CALCULATION OF ELUTION PEAK POSITIONS IN GRADIENT ELUTION CHROMATOGRAPHY WITH AN ION EXCHANGER

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INTRODUCTION

Gradient elution chromatography is an excellent method for the separation of a series of similar ionic species with an ion exchanger. The most convenient apparatus for the gradient elution is the one illustrated in Fig. 1. This apparatus has a constant-volume mixing bottle which delivers an eluent solution whose concentration follows the equation,

$$C = C_r - (C_r - C_o) \cdot \exp(-V/V_m) \quad (1)$$

where C denotes the concentration of the eluent when V ml of the eluent solution has flowed from the mixing bottle, C_o the initial concentration of the eluent in the mixing bottle, C_r the concentration of the eluent in the reservoir, and V_m the constant volume of the eluent solution in the mixing bottle.

Some equations have been proposed for calculating where an elution peak will

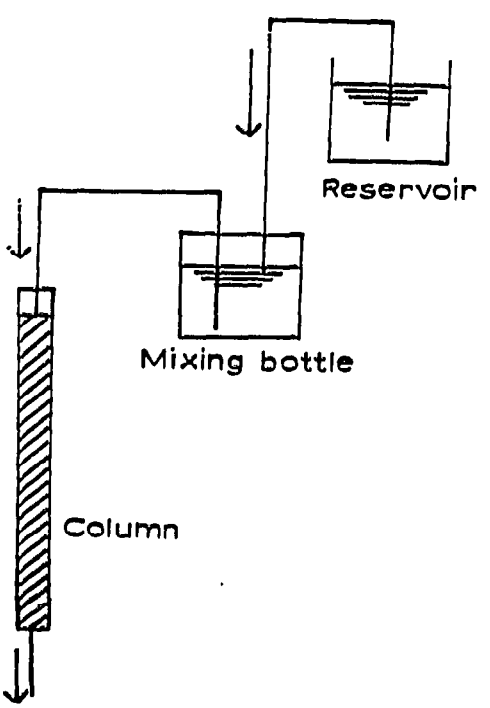


Fig. 1. Apparatus for gradient elution.

appear in such a gradient elution. SCHWAB, RIEMAN AND VAUGHAN[1] have derived equations for the gradient elution of uni-, bi-, and tervalent ions, and KOGUCHI, WAKI AND OHASHI[2] have derived equations for ions with any integral charge. Since anions of a polybasic acid are present as an equilibrium mixture of more than one ionic species, the mean charge of the anions deviates from an integral value in most cases. The purpose of this paper is to derive more generally applicable equations for elution peak positions in the gradient elution of ions whose charges are not necessarily integral and to present a method for calculating their elution peak positions.

DERIVATION OF EQUATIONS

The fundamental equation for the elution peak position, which has been derived in a previous paper[2], is:

$$D_r S = \int_0^{V_{max}} \{1 - \alpha \cdot \exp(-V/V_m)\}^n dV \qquad (2)$$

where V_{max} is the effluent volume at the peak; D_r the distribution ratio of given sample ions at a concentration C_r, *viz.*:

$$D_r = \frac{\text{the amount of the sample ions in a unit volume of resin}}{\text{the amount of the sample ions in a unit volume of solution}}.$$

n is a constant given in eqn. (4) below, which is equal to the mean charge of the sample ions in an ideal system; S the volume of the resin bed; dV the increment of eluent solution; and α is a parameter concerned with the concentration gradient of the eluent, as shown in the following equation:

$$\alpha = (C_r - C_0)/C_r \qquad (3)$$

Eqn. (2) has been derived on the following assumptions: (1) the plate theory holds in all the processes of ion exchange, (2) the volume of the solution in the tubing between the mixing bottle and the column, and the interstitial and dead volumes of the resin bed are negligibly small compared with the effluent volume at the peak, and (3) at any concentration of the eluent the following relation holds with respect to the distribution ratio of the sample ions:

$$D = aC^{-n} \qquad (4)$$

where a and n are constants.

In order to solve eqn. (2), the variables are changed as follows:

$$V/V_m = t,\ V_{max}/V_m = x,\ D_r S/V_m = y,\ dV = V_m dt$$

Then eqn. (2) can be written as follows:

$$y = \int_0^x (1 - \alpha e^{-t})^n dt \qquad (5)$$

Next the variable t is denoted in terms of u where:

$\alpha e^{-t} = u$, and $dt = -(1/u)du$

Hence:

$$y = \int_{\alpha}^{\alpha e^{-x}} -\{(1-u)^n/u\}du = -\int_{\alpha}^{\alpha e^{-x}} (1/u)du + \int_{\alpha}^{\alpha e^{-x}} \{1-(1-u)^n\}\cdot(1/u)du =$$

$$= x - \int_0^{\alpha}\{1-(1-u)^n\}\cdot(1/u)du + \int_0^{\alpha e^{-x}}\{1-(1-u)^n\}\cdot(1/u)du =$$

$$= x - f_n(\alpha) + f_n(\alpha e^{-x}) \equiv G(x) \qquad (6)$$

where:

$$f_n(z) = \int_0^z \{1-(1-u)^n\}\cdot(1/u)du \qquad (7)$$

If one puts,

$1 - u = v$, $du = -dv$

eqn. (7) can be represented by:

$$f_n(z) = \int_{1-z}^{1} \{(1-v^n)/(1-v)\}\,dv \qquad (8)$$

As the function $f_n(z)$ is very complicated, it is difficult to solve this function with respect to any value of n. However, it is possible to integrate the right hand side of eqn. (8), when n is n_o, $n_o + (1/2)$, $n_o + (1/4)$, and $n_o + (3/4)$, where n_o is an integer. The results are given below for:

$n = n_o$:

$$f_n(z) = 1 + (1/2) + (1/3) + \cdots + (1/n_o) - \{1 - z + (1-z)^2\cdot(1/2) +$$

$$+ (1-z)^3\cdot(1/3) + \cdots + (1-z)^{n_o}\cdot(1/n_o)\} \qquad (9)$$

$n = n_o + (1/2)$:

$$f_n(z) = 2 + (2/3) + (2/5) + \cdots + \{2/(2n_o+1)\} - 2\log 2 - 2(1-z)^{1/2}\cdot$$

$$\cdot[1 + (1-z)\cdot(1/3) + (1-z)^2\cdot(1/5) + \cdots + (1-z)^{n_o}\cdot\{1/(2n_o+1)\}] +$$

$$+ 2\log\{1 + (1-z)^{1/2}\} \qquad (10)$$

$n = n_o + (1/4)$:

$$f_n(z) = 4 + (4/5) + 4/9) + \cdots + \{4/(4n_o+1)\} - 3\log 2 - (\pi/2) -$$

$$- 4(1-z)^{1/4}\cdot[1 + (1-z)\cdot(1/5) + (1-z)^2\cdot(1/9) + \cdots + (1-z)^{n_o}\cdot$$

$$\cdot\{1/(4n_o+1)\}] + \log\{1 + (1-z)^{1/2}\} + 2\log\{1 + (1-z)^{1/4}\} +$$

$$+ 2\tan^{-1}(1-z)^{1/4} \qquad (11)$$

$n = n_0 + (3/4)$:

$$f_n(z) = (4/3) + (4/7) + (4/11) + \cdots + \{4/(4n_0 + 3)\} - 3 \log 2 + (\pi/2) - \\ - 4(1 - z)^{3/4} \cdot [(1/3) + (1 - z) \cdot (1/7) + (1 - z)^2 \cdot (1/11) + \cdots + (1 - z)^{n_0} \cdot \\ \cdot \{1/(4n_0 + 3)\}] + \log \{1 + (1 - z)^{1/2}\} + 2 \log \{1 + (1 - z)^{1/4}\} - \\ - 2 \tan^{-1} (1 - z)^{1/4} \qquad (12)$$

METHODS OF CALCULATION

One of the purposes of this work is to calculate x when y is given experimentally. However, eqn. (6) is implicit with respect to x. Therefore, one must calculate y at a given x and examine the relation between x and y graphically. Before these calculations are performed, the ranges of the variables in eqn. (6) should be established. The values of n encountered in many cases are probably smaller than 6. Thus, n was taken to be in the range from 0.25 to 6.00 in intervals of 0.25. The values of α were chosen to be in the range from 0.5 to 1.0 with 0.1 intervals. When $\alpha = 1.0$, $C_0 = 0$, *i.e.*, the mixing bottle contains initially no eluent. When $\alpha = 0.5$, $C_0 = (1/2)C_r$. If α is smaller than 0.5, the concentration gradient between the reservoir and mixing bottle may be too small to perform efficiently the gradient elution. The values of x were taken to be in the range from 0 to 5.00, at intervals of 0.1, because the concentration gradient is too small when $x > 5.00$. By the use of a computor, ALGOL-H, at Kyushu University, 7,200 values of y were calculated for combinations of the variables mentioned above. In the same way, 2,400 values of $f_n(z)$ were calculated for values of z in the range from 0 to 1.00 at intervals of 0.01, because the lower and upper limits of z are 0 and 1.00, respectively.

