THIS BOOK BELONGS TO

Dr. V. S. Ananthanarayanan
422 Winthrop Drive
Ithaca, N. Y. 14850

CLASS OF

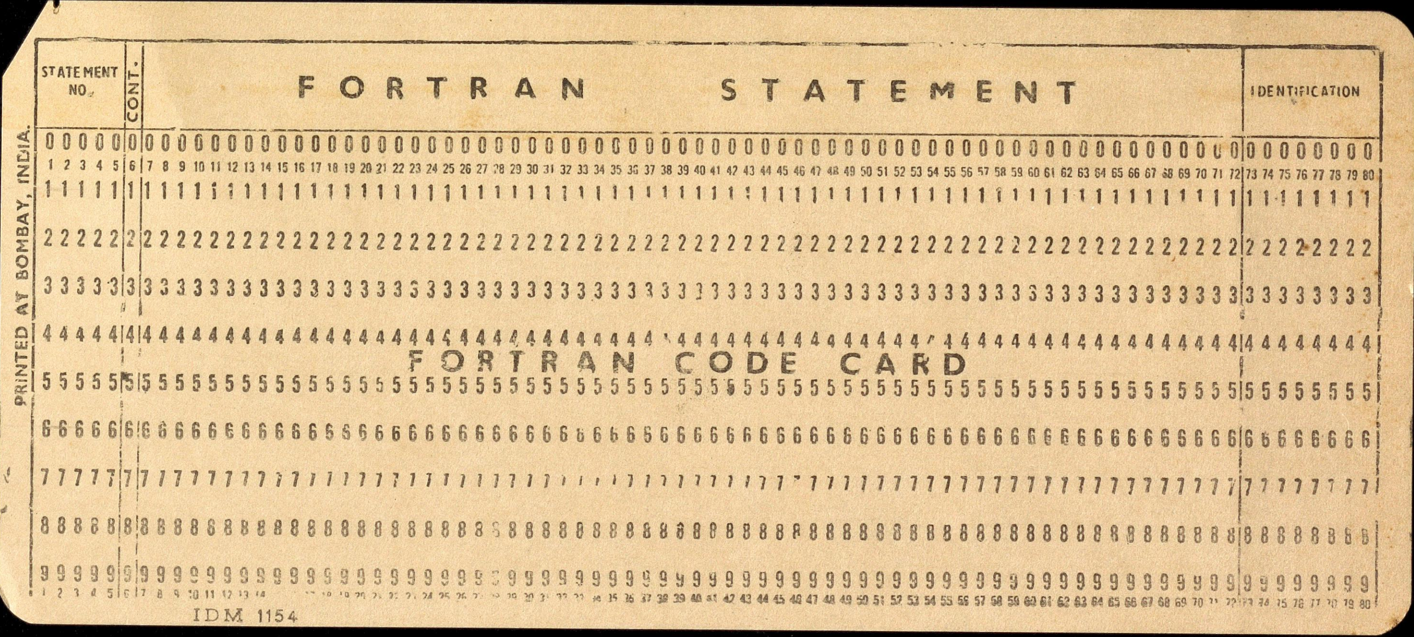
To

Joshi

from

Anantu

23/12



PRINTED AT BOMBAY, INDIA.

STATEMENT NO.

CONT.

