\alpha.12)$$

$$\Delta = \frac{kh^{\frac{1}{4}} \omega^{-\frac{1}{4}}}{4\pi^2} \left(T_c \frac{\partial \kappa^2}{\partial T}\right)^2 f(d) \qquad (\alpha.11)$$

$$\alpha_{ex}/f^2 = \frac{\omega^{-5/4}(\gamma_0 - 1)k}{(n_1+n_2)2\beta C_p} \left(T_c \frac{\partial \kappa^2}{\partial T}\right)^2 h^{\frac{1}{4}} \operatorname{Im} f(d) + B(X,T,f)$$

$$\equiv \mathcal{L}(d) \qquad (V.2)$$

<u>B(X,T,f)</u> represents TR; near X_c and at our low frequencies, its X- and f-dependence are weak, and its T-dependence is weak relative to α_{CR}/f^2; $B \simeq \text{const.}$

We see α_{CR}/f^2 to be a function of the bulk, 'static' parameters ω, n_i, C_p, C_v, β , T_c, and also of the two microscopic parameters l^2 (since $\partial\kappa^2/\partial T = 6/l^2$) and h (<u>d</u> in <u>f</u>(<u>d</u>) is a function of ω, l^2, and h also).

--(2) To develop a bookkeeping for fitting α_{ex}/f^2 to our data, define

$$\alpha_{ex}/f^2 = Af^{-5/4}\mathcal{L}(d) + B \qquad \text{(V.3a)}$$

$$d = C_o|T-T_c|f^{-\frac{1}{2}} \quad . \qquad \text{(V.3b)}$$

Results of the fit to the data, which is a nonlinear fit in C_o, linear in A, B:

-- C_o was scanned to minimize the residual error of the linear fit. Eight data points were fit, four f at each of two T. For $C_o = 0.2$ (f in MHz., α/f^2 in 10^{-17} Np. cm.^{-1} sec.^2), the error was minimized on a crude grid. The error was insensitive to C_o, however. There was a consistent localization of the total error in the f = 7.5 MHz. points, the computed values always being lower; Eq. (V.2) gives a poor shape for α/f^2 vs. f. $\mathcal{L}(d)$ was nearly constant over the d-range we sampled in our 8 data points, so essentially $\alpha_{ex}/f^2 \sim f^{-5/4}$ is predicted.

--Adjustment of T_c was tried, with little result. This is as expected, since it only changes d values, to which the fit is insensitive.

--Separate fits of the four f points were tried for each of the two T; only one degree of freedom is left in both fits. Results are poor; the B term was negative for the best fits, attempting to smooth the poor shape of α_{CR}/f^2. with f.

--Finally, we gave B a temperature dependence, a T-coefficient of +3% deg.^{-1} to -9% deg.^{-1}, with little effect

(C_o changes but the net error is relatively unaffected), since it does not change the problematic f-dependence of α_{ex}/f^2.

Selecting $C_o = 0.20\ \text{MHz.}^{\frac{1}{2}}\text{C.}^{-1}$
$= 2.0\text{x}10^2\ \text{sec.}^{-\frac{1}{2}}\text{C.}^{-1}$,

the corresponding A, B values are

$B = 201\ (\text{x}10^{-17}\text{Np. cm.}^{-1}\text{sec.}^2)$; very reasonable

$A = 7.0\text{x}10^3\ (\text{x}10^{-17}\text{Np. cm.}^{-1}\text{sec.}^2\text{MHz.}^{-5/4})$

$= 2.2\text{x}10^{-6}\ \text{cm.}^{-1}\text{sec.}^{3/4}$; about 0.1 of the value for nitrobenzene: isooctane; reasonable.

--(3) Reduce to the molecular parameters: comparing Eqs. (V.2), (V.3a), we see

$$A = \frac{(2\pi)^{-5/4}(\gamma_o-1)kh^{\frac{1}{4}}}{2\beta C_p(n_1+n_2)}\left(T_c\frac{\partial\kappa^2}{\partial T}\right)^2,$$

and comparing Eqs. (V.1), (V.3b) and using $\kappa^2 = 6|T-T_c|/l^2$,

$$C_o = (2\pi)^{-\frac{1}{2}}\frac{6\ h^{\frac{1}{2}}}{T_c l^2}\ .$$

Now factor all the fixed macroscopic parameters from the A, C_o expressions, leaving only powers of h, l^2:

$$A = \mathfrak{a}\,h^{\frac{1}{4}}/l^4;\quad C_o = \mathfrak{C}\,h^{\frac{1}{2}}/l^2$$

$$\mathfrak{a} = \frac{36(2\pi)^{-5/4}(\gamma_o-1)k}{2\beta C_p(n_1+n_2)}$$

$$\mathfrak{C} = (2\pi)^{-\frac{1}{2}}6/T_c.$$

Reduce the data to $C_o/\mathfrak{C} = \overline{C} = h^{\frac{1}{2}}/l^2$, $A/\mathfrak{a} = \overline{A} = h^{\frac{1}{4}}/l^4$, and get h, l^2 as

$$h = (\overline{C}^2/\overline{A})^{4/3},\quad l^2 = (\overline{C}/\overline{A}^2)^{1/3}$$

--(4) Evaluate $\mathfrak{a}, \mathfrak{C}$; need ω, k, $\gamma_o = (C_p - C_v)/C_v$,

β, $n_1+n_2=\overline{V}^{-1}$, and T_c(take component 1 as water):

$T_c = 306.7$ K.