From the data for the relations between x and y, the present authors concluded that the most practical and convenient way for calculating values of x as accurately as possible is to employ the following two methods depending on whether y is larger or smaller than 0.7.

Method 1 ($y > 0.7$)

When y is large enough, $f_n(\alpha e^{-x})$ is very small as compared with $\{x - f_n(\alpha)\}$ in eqn. (6). Therefore, one can obtain a first approximation value of x, by the equation:

$$x_1 = y + f_n(\alpha) \qquad (13)$$

By means of Newton's method, the second approximate value, x_2, is given as follows:

$$x_2 = x_1 - [\{G(x_1) - y\}/G'(x_1)] \\ = x_1 - [f_n(\alpha e^{-x_1})/(1 - \alpha e^{-x_1})^n] \qquad (14)$$

By using the data for the $f_n(z)$ functions, which are shown in Table I, one can calculate the second approximate value x_2. If n falls between the values given in Table I, the value of $f_n(z)$ must be obtained by interpolation.

TABLE I

VALUES OF $f_n(z)$ FUNCTIONS

z	n											
	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.01	0.0025	0.0050	0.0075	0.0100	0.0125	0.0150	0.0175	0.0200	0.0224	0.0249	0.0274	0.0299
0.02	0.0050	0.0100	0.0150	0.0200	0.0250	0.0299	0.0349	0.0398	0.0447	0.0496	0.0545	0.0594
0.03	0.0075	0.0151	0.0225	0.0300	0.0374	0.0448	0.0522	0.0596	0.0669	0.0742	0.0814	0.0887
0.04	0.0101	0.0201	0.0301	0.0400	0.0499	0.0597	0.0695	0.0792	0.0889	0.0985	0.1081	0.1176
0.05	0.0126	0.0252	0.0376	0.0500	0.0623	0.0745	0.0867	0.0988	0.1107	0.1227	0.1345	0.1463
0.06	0.0152	0.0302	0.0452	0.0600	0.0747	0.0893	0.1038	0.1182	0.1325	0.1466	0.1607	0.1747
0.07	0.0177	0.0353	0.0527	0.0700	0.0871	0.1041	0.1209	0.1376	0.1541	0.1704	0.1867	0.2028
0.08	0.0203	0.0404	0.0603	0.0800	0.0995	0.1188	0.1379	0.1568	0.1755	0.1941	0.2124	0.2306
0.09	0.0229	0.0455	0.0679	0.0900	0.1119	0.1335	0.1548	0.1759	0.1968	0.2175	0.2379	0.2581
0.10	0.0255	0.0506	0.0755	0.1000	0.1242	0.1481	0.1717	0.1950	0.2180	0.2407	0.2632	0.2853
0.11	0.0281	0.0558	0.0831	0.1100	0.1365	0.1627	0.1885	0.2139	0.2390	0.2638	0.2882	0.3123
0.12	0.0307	0.0609	0.0907	0.1200	0.1489	0.1773	0.2052	0.2328	0.2599	0.2867	0.3130	0.3390
0.13	0.0333	0.0661	0.0983	0.1300	0.1611	0.1918	0.2219	0.2515	0.2807	0.3094	0.3376	0.3654
0.14	0.0360	0.0713	0.1060	0.1400	0.1734	0.2063	0.2385	0.2702	0.3013	0.3319	0.3620	0.3915
0.15	0.0386	0.0765	0.1136	0.1500	0.1857	0.2207	0.2551	0.2887	0.3218	0.3543	0.3861	0.4174
0.16	0.0413	0.0817	0.1213	0.1600	0.1979	0.2351	0.2715	0.3072	0.3422	0.3764	0.4100	0.4430
0.17	0.0440	0.0869	0.1289	0.1700	0.2102	0.2495	0.2879	0.3255	0.3624	0.3984	0.4337	0.4683
0.18	0.0466	0.0922	0.1366	0.1800	0.2224	0.2638	0.3043	0.3438	0.3825	0.4202	0.4572	0.4933
0.19	0.0493	0.0974	0.1443	0.1900	0.2346	0.2781	0.3205	0.3619	0.4024	0.4419	0.4805	0.5181
0.20	0.0520	0.1027	0.1520	0.2000	0.2468	0.2923	0.3367	0.3800	0.4222	0.4633	0.5035	0.5427
0.21	0.0548	0.1080	0.1597	0.2100	0.2589	0.3065	0.3529	0.3980	0.4419	0.4846	0.5263	0.5669
0.22	0.0575	0.1133	0.1674	0.2200	0.2711	0.3207	0.3689	0.4158	0.4614	0.5058	0.5489	0.5909
0.23	0.0602	0.1186	0.1752	0.2300	0.2832	0.3348	0.3849	0.4336	0.4808	0.5267	0.5713	0.6147
0.24	0.0630	0.1239	0.1829	0.2400	0.2953	0.3489	0.4008	0.4512	0.5001	0.5475	0.5935	0.6382
0.25	0.0658	0.1293	0.1907	0.2500	0.3074	0.3629	0.4167	0.4688	0.5192	0.5681	0.6155	0.6615
0.26	0.0685	0.1346	0.1984	0.2600	0.3195	0.3769	0.4325	0.4862	0.5382	0.5885	0.6372	0.6845
0.27	0.0713	0.1400	0.2062	0.2700	0.3315	0.3909	0.4482	0.5035	0.5570	0.6088	0.6588	0.7072
0.28	0.0741	0.1454	0.2140	0.2800	0.3436	0.4048	0.4638	0.5208	0.5758	0.6289	0.6801	0.7297
0.29	0.0770	0.1508	0.2218	0.2900	0.3556	0.4187	0.4794	0.5379	0.5944	0.6488	0.7013	0.7520
0.30	0.0798	0.1563	0.2296	0.3000	0.3676	0.4325	0.4949	0.5550	0.6128	0.6685	0.7222	0.7740
0.31	0.0827	0.1617	0.2375	0.3100	0.3796	0.4463	0.5104	0.5719	0.6311	0.6881	0.7429	0.7958
0.32	0.0855	0.1672	0.2453	0.3200	0.3915	0.4600	0.5258	0.5888	0.6493	0.7075	0.7635	0.8173
0.33	0.0884	0.1727	0.2532	0.3300	0.4035	0.4738	0.5411	0.6055	0.6674	0.7268	0.7838	0.8386
0.34	0.0913	0.1782	0.2610	0.3400	0.4154	0.4874	0.5563	0.6222	0.6853	0.7459	0.8039	0.8597