$\Longrightarrow \mathcal{C} = 7.80\text{x}10^{-3}\ \text{K}^{-1}$

$= 1566$ m. sec.$^{-1}$, measured

C_p, C_v--not measured independently; estimate C_p from the pure fluid values

$C_p \simeq X_1C_p^1 + X_2C_p^2$; C_p^2 estimated from other pyridine, heterocycle values

$= 0.935(18\ \text{cal.C.}^{-1}\text{mole}^{-1}) + 0.065(50\ \text{cal.C}^{-1}\ \text{mole}^{-1})$

$= 20$ cal. C.$^{-1}$ mole^{-1}

and get C_v from $C_p - C_v = T\overline{V}\theta^2/\kappa_T$, notation of paper I:

$$\theta = -(\partial\rho/\partial T)/\rho \simeq -(\Delta\rho/\Delta T)/\rho$$

For our mixture at X_c, between T = 32.65 and 34.65 C., our initial $\rho \leftrightarrow X$ data give $\rho = 0.98900$, 0.98759:

$$\theta \simeq 7.1\text{x}10^{-4}\ \text{C.}^{-1}$$

κ_T also was not measured; use $\kappa_T = \kappa_S + T\overline{V}\theta^2/C_p$

$\kappa_S = 1/\rho\beta^2$, $\rho = 0.98900\text{x}10^3$ kg. m.$^{-3}$

$= 0.413\text{x}10^{-9}$ nt.$^{-1}$m.^{2}

$$\overline{V} = \frac{X_1 MW_1 + X_2 MW_2}{\rho_{\text{soln.}}}$$

$$= \frac{0.065(107) + 0.935(18)}{0.989}\ \text{cc. mole}^{-1}$$

$= 24.1\text{x}10^{-6}$ m.^{3} mole^{-1}

$\kappa_T \simeq 0.458\text{x}10^{-9}$ nt.$^{-1}$ m.^{2}

$C_p - C_v \simeq 1.94$ cal. C.$^{-1}$mole^{-1}

$\gamma_0 - 1 = 0.107$

$a = 0.491\text{x}10^{-33}$ m.^{2}molecule^{-1}sec.

$\overline{A} = A/a = 4.47\text{x}10^{29}$ m.$^{-3}$sec.$^{-\frac{1}{4}}$molecule

$\overline{C} = C_o/C = 2.56 \times 10^4 \text{sec.}^{-\frac{1}{2}}$

$h = 1.66 \times 10^{12}$ Å^4 sec.$^{-1}$; reasonable size of pair diffusion constant

$l^2 = 50.5$ Å^2; reasonable in comparison to other systems

These values are not final; they are adjusted for Fixman's oversight, as noted in paper I.

--(4) Reduce <u>h</u> further, to a molecular friction constant ζ, as does Fixman (his ρ), from his Eq. (κ.5):

$$h = \frac{(n_1+n_2)\overline{V}_1^2 \phi_1 kT_c}{m_1 c_2 2\pi a\zeta} \equiv \mathcal{H}/a\zeta$$

n_1 in molecules/unit vol.

$\overline{V}_1$ in vol./molecule

c_2 = weight fraction of component 2 (lut.)

$\overline{V}_1 = 18.07$ cc. mole^{-1} $= 3.00 \times 10^{-23}$ cc. molecule^{-1}

$\phi_1 = n_1 \overline{V}_1$

$n_1 = \rho \frac{X_1}{X_1 MW_1 + X_2 MW_2} = 0.0376$ moles cc.$^{-1}$

$\phi_1 = 0.680$

$c_2 = X_2 MW_2/(X_1 MW_1 + X_2 MW_2) = 0.708$

$\mathcal{H} = 48.8 \times 10^{-26}$ m.^{5}molecule^{-1} sec.$^{-2}$

$\overline{H} = h/\mathcal{H} = 3.4 \times 10^{-14}$ Å^{-1}sec.

$a\zeta = 1/\overline{H} = 2.94 \times 10^{13}$Å sec.$^{-1}$

Now, Fixman derives $a = 3\overline{V}_2/2\pi l^2$ from the <u>Flory-Huggins</u> <u>model</u>:

$a = 1.84$ Å; very low compared to other consolutes

$\zeta = 1.6 \times 10^{13}$ sec.$^{-1}$; small; corrected to 0.32 in paper II, for Fixman's oversight.

(B) Derivation of Correction Factors for 1, γ from Fixman's original results, due to Fixman's oversight in the form of f(d)--faulty translation of singlet→ pair diffusion:

Fixman derived a pair diffusion equation for G(r) or its Fourier transform G_k (Eq. 40, viscosity paper), leading to our Eq. (I.33). The diffusion constant h appears in two places in the incremental heat capacity (or α, α/f^2)--as a factor in the numerator, and buried in the denominator of the integrals I or f(d). But we showed in our redevelopment that h should be replaced by h/2 in the latter place. We indicated that this requires adjustment of Fixman's 1, γ by 1.26, 0.20, respectively. We derive these factors here:

Proper form:

$$\Delta = \frac{kh'}{4n^2} \left(T_c \frac{\partial \kappa^2}{\partial T}\right)^2 I'$$

$$I' = \int \frac{dk\ k^4}{(k^2+ {}^2)(i\omega + \frac{h'}{2}k^2[k^2+\kappa^2])}$$

h' is the proper diffusion constant

Performing the change of variables

$$x = k/\kappa,\ d = \kappa^2 (h'/2\omega)^{\frac{1}{2}},\text{ similarly to before,}$$

we get

$$I' = \frac{2}{h'}\left(\frac{h'}{2}\right)^{\frac{1}{4}} f(d) = 2^{3/4}\frac{\omega^{-\frac{1}{4}}}{h'^{3/4}} f(d),$$

with f(d) the same mathematical form as before. Thus in our forms $\alpha/f^2 = Af^{-5/4}\mathcal{L}(d) + B$, $d = C_o f^{-\frac{1}{2}}|T-T_c|$, we have really

$$A = 2^{3/4} a (h')^{\frac{1}{4}}/(1')^4$$

$$C = \mathcal{C}\, 2^{-\frac{1}{2}} (h')^{\frac{1}{2}} / (l')^2$$

and

$$h' = 2^{7/3} (\bar{C}^2 / \bar{A})^{4/3} = 2^{7/3} h_{old} = 5.04\ h_{old}$$

$$\Longrightarrow \zeta' = 0.20\ \zeta_{old}$$

$$l' = 2^{1/3} (\bar{C} / \bar{A}^2)^{1/6} = 2^{1/3}\ l_{old} = 1.26\ l_{old}.$$

(C) Proving Fixman's expression for the diffusion constant h,

$$h = \frac{kT\phi_1 \bar{V}_1^2 (n_1 + n_2)}{m_1 c_2 2\pi a \zeta} \qquad (\alpha.5)$$

There are some difficulties in verifying this relation: 1) Fixman commonly does not label the variables held fixed in his partial derivatives; 2) he changes notation in transit, or makes errors in notation corrected implicitly in later papers; 3) he sometimes uses approximate equalities in derivations but quotes them as equalities. These three problems plus the spreading of his total derivation over 4 papers are great obstacles to following his line of reasoning. We have corrected some implicit assumptions of the types above in our paper I, but we still have to verify the above equation.