0.35	0.0942	0.1837	0.2689	0.3500	0.4273	0.5010	0.5714	0.6387	0.7031	0.7648	0.8239	0.8805
0.36	0.0971	0.1893	0.2768	0.3600	0.4392	0.5146	0.5865	0.6552	0.7208	0.7835	0.8436	0.9012
0.37	0.1001	0.1948	0.2847	0.3700	0.4510	0.5281	0.6016	0.6715	0.7383	0.8021	0.8631	0.9215
0.38	0.1030	0.2004	0.2926	0.3800	0.4629	0.5416	0.6165	0.6878	0.7557	0.8206	0.8825	0.9417
0.39	0.1060	0.2060	0.3006	0.3900	0.4747	0.5551	0.6314	0.7039	0.7730	0.8388	0.9016	0.9616
0.40	0.1090	0.2117	0.3085	0.4000	0.4865	0.5685	0.6462	0.7200	0.7902	0.8569	0.9206	0.9813
0.41	0.1120	0.2173	0.3165	0.4100	0.4983	0.5818	0.6609	0.7359	0.8072	0.8749	0.9394	1.0008
0.42	0.1150	0.2230	0.3245	0.4200	0.5101	0.5952	0.6756	0.7518	0.8241	0.8927	0.9579	1.0201
0.43	0.1181	0.2287	0.3324	0.4300	0.5218	0.6084	0.6902	0.7675	0.8408	0.9103	0.9763	1.0392
0.44	0.1211	0.2344	0.3405	0.4400	0.5336	0.6217	0.7047	0.7832	0.8574	0.9278	0.9945	1.0580
0.45	0.1242	0.2401	0.3485	0.4500	0.5453	0.6348	0.7192	0.7987	0.8739	0.9451	1.0126	1.0766
0.46	0.1273	0.2459	0.3565	0.4600	0.5570	0.6480	0.7336	0.8142	0.8903	0.9623	1.0304	1.0950
0.47	0.1304	0.2516	0.3646	0.4700	0.5686	0.6611	0.7479	0.8295	0.9065	0.9793	1.0481	1.1133
0.48	0.1335	0.2574	0.3726	0.4800	0.5803	0.6741	0.7621	0.8448	0.9227	0.9961	1.0655	1.1313
0.49	0.1367	0.2632	0.3807	0.4900	0.5919	0.6871	0.7763	0.8599	0.9386	1.0128	1.0828	1.1491
0.50	0.1399	0.2691	0.3888	0.5000	0.6035	0.7001	0.7904	0.8750	0.9545	1.0293	1.0999	1.1667
0.51	0.1430	0.2750	0.3969	0.5100	0.6151	0.7130	0.8044	0.8899	0.9702	1.0457	1.1169	1.1841
0.52	0.1463	0.2809	0.4051	0.5200	0.6266	0.7258	0.8183	0.9048	0.9858	1.0620	1.1336	1.2013
0.53	0.1495	0.2868	0.4132	0.5300	0.6382	0.7386	0.8322	0.9195	1.0013	1.0781	1.1502	1.2183
0.54	0.1527	0.2927	0.4214	0.5400	0.6497	0.7514	0.8460	0.9342	1.0167	1.0940	1.1666	1.2351
0.55	0.1560	0.2987	0.4296	0.5500	0.6612	0.7641	0.8597	0.9487	1.0319	1.1098	1.1829	1.2517
0.56	0.1593	0.3047	0.4378	0.5600	0.6726	0.7768	0.8734	0.9632	1.0470	1.1254	1.1990	1.2681
0.57	0.1627	0.3107	0.4460	0.5700	0.6841	0.7894	0.8869	0.9775	1.0620	1.1409	1.2149	1.2844
0.58	0.1660	0.3168	0.4542	0.5800	0.6955	0.8020	0.9004	0.9918	1.0768	1.1563	1.2306	1.3004
0.59	0.1694	0.3229	0.4625	0.5900	0.7069	0.8145	0.9139	1.0059	1.0916	1.1714	1.2462	1.3163
0.60	0.1728	0.3290	0.4708	0.6000	0.7183	0.8270	0.9272	1.0200	1.1062	1.1865	1.2616	1.3320
0.61	0.1762	0.3351	0.4790	0.6100	0.7296	0.8394	0.9405	1.0340	1.1207	1.2014	1.2768	1.3475
0.62	0.1797	0.3413	0.4874	0.6200	0.7410	0.8518	0.9537	1.0478	1.1350	1.2162	1.2919	1.3628
0.63	0.1831	0.3475	0.4957	0.6300	0.7523	0.8641	0.9668	1.0615	1.1493	1.2308	1.3068	1.3780
0.64	0.1866	0.3537	0.5040	0.6400	0.7636	0.8764	0.9799	1.0752	1.1634	1.2453	1.3216	1.3930
0.65	0.1902	0.3600	0.5124	0.6500	0.7748	0.8886	0.9928	1.0887	1.1774	1.2596	1.3362	1.4078
0.66	0.1937	0.3663	0.5208	0.6600	0.7860	0.9008	1.0057	1.1022	1.1913	1.2738	1.3507	1.4224
0.67	0.1973	0.3726	0.5292	0.6700	0.7972	0.9129	1.0186	1.1155	1.2050	1.2879	1.3649	1.4369
0.68	0.2010	0.3790	0.5377	0.6800	0.8084	0.9250	1.0313	1.1288	1.2186	1.3018	1.3791	1.4512
0.69	0.2046	0.3854	0.5461	0.6900	0.8196	0.9370	1.0440	1.1419	1.2322	1.3156	1.3931	1.4654
0.70	0.2083	0.3918	0.5546	0.7000	0.8307	0.9490	1.0565	1.1550	1.2455	1.3292	1.4069	1.4793
0.71	0.2121	0.3983	0.5631	0.7100	0.8418	0.9609	1.0691	1.1679	1.2588	1.3427	1.4206	1.4932
0.72	0.2158	0.4048	0.5716	0.7200	0.8529	0.9727	1.0815	1.1808	1.2720	1.3561	1.4342	1.5068
0.73	0.2196	0.4114	0.5802	0.7300	0.8639	0.9845	1.0938	1.1935	1.2850	1.3694	1.4475	1.5203
0.74	0.2235	0.4180	0.5888	0.7400	0.8749	0.9963	1.1061	1.2062	1.2979	1.3825	1.4608	1.5337
0.75	0.2274	0.4246	0.5974	0.7500	0.8859	1.0080	1.1183	1.2188	1.3107	1.3955	1.4739	1.5469
0.76	0.2313	0.4313	0.6060	0.7600	0.8969	1.0196	1.1304	1.2312	1.3234	1.4083	1.4869	1.5599
0.77	0.2353	0.4381	0.6147	0.7700	0.9078	1.0312	1.1425	1.2435	1.3360	1.4210	1.4997	1.5728
0.78	0.2393	0.4448	0.6234	0.7800	0.9187	1.0427	1.1544	1.2558	1.3484	1.4336	1.5124	1.5856
0.79	0.2433	0.4517	0.6321	0.7900	0.9296	1.0542	1.1663	1.2679	1.3608	1.4461	1.5250	1.5982

z	n											
	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25	5.50	5.75	6.00
0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.01	0.0323	0.0348	0.0372	0.0397	0.0422	0.0446	0.0471	0.0495	0.0519	0.0544	0.0568	0.0593
0.02	0.0643	0.0691	0.0740	0.0788	0.0836	0.0884	0.0932	0.0980	0.1028	0.1076	0.1123	0.1171
0.03	0.0959	0.1031	0.1102	0.1173	0.1244	0.1315	0.1386	0.1456	0.1526	0.1596	0.1665	0.1734
0.04	0.1271	0.1365	0.1459	0.1553	0.1646	0.1738	0.1830	0.1922	0.2013	0.2104	0.2194	0.2284
0.05	0.1580	0.1696	0.1812	0.1927	0.2041	0.2154	0.2267	0.2379	0.2490	0.2601	0.2711	0.2821
0.06	0.1885	0.2023	0.2159	0.2295	0.2429	0.2563	0.2695	0.2827	0.2958	0.3087	0.3216	0.3344
0.07	0.2187	0.2345	0.2502	0.2658	0.2812	0.2964	0.3116	0.3266	0.3415	0.3563	0.3709	0.3854
0.08	0.2486	0.2664	0.2840	0.3015	0.3188	0.3359	0.3529	0.3697	0.3863	0.4028	0.4191	0.4353
0.09	0.2781	0.2978	0.3173	0.3367	0.3558	0.3747	0.3934	0.4118	0.4301	0.4482	0.4662	0.4839
0.10	0.3072	0.3288	0.3502	0.3713	0.3922	0.4128	0.4331	0.4532	0.4731	0.4927	0.5121	0.5313
0.11	0.3361	0.3595	0.3826	0.4054	0.4280	0.4502	0.4721	0.4938	0.5151	0.5362	0.5570	0.5776
0.12	0.3645	0.3897	0.4146	0.4391	0.4632	0.4870	0.5104	0.5335	0.5563	0.5788	0.6009	0.6228
0.13	0.3927	0.4196	0.4461	0.4722	0.4978	0.5231	0.5480	0.5725	0.5966	0.6204	0.6438	0.6669
0.14	0.4206	0.4491	0.4772	0.5048	0.5319	0.5586	0.5848	0.6107	0.6361	0.6611	0.6857	0.7099
0.15	0.4481	0.4782	0.5078	0.5369	0.5654	0.5935	0.6210	0.6481	0.6748	0.7009	0.7266	0.7519
0.16	0.4753	0.5069	0.5380	0.5685	0.5984	0.6278	0.6566	0.6849	0.7126	0.7399	0.7667	0.7930
0.17	0.5021	0.5353	0.5678	0.5996	0.6309	0.6614	0.6914	0.7209	0.7497	0.7780	0.8058	0.8330
0.18	0.5287	0.5633	0.5972	0.6303	0.6628	0.6945	0.7257	0.7562	0.7860	0.8153	0.8440	0.8722
0.19	0.5550	0.5909	0.6261	0.6605	0.6942	0.7271	0.7593	0.7908	0.8216	0.8518	0.8814	0.9104
0.20	0.5809	0.6182	0.6547	0.6903	0.7250	0.7590	0.7923	0.8247	0.8565	0.8876	0.9180	0.9477
0.21	0.6065	0.6451	0.6828	0.7196	0.7554	0.7904	0.8246	0.8580	0.8906	0.9225	0.9537	0.9842
0.22	0.6319	0.6717	0.7106	0.7484	0.7853	0.8213	0.8564	0.8907	0.9241	0.9568	0.9886	1.0198
0.23	0.6569	0.6980	0.7379	0.7768	0.8147	0.8516	0.8876	0.9227	0.9569	0.9903	1.0228	1.0546
0.24	0.6816	0.7238	0.7649	0.8048	0.8436	0.8814	0.9182	0.9541	0.9890	1.0231	1.0563	1.0886
0.25	0.7061	0.7494	0.7915	0.8324	0.8721	0.9107	0.9483	0.9849	1.0205	1.0552	1.0890	1.1219
0.26	0.7302	0.7746	0.8177	0.8595	0.9001	0.9395	0.9778	1.0151	1.0514	1.0866	1.1210	1.1544
0.27	0.7541	0.7995	0.8435	0.8862	0.9276	0.9678	1.0068	1.0448	1.0816	1.1174	1.1523	1.1862
0.28	0.7777	0.8241	0.8690	0.9125	0.9547	0.9956	1.0353	1.0738	1.1112	1.1476	1.1829	1.2173
0.29	0.8010	0.8483	0.8941	0.9385	0.9814	1.0230	1.0633	1.1024	1.1403	1.1771	1.2129	1.2477
0.30	0.8240	0.8722	0.9189	0.9640	1.0076	1.0498	1.0907	1.1304	1.1688	1.2061	1.2423	1.2774
0.31	0.8467	0.8959	0.9433	0.9891	1.0334	1.0762	1.1177	1.1578	1.1967	1.2344	1.2710	1.3065
0.32	0.8692	0.9192	0.9674	1.0139	1.0588	1.1022	1.1442	1.1848	1.2241	1.2622	1.2992	1.3350
0.33	0.8914	0.9422	0.9911	1.0383	1.0838	1.1277	1.1702	1.2112	1.2510	1.2894	1.3267	1.3628
0.34	0.9133	0.9648	1.0145	1.0623	1.1083	1.1528	1.1957	1.2372	1.2773	1.3161	1.3537	1.3901
0.35	0.9350	0.9872	1.0375	1.0859	1.1325	1.1775	1.2208	1.2627	1.3032	1.3423	1.3801	1.4168
0.36	0.9563	1.0093	1.0602	1.1092	1.1563	1.2017	1.2455	1.2877	1.3285	1.3679	1.4061	1.4429
0.37	0.9775	1.0311	1.0827	1.1322	1.1798	1.2256	1.2697	1.3123	1.3534	1.3931	1.4314	1.4685
0.38	0.9984	1.0527	1.1047	1.1547	1.2028	1.2490	1.2935	1.3364	1.3778	1.4177	1.4563	1.4936
0.39	1.0190	1.0739	1.1265	1.1770	1.2255	1.2721	1.3169	1.3601	1.4017	1.4419	1.4807	1.5182
0.40	1.0394	1.0949	1.1480	1.1989	1.2478	1.2948	1.3399	1.3834	1.4253	1.4656	1.5046	1.5423
0.41	1.0595	1.1155	1.1692	1.2205	1.2698	1.3171	1.3625	1.4062	1.4483	1.4889	1.5281	1.5659
0.42	1.0794	1.1359	1.1900	1.2418	1.2914	1.3390	1.3847	1.4287	1.4710	1.5117	1.5511	1.5890
0.43	1.0990	1.1561	1.2106	1.2628	1.3127	1.3606	1.4066	1.4507	1.4932	1.5342	1.5736	1.6117
0.44	1.1184	1.1760	1.2309	1.2834	1.3337	1.3818	1.4280	1.4724	1.5151	1.5561	1.5957	1.6339
0.45	1.1375	1.1956	1.2509	1.3037	1.3543	1.4027	1.4491	1.4937	1.5365	1.5777	1.6174	1.6557
0.46	1.1565	1.2149	1.2706	1.3238	1.3746	1.4232	1.4699	1.5146	1.5576	1.5989	1.6388	1.6771
0.47	1.1752	1.2340	1.2901	1.3435	1.3946	1.4435	1.4903	1.5352	1.5783	1.6197	1.6597	1.6981
0.48	1.1936	1.2529	1.3092	1.3630	1.4143	1.4634	1.5103	1.5554	1.5986	1.6402	1.6802	1.7188
0.49	1.2118	1.2715	1.3281	1.3822	1.4337	1.4829	1.5301	1.5753	1.6186	1.6603	1.7004	1.7390
0.50	1.2299	1.2898	1.3468	1.4010	1.4528	1.5022	1.5495	1.5948	1.6383	1.6800	1.7202	1.7589
0.51	1.2476	1.3079	1.3652	1.4197	1.4716	1.5212	1.5686	1.6140	1.6576	1.6994	1.7396	1.7784
0.52	1.2652	1.3258	1.3833	1.4380	1.4901	1.5398	1.5874	1.6329	1.6765	1.7185	1.7587	1.7975
0.53	1.2826	1.3434	1.4012	1.4561	1.5084	1.5582	1.6059	1.6515	1.6952	1.7372	1.7775	1.8164
0.54	1.2997	1.3608	1.4188	1.4739	1.5263	1.5763	1.6241	1.6698	1.7136	1.7556	1.7960	1.8349
0.55	1.3166	1.3780	1.4362	1.4915	1.5440	1.5941	1.6420	1.6878	1.7316	1.7737	1.8141	1.8530
0.56	1.3334	1.3950	1.4534	1.5088	1.5615	1.6117	1.6596	1.7055	1.7494	1.7915	1.8320	1.8709
0.57	1.3499	1.4117	1.4703	1.5258	1.5787	1.6290	1.6770	1.7229	1.7669	1.8090	1.8495	1.8885
0.58	1.3662	1.4282	1.4870	1.5427	1.5956	1.6460	1.6941	1.7400	1.7841	1.8263	1.8668	1.9058
0.59	1.3823	1.4446	1.5034	1.5592	1.6123	1.6628	1.7109	1.7569	1.8010	1.8432	1.8838	1.9228
0.60	1.3982	1.4606	1.5197	1.5756	1.6287	1.6793	1.7275	1.7736	1.8176	1.8599	1.9005	1.9395
0.61	1.4139	1.4765	1.5357	1.5917	1.6449	1.6955	1.7438	1.7899	1.8340	1.8763	1.9170	1.9560
0.62	1.4295	1.4922	1.5515	1.6076	1.6609	1.7116	1.7599	1.8060	1.8502	1.8925	1.9331	1.9722
0.63	1.4448	1.5077	1.5671	1.6233	1.6767	1.7274	1.7757	1.8219	1.8661	1.9084	1.9491	1.9882
0.64	1.4600	1.5230	1.5825	1.6388	1.6922	1.7430	1.7914	1.8376	1.8818	1.9241	1.9648	2.0039
0.65	1.4749	1.5381	1.5977	1.6540	1.7075	1.7583	1.8068	1.8530	1.8972	1.9396	1.9803	2.0193
0.66	1.4897	1.5530	1.6127	1.6691	1.7226	1.7735	1.8219	1.8682	1.9124	1.9548	1.9955	2.0346
0.67	1.5043	1.5677	1.6274	1.6839	1.7375	1.7884	1.8369	1.8832	1.9274	1.9698	2.0105	2.0496
0.68	1.5188	1.5822	1.6420	1.6986	1.7522	1.8031	1.8516	1.8979	1.9422	1.9846	2.0253	2.0644
0.69	1.5330	1.5966	1.6564	1.7130	1.7667	1.8176	1.8662	1.9125	1.9568	1.9992	2.0399	2.0790
0.70	1.5471	1.6107	1.6707	1.7273	1.7810	1.8320	1.8805	1.9268	1.9711	2.0135	2.0542	2.0934
0.71	1.5610	1.6247	1.6847	1.7414	1.7951	1.8461	1.8946	1.9410	1.9853	2.0277	2.0684	2.1075
0.72	1.5748	1.6385	1.6986	1.7553	1.8090	1.8600	1.9086	1.9549	1.9992	2.0417	2.0824	2.1215
0.73	1.5883	1.6522	1.7122	1.7690	1.8227	1.8738	1.9224	1.9687	2.0130	2.0555	2.0962	2.1353
0.74	1.6018	1.6656	1.7258	1.7825	1.8363	1.8873	1.9359	1.9823	2.0266	2.0691	2.1098	2.1489
0.75	1.6150	1.6790	1.7391	1.7959	1.8497	1.9007	1.9493	1.9957	2.0400	2.0825	2.1232	2.1623
0.76	1.6281	1.6921	1.7523	1.8091	1.8629	1.9140	1.9626	2.0089	2.0533	2.0957	2.1364	2.1756
0.77	1.6411	1.7051	1.7653	1.8221	1.8759	1.9270	1.9756	2.0220	2.0663	2.1088	2.1495	2.1886
0.78	1.6539	1.7179	1.7782	1.8350	1.8888	1.9399	1.9885	2.0349	2.0792	2.1217	2.1624	2.2015
0.79	1.6666	1.7306	1.7909	1.8477	1.9015	1.9526	2.0013	2.0476	2.0920	2.1344	2.1751	2.2143