The diffusion equation outside the critical region (I.12) has a diffusion constant

$$D = \kappa (\partial \mu / \partial c_2) \qquad (1)$$

which is retained in the critical region (only the driving terms are altered) but written as

$$D = \frac{h\rho}{2} \kappa^2 .$$

Clearly,

$$h = \frac{2\alpha}{\rho\kappa^2}\left(\frac{\partial\mu}{\partial c_2}\right)_{P,T}$$

and from this we must derive Eq. (α.5). Let us reduce Eq. (1). First, we take, as does Fixman, c_2 to be the mass fraction of component 2. Correspondingly, μ is the difference in chemical potentials per unit concentration $\mu_2-\mu_1$. As Fixman later uses μ_1 as the chemical potential per molecule, we must convert

$$\mu = \mu_2/m_2-\mu_1/m_1$$
$$d\mu = d\mu_2/m_2 - d\mu_1/m_1 .$$

By the Gibbs-Duhem relation, μ_1 and μ_2 are constrained to vary as

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$
$$\Longrightarrow d\mu = \frac{n_1m_1 + n_2m_2}{n_2m_1m_2}\, d\mu_1 = \frac{\rho}{n_2m_1m_2}\, d\mu_1 ,$$

and thus

$$D = \frac{\alpha\rho}{n_2m_1m_2}\left(\frac{\partial\mu_1}{\partial c_2}\right)_{P,T} .$$

-- Now, in his viscosity paper, Fixman derives a relation (Sec. A) between $\partial\mu_1/\partial\phi_2$ [or $\partial\mu_1/\partial n_2$, as easily] and the microscopic parameters *a* and κ^2, through the relation of osmotic pressure π and the correlation function $G_{22}(r)$:

$$\frac{\partial\pi}{\partial n_2} = kT\left[1 + n_2\int G_{22}(r)\, d\vec{r}\right]^{-1} \equiv \left(\frac{\partial P}{\partial n_2}\right)_{\mu_1,T}$$
$$= \left(\frac{\partial\mu_1}{\partial n_2}\right)_{P,T}\left(\frac{\partial P}{\partial\mu_1}\right)_{n_2,T} .$$

He uses a Maxwell relation

$$\left(\frac{\partial V}{\partial N_1}\right)_{P,T,N_2} = \left(\frac{\partial \mu_1}{\partial P}\right)_{T,N_1,N_2}$$

and an assumption of small compressibility of the mixture,

$$\left(\frac{\partial \mu_1}{\partial P}\right)_{T,N_1,N_2} \simeq \left(\frac{\partial \mu_1}{\partial P}\right)_{n_2,T} = -\bar{V}_1$$

to get

$$\frac{\partial \pi}{\partial n_2} \simeq -\frac{1}{\bar{V}_1}\left(\frac{\partial \mu_1}{\partial n_2}\right)_{P,T} .$$

Now, in the critical region, according to the Ornstein-Zernike model of classical thermodynamics,

$$\int G_{22}(r)\, d\vec{r} = 4\pi a/\kappa^2$$

$$\Longrightarrow \frac{4na}{\kappa^2} = -\frac{\bar{V}_1}{n_2}\left[\frac{kT}{(\partial \mu_1/\partial n_2)} + \frac{1}{\bar{V}_1}\right]. \qquad \text{(I.26)}$$

The second term in brackets is negligible relative to the first when $\partial \mu_1/\partial n_2 \rightarrow 0$, as in the critical region --unless we are trying to get the dependence of absorption on composition away from X_c (Puls' thesis, e.g.). Thus

$$\frac{\partial u_1}{\partial n_2} \simeq \frac{\bar{V}_1 kT \kappa^2}{4\pi a n_2} .$$

--We must put this in terms of $\partial \mu_1/\partial c_2$:

$$\frac{\partial \mu_1}{\partial c_2} = \left(\frac{\partial \mu_1}{\partial n_2}\right)\left(\frac{\partial n_2}{\partial c_2}\right)_{\bar{V}} .$$

The chain rule is justified, since c_2 (with P, T) is a complete description. We need a condition on the latter partial to reflect the P, T constancy, and we choose $d\bar{V}=0$ (low compressibility; also consistent with relation I.17

between δG and $[\delta n_2]^2$):

$$dc_2 = \left(\frac{\partial c_2}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial c_2}{\partial n_2}\right)_{n_1} dn_2$$

$$c_2 = \frac{n_2 m_2}{\rho} \Longrightarrow \frac{\partial c_2}{\partial n_1} = -\frac{n_2 m_1 m_2}{\rho^2}$$

$$\frac{\partial c_2}{\partial n_2} = \frac{n_1 m_1 m_2}{\rho^2}$$

$$dc_2 = \frac{m_1 m_2}{\rho^2}\left[-n_2 dn_1 + n_1 dn_2\right]$$

$$dV = \bar{V}_1 dn_1 + \bar{V}_2 dn_2 \Longrightarrow dn_1 = -\frac{\bar{V}_2}{\bar{V}_1} dn_2$$

$$dc_2 = \frac{m_1 m_2}{\rho^2}\left[\frac{\overset{\longrightarrow\,=1}{\cancel{n_2\bar{V}_2 + n_1\bar{V}_1}}}{\bar{V}_1}\right] dn_2$$

$$\left(\frac{\partial c_2}{\partial n_2}\right)_{\bar{V}} = \frac{m_1 m_2}{\rho^2 \bar{V}_1} = \frac{m_1 c_2}{\rho \bar{V}_1 n_2}$$

Thus

$$\frac{\partial u_1}{\partial c_2} \simeq \frac{\rho \bar{V}_1 \cancel{n}_2}{m_1 c_2} \cdot \frac{\bar{V}_1 kT \kappa^2}{4\pi\eta a \cancel{n}_2}$$

$$D = \frac{\alpha \rho^2}{n_2 m_1^{\text{②}} m_2} \cdot \frac{\cancel{\rho}\bar{V}_1^2 kT \kappa^2}{\cancel{m}_1 c_2 4\pi\eta a}$$

$$h = \frac{\alpha \rho \bar{V}_1^2 kT}{n_2 m_1^2 m_2 c_2 2\pi\eta a}$$

---Fixman uses an intermolecular friction constant ζ in preference to α, converting through an ideal diffusion constant D_{id}. In Sec. VIII in his viscosity paper, he derives a rigorous relation

$$D_{id} = \frac{\alpha \rho kT}{m_1 m_2{}^2 n_1} \left(\frac{\partial \ln X_2}{\partial n_2} \right)_{\overline{V}} = \frac{\alpha \rho kT}{m_1 m_2{}^2 n_1 n_2 (n_1+n_2) \overline{V}_1}$$

and then defines

$$\zeta \equiv \frac{kT}{m_2 D_{id}}$$

$$\Longrightarrow \alpha = \frac{m_1 m_2{}^2 n_1 n_2 (n_1+n_2) \overline{V}_1}{\rho kT} D_{id}$$

$$= \frac{m_1 m_2 n_1 n_2 (n_1+n_2) \overline{V}_1}{\rho \zeta}$$

$$h = \frac{\cancel{\rho} \overline{V}_1^2 kT}{\cancel{n_2} m_1{}^{\cancel{2}} \cancel{m_2} c_2 2\pi a} \cdot \frac{\cancel{m_1} \cancel{m_2} n_1 \cancel{n_2} (n_1+n_2) \overline{V}_1}{\cancel{\rho} \zeta}$$

and using $n_1 \overline{V}_1 = \phi_1$, we get

$$h = \frac{\overline{V}_1{}^2 kT (n_1+n_2) \phi_1}{m_1 c_2 2\pi a \zeta} \quad , \text{ Q.E.D.}$$

(D) A <u>Comment</u> on Fixman's choice of the dissipative equation and its driving force: Fixman's earlier papers on general critical region thermodynamics and on ultrasonic attenuation focus on the equations of motion for the singlet and pair densities, rather than the singlet and pair concentration deviations. The latter obey a purely dissipative equation, modified from the standard non-critical diffusion equation; the choice of thermodynamic description for the entropy production and the choice of driving term are well justified. The density equations of motion, on the other hand, are mixed propagative-dissipative and encompass the anomalous entropy production or sound absorption only for the gas-liquid critical point, and then in a non-obvious way. Fixman's first attempts to describe the liquid-liquid critical absorption failed for this reason.

(E) Estimation of the pressure-driven contribution to the critical absorption, relative to the thermal absorption: The δT term in the driven entropy fluctuation, hence in α, originated in the derivative

$$\left(\frac{\partial \kappa^2}{\partial T}\right)\delta T \sim \left(\frac{\partial^2 \mu_1}{\partial T \partial c_2}\right)\delta T = \frac{\partial^2}{\partial T \partial c_2}\left(\frac{\partial G_{mix}}{\partial N_1}\right)_{N_2},$$

where G_{mix} is the free energy change for an arbitrary mass of solution and the N_i are total numbers of moles (or molecules, if one prefers). The analogous δP-driven term is proportional, with the same constant of proportionality, to

$$\frac{\partial^3 G_{mix}}{\partial P \partial c_2 \partial N_1} = \frac{\partial}{\partial c_2}\left(\frac{\partial}{\partial N_1}\right)_{N_2} \Delta V_{mix} .$$

The derivative $(\partial/\partial N_1)_{N_2}$ factors as

$$\left(\frac{\partial}{\partial N_1}\right)_{N_2} = \left(\frac{\partial N}{\partial N_1}\right)_{N_2}\left(\frac{\partial}{\partial N}\right)_{X_2} + \left(\frac{\partial X_2}{\partial N_1}\right)_{N_2}\left(\frac{\partial}{\partial X_2}\right)_N$$

$$N = N_1 + N_2$$

$$= \left(\frac{\partial}{\partial N}\right)_{X_2} - \frac{X_2}{N}\left(\frac{\partial}{\partial X_2}\right)_N$$

and clearly $\Delta V_{mix} = N \Delta \bar{V}_{mix}$, where the bar denotes the molar quantity. Then the δP term measure becomes, for $c_2 = X_2$,

$$\frac{\partial \Delta \bar{V}_{mix}}{\partial X_2} - X_2 \frac{\partial^2 \Delta \bar{V}_{mix}}{\partial X_2^2}$$

and

$$\Delta\overline{V}_{mix} = V^E = \frac{X_1MW_1+X_2MW_2}{\rho_s} - \frac{X_1MW_1}{\rho_1} - \frac{X_2MW_2}{\rho_2}$$

$$\frac{\partial\Delta\overline{V}_{mix}}{\partial X_2} = \frac{(MW_2-MW_1)}{\rho_s} - \frac{\Delta\overline{V}_{mix}}{\rho_s}\left(\frac{\partial\rho_s}{o X_2}\right) - \frac{MW_2}{\rho_2} + \frac{MW_1}{\rho_1}$$

$$\rho_s{}^2\left(\frac{\partial^2\Delta\overline{V}_{mix}}{\partial X_2{}^2}\right) = -(MW_2-MW_1)\left(\frac{\partial\rho_s}{\partial X_2}\right) - \rho_s\left(\frac{\partial\Delta\overline{V}_{mix}}{\partial X_2}\right)\left(\frac{\partial\rho_s}{\partial X_2}\right)$$

$$+ \Delta\overline{V}_{mix}\left[\left(\frac{\partial\rho_s}{\partial X_2}\right)^2 - \rho_s\left(\frac{\partial^2\rho_s}{\partial X_2{}^2}\right)\right]$$

The ratio R of the pressure-induced to the temperature-induced absorption is

$$R = \frac{\left[\dfrac{\partial\Delta\overline{V}_{mix}}{\partial X_2} - X_2\,\dfrac{\partial^2\Delta\overline{V}_{mix}}{\partial X_2{}^2}\right]}{(\,\partial^2\mu_1/\partial T\partial X_2)}\cdot\frac{C_p}{TV\theta}\,,$$

since for $\delta S = 0$, $\frac{C_p}{T}\,\delta T - V\theta\delta P = 0$.