(continued on p. 220)

TABLE I (*continued*)

VALUES OF $f_n(z)$ FUNCTIONS

z	n											
	0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00
0.80	0.2475	0.4586	0.6408	0.8000	0.9405	1.0656	1.1781	1.2800	1.3730	1.4584	1.5374	1.6107
0.81	0.2516	0.4655	0.6496	0.8100	0.9513	1.0769	1.1898	1.2919	1.3851	1.4707	1.5497	1.6230
0.82	0.2558	0.4725	0.6584	0.8200	0.9620	1.0882	1.2014	1.3038	1.3971	1.4827	1.5618	1.6352
0.83	0.2601	0.4795	0.6673	0.8300	0.9728	1.0995	1.2130	1.3155	1.4090	1.4947	1.5738	1.6472
0.84	0.2645	0.4867	0.6761	0.8400	0.9835	1.1107	1.2244	1.3272	1.4208	1.5066	1.5857	1.6592
0.85	0.2689	0.4938	0.6850	0.8500	0.9942	1.1218	1.2358	1.3388	1.4324	1.5183	1.5975	1.6710
0.86	0.2734	0.5011	0.6940	0.8600	1.0048	1.1328	1.2471	1.3502	1.4440	1.5299	1.6091	1.6826
0.87	0.2779	0.5084	0.7030	0.8700	1.0155	1.1438	1.2583	1.3615	1.4554	1.5414	1.6206	1.6942
0.88	0.2825	0.5158	0.7120	0.8800	1.0260	1.1547	1.2695	1.3728	1.4667	1.5527	1.6320	1.7056
0.89	0.2873	0.5232	0.7211	0.8900	1.0366	1.1656	1.2805	1.3839	1.4779	1.5640	1.6433	1.7168
0.90	0.2921	0.5308	0.7302	0.9000	1.0471	1.1764	1.2915	1.3950	1.4890	1.5751	1.6544	1.7280
0.91	0.2970	0.5384	0.7393	0.9100	1.0576	1.1871	1.3023	1.4059	1.5000	1.5861	1.6655	1.7390
0.92	0.3020	0.5462	0.7486	0.9200	1.0680	1.1978	1.3131	1.4168	1.5109	1.5970	1.6764	1.7500
0.93	0.3072	0.5540	0.7578	0.9300	1.0784	1.2083	1.3238	1.4275	1.5217	1.6078	1.6872	1.7608
0.94	0.3125	0.5620	0.7671	0.9400	1.0887	1.2189	1.3344	1.4382	1.5324	1.6185	1.6979	1.7715
0.95	0.3179	0.5701	0.7765	0.9500	1.0990	1.2293	1.3449	1.4487	1.5429	1.6291	1.7085	1.7820
0.96	0.3236	0.5783	0.7860	0.9600	1.1093	1.2397	1.3553	1.4592	1.5534	1.6396	1.7189	1.7925
0.97	0.3295	0.5868	0.7955	0.9700	1.1195	1.2500	1.3657	1.4695	1.5638	1.6499	1.7293	1.8029
0.98	0.3356	0.5954	0.8051	0.9800	1.1296	1.2602	1.3759	1.4798	1.5740	1.6602	1.7396	1.8131
0.99	0.3423	0.6043	0.8148	0.9900	1.1397	1.2703	1.3861	1.4899	1.5842	1.6703	1.7497	1.8233
1.00	0.3498	0.6137	0.8247	1.0000	1.1498	1.2804	1.3961	1.5000	1.5942	1.6804	1.7598	1.8333

TABLE II

ERRORS OF x_2 CALCULATED BY METHOD I

n	α	x	y	x_1	x_2	$100\,(x_2 - x)/x$
0.25	0.5	0.700	0.6254	0.7653	0.700	0.0
0.25	0.5	1.000	0.9078	1.0487	1.000	0.0
0.25	1.0	0.900	0.6612	1.0110	0.901	0.1
0.25	1.0	1.000	0.7497	1.0995	1.001	0.1
6.00	0.5	1.000	0.1285	1.8874	1.221	22.1
6.00	0.5	2.000	0.6148	2.3737	2.023	1.2
6.00	0.5	2.100	0.6819	2.4408	2.119	0.9
6.00	0.5	3.000	1.3860	3.1449	3.002	0.1
6.00	1.0	2.000	0.2400	2.6900	2.127	6.4
6.00	1.0	2.600	0.5569	3.0069	2.629	1.1
6.00	1.0	2.900	0.6213	3.0713	2.722	0.8
6.00	1.0	3.000	0.8309	3.2809	3.010	0.3

	n											
	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00	5.25	5.50	5.75	6.00
.80	1.6791	1.7431	1.8034	1.8603	1.9141	1.9652	2.0138	2.0602	2.1045	2.1470	2.1877	2.2269
.81	1.6914	1.7555	1.8158	1.8727	1.9265	1.9776	2.0262	2.0726	2.1170	2.1594	2.2001	2.2393
.82	1.7036	1.7678	1.8280	1.8849	1.9388	1.9899	2.0385	2.0849	2.1292	2.1717	2.2124	2.2516
.83	1.7157	1.7798	1.8401	1.8970	1.9509	2.0020	2.0506	2.0970	2.1413	2.1838	2.2245	2.2637
.84	1.7277	1.7918	1.8521	1.9090	1.9629	2.0140	2.0626	2.1090	2.1533	2.1958	2.2365	2.2756
.85	1.7395	1.8036	1.8639	1.9208	1.9747	2.0258	2.0744	2.1208	2.1652	2.2076	2.2483	2.2875
.86	1.7511	1.8153	1.8756	1.9325	1.9864	2.0375	2.0861	2.1325	2.1768	2.2193	2.2600	2.2992
.87	1.7627	1.8269	1.8872	1.9441	1.9979	2.0490	2.0977	2.1441	2.1884	2.2309	2.2716	2.3107
.88	1.7741	1.8383	1.8986	1.9555	2.0094	2.0605	2.1091	2.1555	2.1998	2.2423	2.2830	2.3222
.89	1.7854	1.8496	1.9099	1.9668	2.0207	2.0718	2.1204	2.1668	2.2111	2.2536	2.2943	2.3335
.90	1.7966	1.8607	1.9211	1.9780	2.0318	2.0829	2.1316	2.1780	2.2223	2.2648	2.3055	2.3446
.91	1.8076	1.8718	1.9321	1.9890	2.0429	2.0940	2.1426	2.1890	2.2334	2.2758	2.3165	2.3557
.92	1.8185	1.8827	1.9430	2.0000	2.0538	2.1049	2.1536	2.2000	2.2443	2.2867	2.3275	2.3666
.93	1.8293	1.8935	1.9538	2.0108	2.0646	2.1157	2.1644	2.2108	2.2551	2.2976	2.3383	2.3774
.94	1.8400	1.9042	1.9645	2.0215	2.0753	2.1264	2.1751	2.2215	2.2658	2.3083	2.3490	2.3881
.95	1.8506	1.9148	1.9751	2.0320	2.0859	2.1370	2.1857	2.2320	2.2764	2.3188	2.3596	2.3987
.96	1.8611	1.9253	1.9856	2.0425	2.0964	2.1475	2.1961	2.2425	2.2868	2.3293	2.3700	2.4092
.97	1.8714	1.9356	1.9960	2.0529	2.1067	2.1578	2.2065	2.2529	2.2972	2.3397	2.3804	2.4195
.98	1.8817	1.9459	2.0062	2.0631	2.1170	2.1681	2.2167	2.2631	2.3075	2.3499	2.3907	2.4298
.99	1.8918	1.9560	2.0164	2.0733	2.1271	2.1783	2.2269	2.2733	2.3176	2.3601	2.4008	2.4399
.00	1.9019	1.9661	2.0264	2.0833	2.1372	2.1883	2.2369	2.2833	2.3277	2.3701	2.4109	2.4500