A modified Flory-Huggins model will be used for the term $\partial^2\mu_1/\partial X_2\partial T$, in terms of mole fractions rather than volume fractions:

$$\frac{\partial\mu_1}{\partial X_2} = -\frac{R_gT}{(X_2{}^c)^2}\left[\frac{1}{X_1} - \frac{2}{X_1{}^c} + \frac{T_c}{T}\,\frac{X_1}{(X_1{}^c)^2}\right],$$

which is a form satisfying $\partial\mu_1/\partial X_2 = 0 = \partial^2\mu_1/\partial X_2{}^2$ at $X_2 = X_2{}^c$, and $\partial^3\mu_1/\partial X_2{}^2\partial T > 0$ appropriate to a lower consolute. Then

$$\frac{\partial^2\mu_1}{\partial X_2\partial T} = -\frac{R_g}{(X_2{}^c)^2}\left[\frac{1}{X_1} - \frac{2}{X_1{}^c}\right] \rightarrow \frac{R_g}{(X_2{}^c)^2X_1{}^c} \text{ at } X_c\,.$$

Numerical evaluation (let component 1 be water), T = 33.2 C. and $X = X_c = 0.065$ lutidine:

$MW_1 = 18$ g. mole^{-1}

$MW_2 = 107$ g. mole^{-1}

$\rho_1 = 0.91035$ g. cc.$^{-1}$

$\rho_2 = 0.99467$ g. cc.$^{-1}$

$\rho_s = 0.98852$ g. cc.$^{-1}$

$$\frac{\partial \rho_s}{\partial X_2} \simeq \frac{-0.00087 \text{ g. cc.}^{-1}}{0.0100} = -0.087 \text{ g. cc.}^{-1},$$ graphically

$\Delta \overline{V}_{mix} = -0.504$ cc. mole^{-1}

$R_g = 1.987$ cal. C.$^{-1}$ mole^{-1}

C_p, T, $\overline{V}$, θ have been listed in section (A).

$$\frac{\partial \Delta \overline{V}_{mix}}{\partial X_2} = -9.45 \text{ cc. mole}^{-1}$$

$$\frac{\partial^2 \Delta \overline{V}_{mix}}{\partial X_2^2} = +7.09 \text{ cc. mole}^{-1}$$

$\partial^2 \mu_1 / \partial X_2 \partial T = 503$ cal. C.$^{-1}$ mole^{-1}

$R = -0.079 = -7.9\%$

Part II: Chemical Theory of Solution Thermodynamics and of Ultrasonic Relaxation.

The thermodynamics of our lutidine: water mixtures, as of other aqueous amine or heterocycle solutions, points to strong A-B association through hydrogen-bonding. The phase behavior is affected: a lower consolute or critical mixing point is generated. The strong association equilibria also relax ultrasonically to yield a strong absorption. The latter effect has been studied by Andreae, et al.[1] with simple and not very successful models or chemical theories, and pointedly ignoring the former effect. The critical absorption phenomena have been studied only for upper consolute mixtures (with one exception), dominated by 'physical' rather than 'chemical' interactions of mixing. Our solution seems to be the first[2] calling for a careful modelling of both absorption effects in a common framework, to separate and interpret the effects which are of comparable magnitude in the critical region of interest. We have only limited guides in constructing such a theory; the chemical models of thermal relaxation are not very satisfactory as we have noted, and the models for the critical thermodynamics have been elementary physical solution theories (not beyond Flory-Huggins) used empirically, far from the more complex chemical theories. Our rather piecemeal attempts at the total theory are presented below.

Assume some model for the self-association of water, and likewise for lutidine-water complexation:

$$A + A_{n-1} \rightleftharpoons A_n$$

$$B + A_n \rightleftharpoons BA_n \ .$$

Each equilibrium is characterized by an equilibrium constant, enthalpy change, volume change, and (for relaxation) forward rate constant. Let us denote these for the association equilibria as K_n, H_n, V_n, and k_{fn}, respectively, and with primes for the complexation equilibria. With modern computers it is possible to solve for the 'true' species concentrations given a large but finite set of equilibria with an arbitrary progression of K_n, etc. with n, and from there to compute the net thermodynamic functions of mixing and the relaxation strengths, both as functions of the macroscopic composition as perhaps measured by the mole fraction X_B. This reduces to an exercise in curve fitting with an enormous number of parameters. Our limited data on the phase diagram and on absorption do not justify such an exacting treatment, which is of limited interpretive value in any case. Our models are therefore limited to some simple progressions of the K_n, V_n, etc., such as the geometric one, $K_n = \alpha K_{n-1}$. We obtain low-order polynomial equations for the mole fractions δ_n, δ_B, and δ_{Bn} of the true species A_n, B, and BA_n, to be solved numerically for any composition X_B.

The molar free energy of mixing can be computed from the true species concentrations rather straightforwardly,

$$G_{mix} = RT\left[X_A \ln \delta_A + X_B \ln \delta_B\right] , \qquad (II.10)$$

under the assumption that the 'true' species form an ideal solution, in which case the activities of the monomers A, B equal the corresponding true mole fractions δ_A, δ_B. (A reasonable assumption to go with this is that the parameters K_n, etc. are independent of composition; this keeps things simple.) The condition for instability (immiscibility)

$$\frac{\partial^2 G_{mix}}{\partial X_A{}^2} < 0$$

maps the region of phase separation. The chemical term above $G_{mix} = G_{chem}$ is not sufficient to cause such a condition, but it helps it to occur and partly determines the particular mole fraction whre it occurs.

Aside from phase behavior, our model must give the correct relaxation strength Z as a function of macroscopic composition X_B. For a single general reaction

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots$$

Herzfeld and Litovitz[3] develop a relaxation equation. Let ξ define an extent of reaction from some arbitrary initial state and let its first order disturbance (from the ultrasound) be $\delta\xi$,

$$\delta\xi = \frac{\delta n_C}{c} = \frac{\delta n_D}{d} = \frac{-\delta n_A}{a} = \frac{-\delta n_B}{b} = \ldots,$$

n_i = no. of moles of species $\underline{i}$.

Defining the forward and backward rate constants $\tilde{k}$ and $\bar{k}$, they derive to first order (for the case $aA+bB \rightleftharpoons cC+dD$, to prevent ambiguity of expressions)

$$-\frac{d}{dt}\,\delta\xi = \overline{k}(\delta_C^o)^c(\delta_D^o)^d\left[\left\{\frac{a^2}{\delta_A}+\frac{b^2}{\delta_B}+\frac{c^2}{\delta_C}+\frac{d^2}{\delta_D}-(\Delta n)^2\right\}\delta\xi \right.$$

$$\left. -n\,\delta\ln K\right]$$

$\Delta n = c+d-a-b$

δ_i^o = equilibrium value of δ_i.

Since $\delta \ln K = \frac{\Delta\overline{H}}{RT^2}\,\delta T + \frac{\Delta\overline{V}}{RT}\,\delta P$, we can write this as

$$-\frac{d}{dt}\,\delta\xi = \frac{1}{\tau}\left[\delta\xi - \frac{H'}{T}\delta T - V'\delta P\right],$$

the general form of irreversible thermodynamics. Here

$1/\tau = \overline{k}(\delta_C^o)^c(\delta_D^o)^d\phi/RT$

$\phi = RT\left(\frac{a^2}{\delta_A}+\frac{b^2}{\delta_B}+\frac{c^2}{\delta_C}+\frac{d^2}{\delta_D}-(\Delta n)^2\right)$

$H' = n\Delta\overline{H}$

$V' = n\Delta\overline{V}$

and the relaxation strength is as usual

$$Z = \operatorname{Im} K_S(\omega)$$

$$= \frac{(V'-\overline{V}\theta^{\infty}H')^2}{\overline{V}\phi\left[1+(H')^2/TC_p^{\infty}\phi\right]}\,\frac{\omega\tau}{\left[1+\omega^2\tau^2\right]} \qquad \text{(I.9)}$$

For multiple equilibria, the coupling of the reactions (one reaction's product is another's reactant, as for the pair $A+A_{n-1}\rightleftharpoons A_n$, $A+A_n\rightleftharpoons A_{n+1}$) must be removed by taking appropriate linear combinations of reactions, 'normal modes' of reaction. Eigen and deMaeyer[4] give the necessary linear algebra. The redefined equilibrium constants, volume changes, etc. can be solved for on a computer--or an analytic solution can be obtained if our choice of progression of the elementary parameters K_n, ΔV_n, etc. is a lucky one.

The expressions for the mixing free energy and for the general relaxation strength are our mainstays in evaluating any model of the equilibria. We require three results for an acceptable model:

(1) Z, summed over the reactions and regarded as a function of the macroscopic composition, must have the correct peaking at $\underline{X}(\text{lutidine}) \cong 0.1$, including width and height. Now, Z is hard to compute for the general case of coupled reactions. However, we do know that the principal contributor to relaxation is the complexation A-B, and not the water self-association, since pure water absorbs very little. If we assume the complexation reactions are all uncoupled, then at a frequency $f \ll 1/\tau_i$ for all τ_i such as we use,

$$\begin{aligned}\alpha/f^2 &\sim \sum_n Z_n \tau_n \\ &= \sum_n \frac{(V' - \bar{V}\theta^{\infty} H\dot{h}\ )^2}{\bar{V}\phi_n(1+[H'_n]^2/TC_p^{\infty}\phi_n)} \cdot \frac{1}{\bar{k}_n \delta_{Bn}\ \phi_n}\end{aligned} \quad .$$

Under the reasonable assumption that for all $\underline{n}$

$V'_n = V'$

$H'_n = H'$,

and noting that the parameters $\bar{V}$, θ^{∞}, and TC_p^{∞} are independent of $\underline{n}$, the measure of α/f^2 simplifies,

$$\alpha/f^2 \sim \sum_n \frac{1}{\bar{K}_n \delta_{Bn}(\phi_n^2 + \text{const.}\ \phi_n)}$$

At the end points $X_B = 0$ or 1, this can be shown to vanish as it must; $\delta_{Bn}\phi_n \to$ finite limit, $\phi_n \to \infty$.

Practical calculations are easiest and still accurate if we model $\bar{V}, \theta^{\infty}$, and C_p^{∞} as linearly varying with composition. The progression of $\bar{k}_n$ with n must be decided upon. Two simple choices are that they are independent of n or that they follow the same progression as the K_n. Whatever the choice of progression, the sum over n in the α/f^2 measure must be done numerically. Once a reasonable shape for α/f^2 as a function of X_B has been obtained by adjusting the model parameters, it remains to check the absolute magnitude of the calculated α/f^2. While the absolute value can be changed by scaling the $\bar{k}_n$ uniformly, they cannot be adjusted such that $\tau_n \gtrsim 1/f_{max}$, where f_{max} is the upper limit of the dispersion-free frequency range--at least 13.5 MHz. in our system.

In our original calculations on all models, we used a simple and intuitive, but incorrect, measure of α/f^2, namely δ_{AB} itself for the simplest case where B associates only with monomer water A. We therefore do not report our results in this regard. Our conclusions on phase behavior are still valid. The correct measure should be computed and evaluated for our models at some later date, and the problem of reaction coupling should be attacked.

(2) The free energy of mixing must generate a critical point at the proper low mole fraction $X_B = 0.065$. Let us define $\mathcal{G} = G_{mix}/RT$ and $\mathcal{G}' = \partial\mathcal{G}/\partial X_A$, $\mathcal{G}'' = \partial^2\mathcal{G}/\partial X_A{}^2$.

The critical condition is $\mu'' = 0$ at some X_B. It is easy to derive that

$$\mu''_{\text{chem}} = \frac{2}{\delta_A}\delta_A' + \frac{X_A}{\delta_A^2}\left[\delta_A\delta_A'' - (\delta_A')^2\right] - \frac{2}{\delta_B}\delta_B'$$

$$+ \frac{X_B}{\delta_B^2}\left[\delta_B\delta_B'' - (\delta_B')^2\right]$$

where $\delta_A' = \partial\delta_A/\partial X_A$, $\delta_B' = \partial\delta_B/\partial X_A$, etc.