TABLE III

ERRORS OF x_2 CALCULATED BY METHOD 2

n	α	x	y	x_1	x_2	$100\,(x_2 - x)/x$
1.00	1.0	0.10	0.0048	0.08	0.102	2.0
1.00	1.0	0.10	0.0048	0.12	0.101	1.0
2.00	1.0	0.20	0.0023	0.18	0.206	3.0
2.00	1.0	0.20	0.0023	0.22	0.202	1.0
3.00	1.0	0.30	0.0014	0.28	0.301	0.3
3.00	1.0	0.30	0.0014	0.32	0.305	1.7
4.00	1.0	0.40	0.0011	0.38	0.400	0.0
4.00	1.0	0.40	0.0011	0.42	0.406	1.5
5.00	1.0	0.50	0.0009	0.48	0.505	1.0
5.00	1.0	0.50	0.0009	0.52	0.502	0.4
6.00	1.0	0.60	0.0009	0.58	0.608	1.3
6.00	1.0	0.60	0.0009	0.62	0.610	1.7

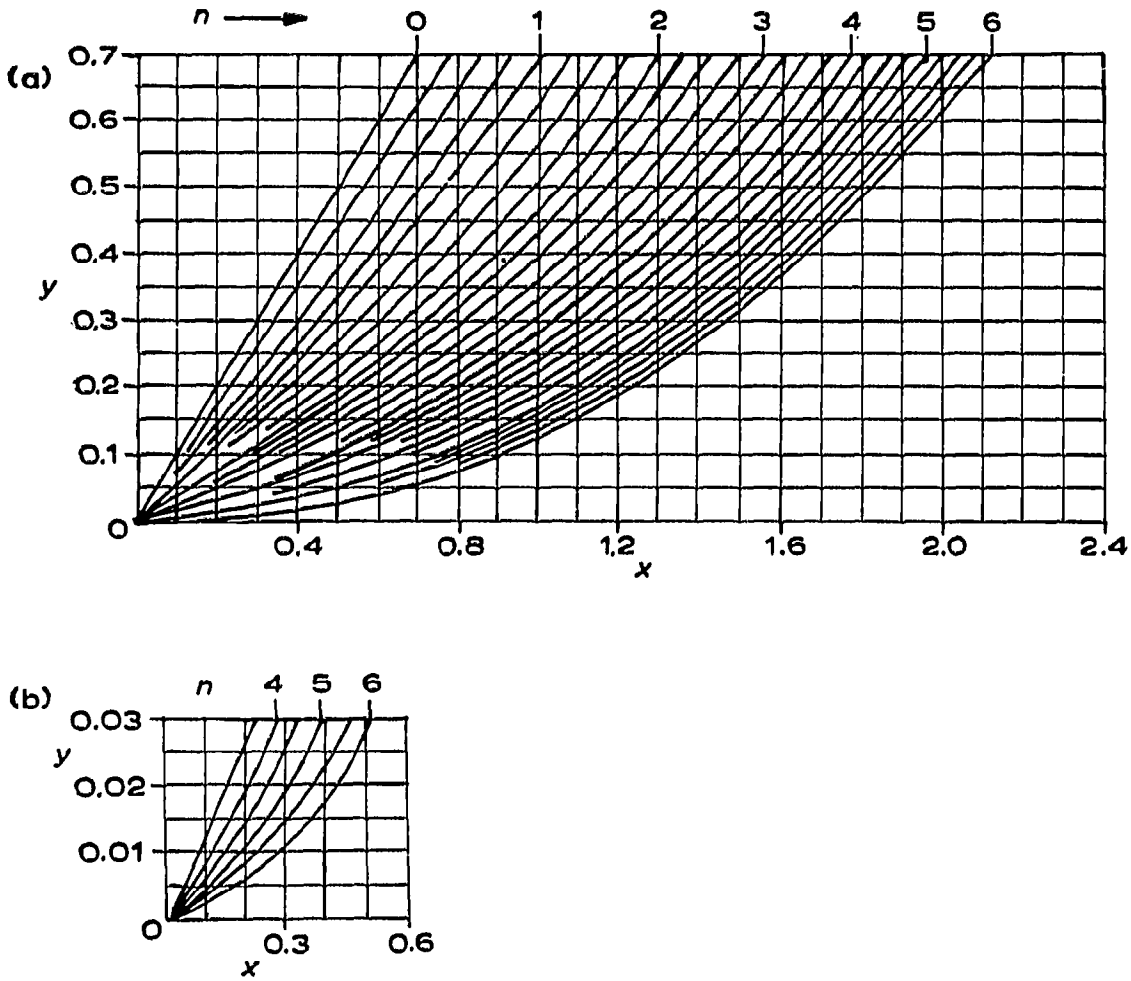


Fig. 2. Relation between x and y. (a) $\alpha = 0.5$; $x = 0 \sim 2.1$; $y = 0 \sim 0.7$; interval of $n = 0.25$. (b) $\alpha = 0.5$; $x = 0 \sim 0.5$; $y = 0 \sim 0.03$; interval of $n = 0.50$.

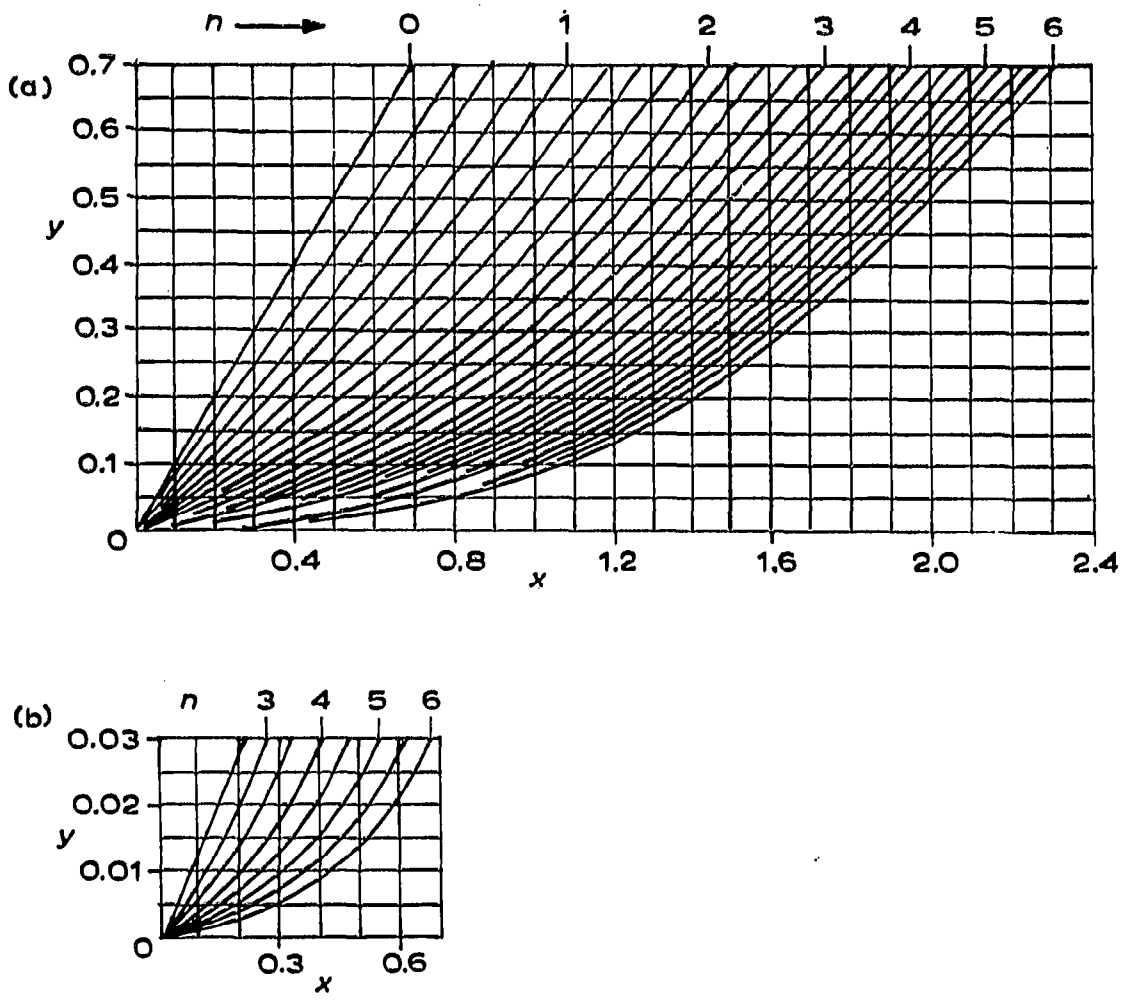
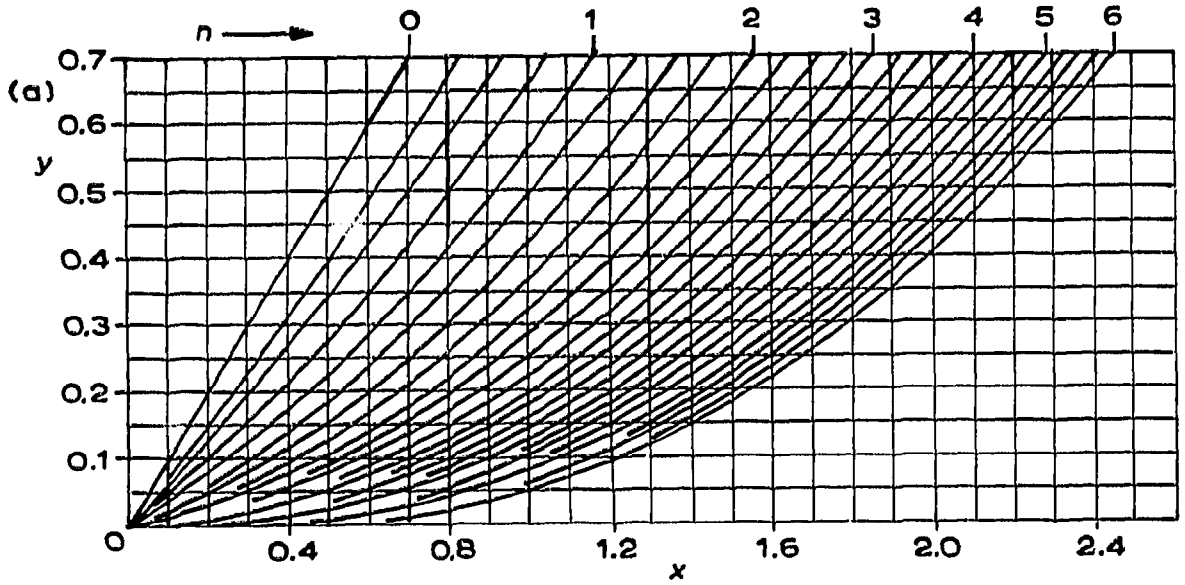