It is simplest to express everything in terms of δ_A and its derivatives, using the chain rules

$$\delta_B' = (\partial\delta_B/\partial\delta_A)\delta_A', \quad \delta_B'' = (\partial\delta_B/\partial\delta_A)\delta_A''.$$

Further, δ_A', δ_A'', and $\partial\delta_B/\partial\delta_A$ are most compactly derived by implicit differentiation--of the polynomial equation for δ_A and X_A for the first two, and of the sum rule relation

$$\delta_B = 1 - \sum_n \delta_n - \sum_n \delta_{Bn} = 1 - \sum_n \delta_n - \delta_B \sum_n K_n' \delta_n$$

$$\Longrightarrow \delta_B = (1 - \sum_n \delta_n)/(1 - \sum_n K_n' \delta_n)$$

for $\partial\delta_B/\partial\delta_A$.

To get a phase separation, we need to add μ_{phys}, some function of composition. Now, μ''_{chem} can bring μ'' close to zero, and certain of the models favor smallness and flatness of μ''_{chem} at low X_B where we require it. A μ_{phys} of the simple form $AX_A{}^n X_B$ can then be added, which peaks at $X_B = 3/(n+4)$. For $X_c = 0.065$ to be generated, n has to be about 50, which is very unrealistic. μ_{phys} becomes a narrow spike. An inverse exponential such as $A\exp(a/(|X_B - X_c| + b))$ might be more realistic. Any form, however, is hard to justify on any grounds over and above the phase behavior.

Finally, we note that $\mathcal{A}_{phys}$ may alter the activity coefficients of the true species, and the equilibria must be correspondingly adjusted.

(3) The net temperature dependence of $\mathcal{A}'' = \mathcal{A}''_{chem} + \mathcal{A}''_{phys}$ must give a lower consolute point,

$$\partial \mathcal{A}''(X_B)/\partial T < 0.$$

The chemical equilibrium constants are all reduced by increased temperature, since the enthalpies of reaction are all negative. $\mathcal{A}''_{chem}$ is consequently changed. In all our models, $\mathcal{A}''_{chem}$ pulled away from zero at extreme mole fractions and bulged toward zero at intermediate X_B, as the temperature rose. To get $\partial \mathcal{A}''/\partial T < 0$ at low X_B, the major temperature dependence must be in $\mathcal{A}''_{phys}$, which is surprising and discouraging. The model for $\mathcal{A}_{phys}$ becomes more arbitrary yet more important for properties. This difficulty is our principle one, as cited in paper II.

Before ending this Appendix by listing the key equations for three chemical models, we mention that two more thermodynamic criteria could be added: accurate predictions of volume and enthalpy changes on mixing, $\Delta\overline{V}_{mix}$ and $\Delta\overline{H}_{mix}$. We do not have any data on the latter for our system, but the former is modestly informative for lutidine: water. An extra use of the volume information is in setting $\overline{V}'$ for the complexation, for use in calculating the relaxation strengths, hence α/f^2. The detailed equations for computing $\overline{V}_{mix}$ are developed as follows:

$$\Delta\overline{V}_{mix} = V^E = \overline{V}(X_B) - \overline{V}_o(X_B)$$

where

$$\overline{V}_o(X_B) = \text{volume per mole of monomers, unmixed}$$

$$\overline{V}(X_B) = \text{volume per mole of monomers, mixed.}$$

In turn,

$$\overline{V}_o(X_B) = X_A\overline{V}_A(0) + X_B\overline{V}_B.$$

There is an X_B-dependence of $\overline{V}_A$ because it self-associates, and even an inert diluent shifts the equilibria. Now,

$$\overline{V}_A(0) = V_t(=\text{total volume})/N_t(=\text{total no. monomers})$$

$$= \sum_k n_k\overline{V}_k / \sum_k kn_k = \sum_k \delta_k\overline{V}_k / \sum_k k\delta_k$$

$$\overline{V}_k = k\overline{V}_o + (k-1)\Delta\overline{V} \text{ (for } \Delta\overline{V}_n = \text{const.} = \Delta\overline{V})$$

$$\overline{V}_A(0) = \overline{V}_o + \Delta\overline{V}(1 - \sum_k \delta_k / \sum_k k\delta_k) \equiv \overline{V}_o + R_o\Delta\overline{V}.$$

Similarly, for the mixture,

$$\overline{V}(X_B) = V_t/N_t$$

$$V_t \sim \sum_k \delta_k\overline{V}_k + \delta_B\overline{V}_B + \sum_k \delta_{Bk}V_{Bk}$$

$$\overline{V}_k = k\overline{V}_o + (k-1)\Delta\overline{V} \text{ , as before}$$

$$\overline{V}_{Bk} = k\overline{V}_o + (k-1)\Delta\overline{V} + \Delta\overline{V}'$$

$$N_t \sim \sum_k k\delta_k + \delta_B + \sum_k (k+1)\delta_{Bk} .$$

Overall, V^E has the form

$$\overline{V}_{mix} = f_1(X_B)\Delta\overline{V} + f_2(X_B)\Delta\overline{V}'.$$

$\Delta\overline{V}$ should be set from the molar volume of pure water $\overline{V}_A(0)$, leaving $\Delta\overline{V}'$ to be set from the least-squares fit of our V^E function to experiment. We take $\overline{V}_o + \Delta\overline{V}$ to represent the molar volume of ice (totally bonded water), and $\overline{V}_o + R_o\Delta\overline{V}$ to be the molar volume of water at some moderately low temperature.

Calculations of the enthalpy of mixing $\Delta\overline{H}_{mix}(X_B)$ follow the exact same outline, and use the same R_o, $f_1(X_B)$, and $f_2(X_B)$.

The chained equilibria of association cause f_1 to peak at very high X_B. For the simplest model of complexation, that of A-B monomer association only ($K_n' = 0$ for $n > 0$), f_2 also peaks at large X_B. However $\Delta\overline{V}_{mix}$ peaks at $X_B \simeq 0.4$, so the simple model is unphysical for at least the excess volume behavior. The other models have not been examined for their volume predictions. Getting the phase behavior, absorption, and volume/enthalpy behavior to be satisfactorily predicted by any chemical model will no doubt be very difficult, if not impossible.