Fig. 3. Relation between x and y. (a) $\alpha = 0.6$; $x = 0 \sim 2.3$; $y = 0 \sim 0.7$; interval of $n = 0.25$. (b) $\alpha = 0.6$; $x = 0 \sim 0.7$; $y = 0 \sim 0.03$; interval of $n = 0.50$.



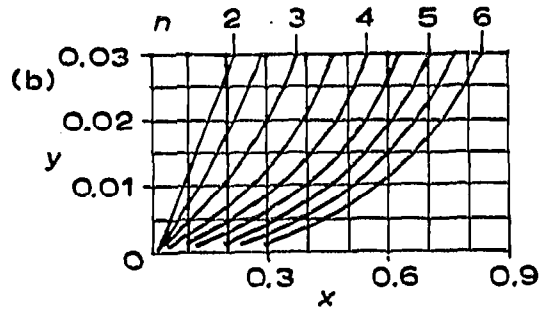


Fig. 4. Relation between x and y. (a) $\alpha = 0.7$; $x = 0 \sim 2.5$; $y = 0 \sim 0.7$; interval of $n = 0.25$. (b) $\alpha = 0.7$; $x = 0 \sim 0.8$; $y = 0 \sim 0.03$; interval of $n = 0.50$.

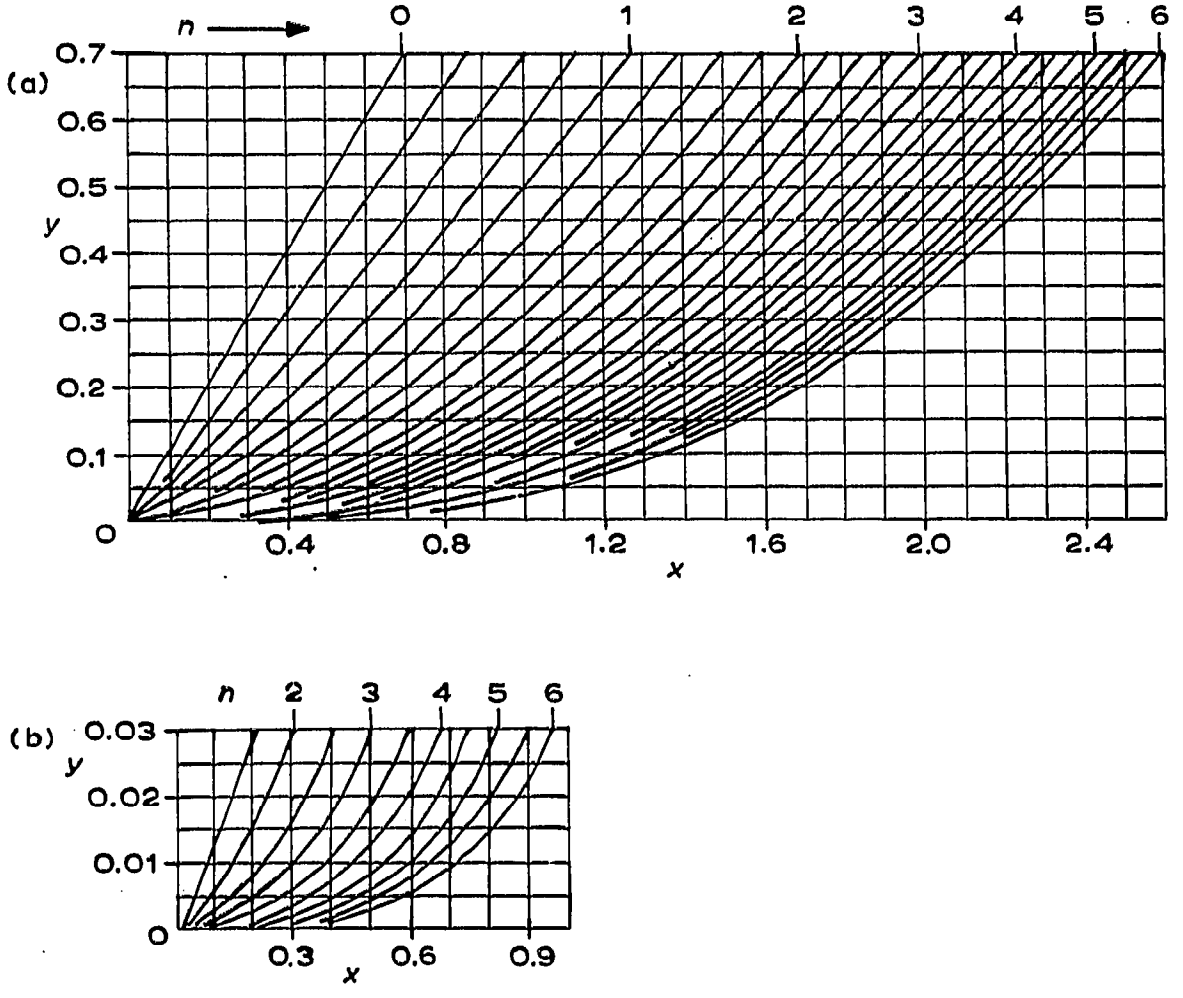


Fig. 5. Relation between x and y. (a) $\alpha = 0.8$; $x = 0 \sim 2.6$; $y = 0 \sim 0.7$; interval of $n = 0.25$. (b) $\alpha = 0.8$; $x = 0 \sim 1.0$; $y = 0 \sim 0.03$; interval of $n = 0.50$.

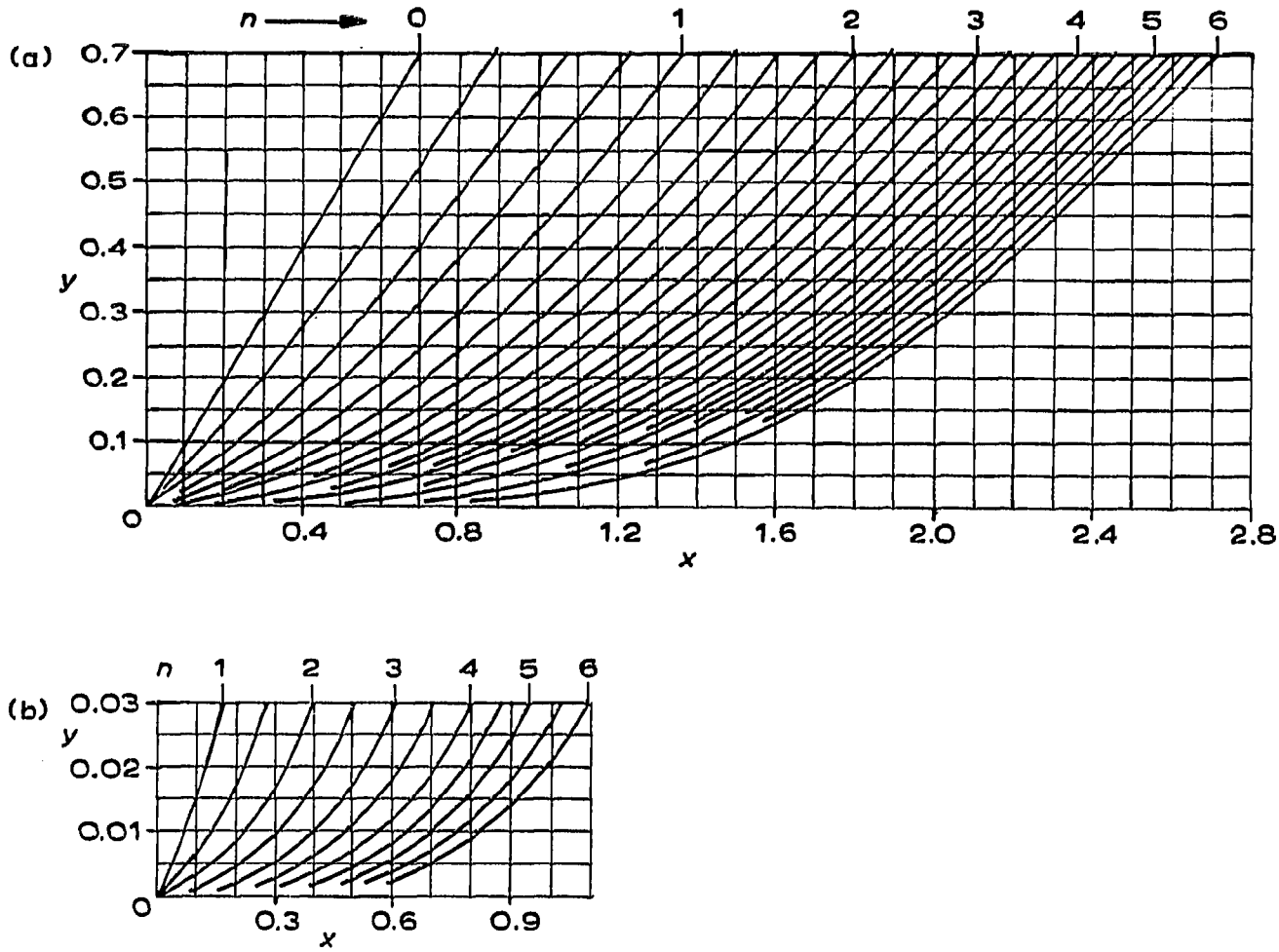


Fig. 6. Relation between x and y. (a) $\alpha = 0.9$; $x = 0 \sim 2.7$; $y = 0 \sim 0.7$; interval of $n = 0.25$. (b) $\alpha = 0.9$; $x = 0 \sim 1.1$; $y = 0 \sim 0.03$; interval of $n = 0.50$.

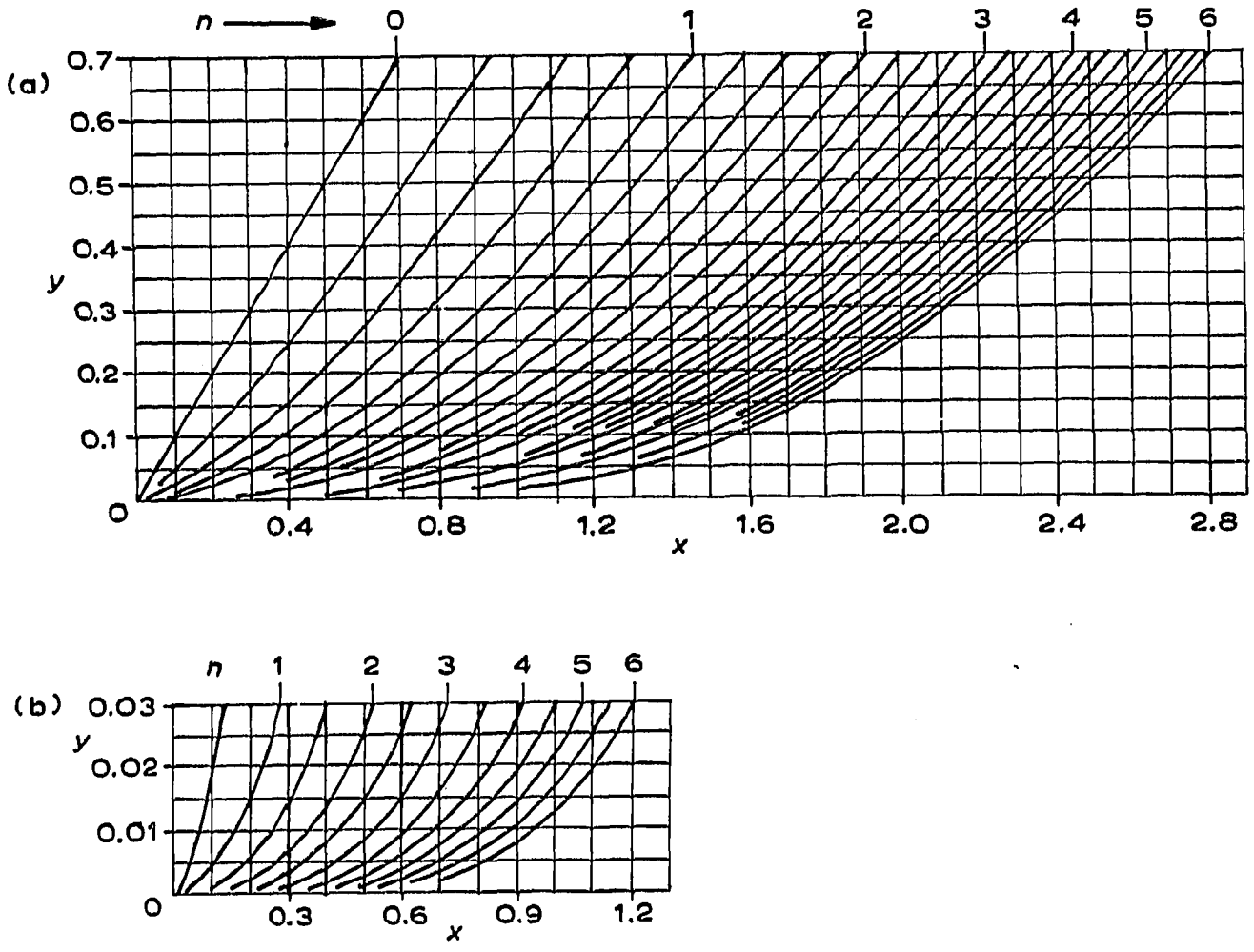


Fig. 7. Relation between x and y. (a) $\alpha = 1.0$; $x = 0 \sim 2.8$; $y = 0 \sim 0.7$; interval of $n = 0.25$. (b) $\alpha = 1.0$; $x = 0 \sim 1.2$; $y = 0 \sim 0.03$; interval of $n = 0.50$.

As has been shown in Table II, the errors for x_2 obtained by this method are always less than 1 %, when y is larger than 0.7. However, when y is smaller than 0.7, this method for calculating x_2 results in large errors, especially when n is large.

Method 2 ($y < 0.7$)

When y is smaller than 0.7, one should use another method for calculating the approximate value of x. The relations between x and y are illustrated graphically in Figs. 2–7 for each value of α. From these figures, one can obtain the first approximate value x_1 for an experimental value of y. By means of Newton's method, the second approximate value x_2 is given by the following equation:

$$x_2 = x_1 - [\{x_1 - f_n(\alpha) + f_n(\alpha e^{-x_1}) - y\}/(1 - \alpha e^{-x_1})^n] \quad (15)$$

Since one can read graphically the first approximate value x_1 with an accuracy of 0.02, the errors of x_2 are within 3 % for the cases shown in Table III.

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SUMMARY

The authors have derived equations for elution peak positions in gradient elution chromatography generally applicable to ions whose mean charge is n_o, $n_o + (1/4)$, $n_o + (1/2)$, or $n_o + (3/4)$, where n_o is an integer. Practical and convenient methods are proposed for calculating the approximate values of elution peak positions.

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