Details

The algebra of the mole fraction equations is very messy and difficult to do correctly, so we present the key equations for three chemical models as a time saver for any future work on these lines.

Model I:

$$A + A_{n-1} \rightleftharpoons A_n \qquad K_n = K = \delta_n / \delta_A \delta_{n-1}$$

$$A + B \rightleftharpoons AB \qquad K' = \delta_{AB} / \delta_A \delta_B$$

$$X_A = \frac{N_A}{N_A + N_B} = \frac{\cancel{N_{tot}}(\sum_n n\delta_n + \delta_{AB})}{\cancel{N_{tot}}(\sum_n n\delta_n + 2\delta_{AB} + \delta_B)}$$

$$= \frac{\delta_A\left[(1+K') - 2KK'\delta_A + KK'(1+K)\delta_A^2\right]}{1 + 2(K'-K)\delta_A + (K - K' + K^2 - 4KK')\delta_A^2 + 2KK'(1+K)\delta_A^3} ,$$

$$\equiv \frac{\delta_A\left[a - b\delta_A + c\delta_A{}^2\right]}{1 + d\delta_A + e\delta_A{}^2 + 2c\delta_A{}^3}$$

which reduces to the cubic form

$$(2cX_A-c)\delta_A^3+(eX_A+b)\delta_A^2+(dX_A-a)\delta_A+X_A= 0.$$

Explicit forms for the solutions to cubic equations are available, as in the Handbook of Chemistry and Physics. Generally there are three real roots δ_A obtained, only one of which satisfies the constraint that all mole fractions δ_A, δ_B, and δ_{AB} be positive.

$$\delta_B = (1-[1+K]\delta_A)/(1-K\delta_A)(1+K'\delta_A)$$

$$\partial\delta_B/\partial\delta_A = -(a + b\delta_A + c\delta_A{}^2)/(1-K\delta_A)(1+K'\delta_A)$$

$$\delta_A' = -(1 + d\delta_A + e\delta_A^2 + 2c\delta_A^3)/D$$

$$D = X_A(d + 2e\delta_A + 6c\delta_A{}^2) - a + 2b\delta_A - 3c\delta_A{}^2$$

$$\delta_A'' = -\frac{\delta_A'}{D}\Big[2(d+2e\delta_A+6c\delta_A{}^2) + X_A(2e\delta_A'+12c\delta_A\delta_A') +2b\delta_A'-6c\delta_A\delta_A'\Big]$$

$\aleph_{\text{chem}}$ is not very flat for this model for any moderate K, K', and δ_{AB} peaks at $X_B = 0.5$.

Model II:

$A + A_{n-1} \rightleftharpoons A_n \qquad K_n = K$

$B + A_n \rightleftharpoons BA_n \qquad K_n' = K'$

$$X_A = \frac{(1+K')\delta_A - K(1+K')\delta_A{}^2}{1 + (2K'-3K)\delta_A + (1+3K)(K-K')\delta_A{}^2 + K(1+K)(K'-K)\delta_A{}^3}$$

$$\equiv \frac{\delta_A[a - b\delta_A]}{1 + c\delta_A + d\delta_A{}^2 + e\delta_A{}^3}\ ,$$

cubic if $K \neq K'$, quadratic if $K = K'$.

$$\delta_B = (1-[1+K]\delta_A)/(1-[K-K']\delta_A)$$

$$\partial\delta_B/\partial\delta_A = -(a - b\delta_A)/(1 -[K-K']\delta_A)^2$$

$$\delta_A' = -(1 + c\delta_A + d\delta_A^2 + e\delta_A^3)/D$$

$$D = X_A(c + 2d\delta_A + 3e\delta_A^2) - a + 2b\delta_A$$

A reasonable model.

Model III:

$$A + A_{n-1} \rightleftharpoons A_n \qquad K_n = K$$

$$B + A_n \rightleftharpoons BA_n \qquad K'_n = K'\alpha^n$$

$$\delta_B = \frac{(1 - [1+K]\delta_A)(1 - \alpha K\delta_A)}{(1 - K\delta_A)(1 + \alpha[K'-K]\delta_A)}$$

$X_A \leftrightarrow \delta_A$ relation is quartic, unless $K = K'$, which we promptly assume:

$$\delta_B = (1 - [1+K]\delta_A)(1 - \alpha K\delta_A)/(1 - K\delta_A)$$

$$X_A = \frac{(1 + \alpha K)\delta_A - 2\alpha K(1+K)\delta_A^2 + \alpha K^2(1+K)\delta_A^3}{1 - 2K\delta_A + K(1 - \alpha + K)\delta_A^2}$$

$$\equiv (a\delta_A + b\delta_A^2 + c\delta_A^3)/(1 + d\delta_A + e\delta_A^2)$$

$$\delta_A' = -(1 + d\delta_A + e\delta_A^2)/D$$

$$D = X_A(d + 2e\delta_A) - a - 2b\delta_A - 3c\delta_A^2$$

$$\partial\delta_B/\partial\delta_A = -(a + b\delta_A + c\delta_A^2)/(1 - K\delta_A)^2$$

also a good model.

We used two more models, one the same as model III but with $K_n' = K'\alpha^{n-1}$, and one with self-association of B. The former is not noticeably different from model III, and the latter is unrealistic for our system.

References for Part II:

1. J. H. Andreae, P. D. Edmonds, and J. F. McKellar, Acustica 15,74(1965).

2. The triethylamine: water lower consolute system studied by Brown and Richardson (Phil. Mag. 4,705 1959) probably shows the same effects as our system, but it was not studied at compositions off X_c so they were not recognized.

3. K. F. Herzfeld and T. A. Litovitz, Absorption and Dispersion of Ultrasonic Waves (Academic, N. Y., 1959).

4. M. Eigen and L. de Maeyer, in Techniques of Organic Chemistry, ed. Weissberger, *et al.* (Wiley, N. Y., 1962), Vol. VIII, Part 2.

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