F O R T R A N   S T A T E M E N T

IDENTIFICATION

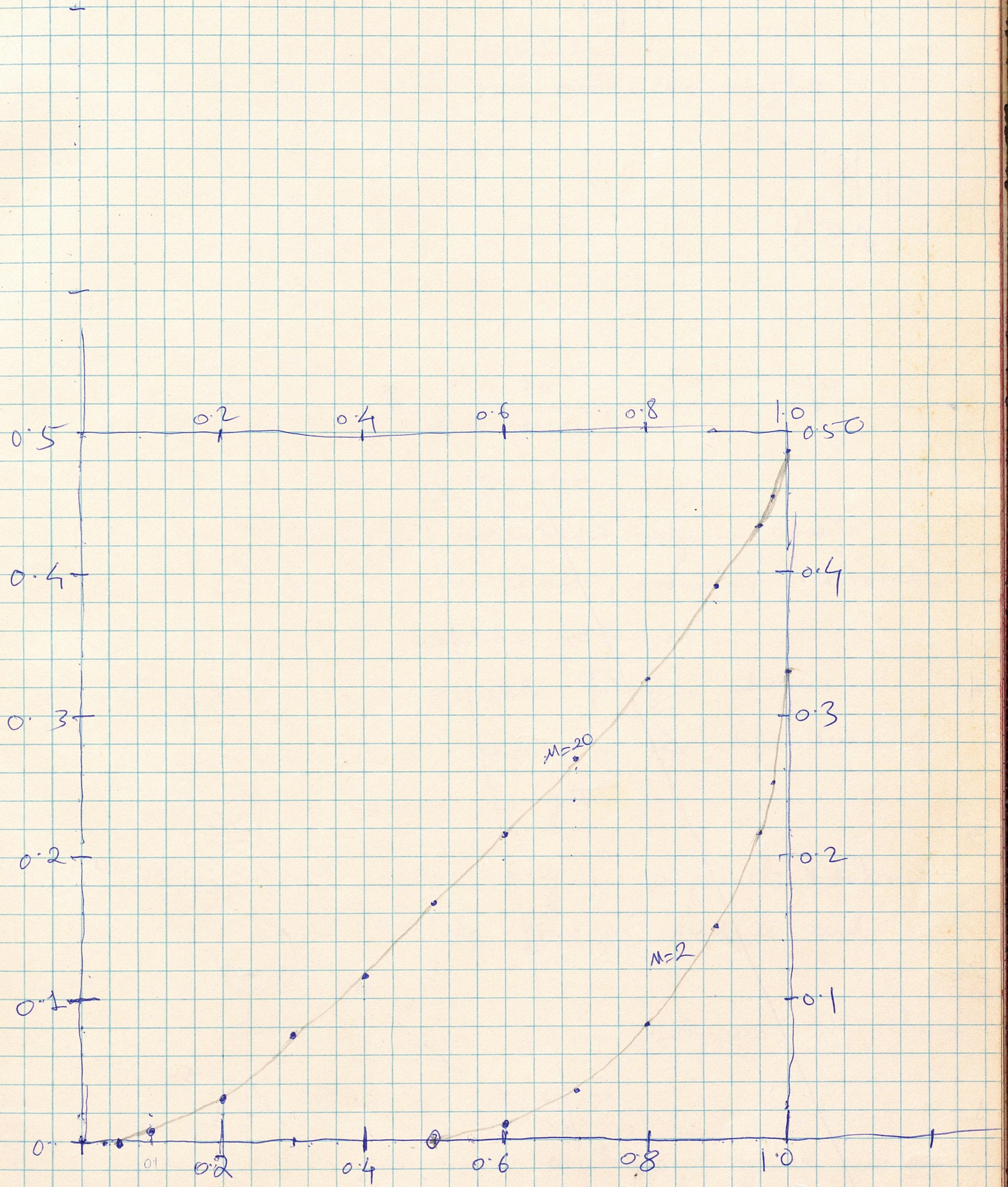
```
00000|0|000000000000000000000000000000000000000000000000000000000000000000|00000000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80
11111|1|111111111111111111111111111111111111111111111111111111111111111111|11111111
22222|2|222222222222222222222222222222222222222222222222222222222222222222|22222222
33333|3|333333333333333333333333333333333333333333333333333333333333333333|33333333
44444|4|444444444444444444444444444444444444444444444444444444444444444444|44444444
55555|5|555555555555555555555555555555555555555555555555555555555555555555|55555555
66666|6|666666666666666666666666666666666666666666666666666666666666666666|66666666
77777|7|777777777777777777777777777777777777777777777777777777777777777777|77777777
88888|8|888888888888888888888888888888888888888888888888888888888888888888|88888888
99999|9|999999999999999999999999999999999999999999999999999999999999999999|99999999
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80
```

FORTRAN CODE CARD

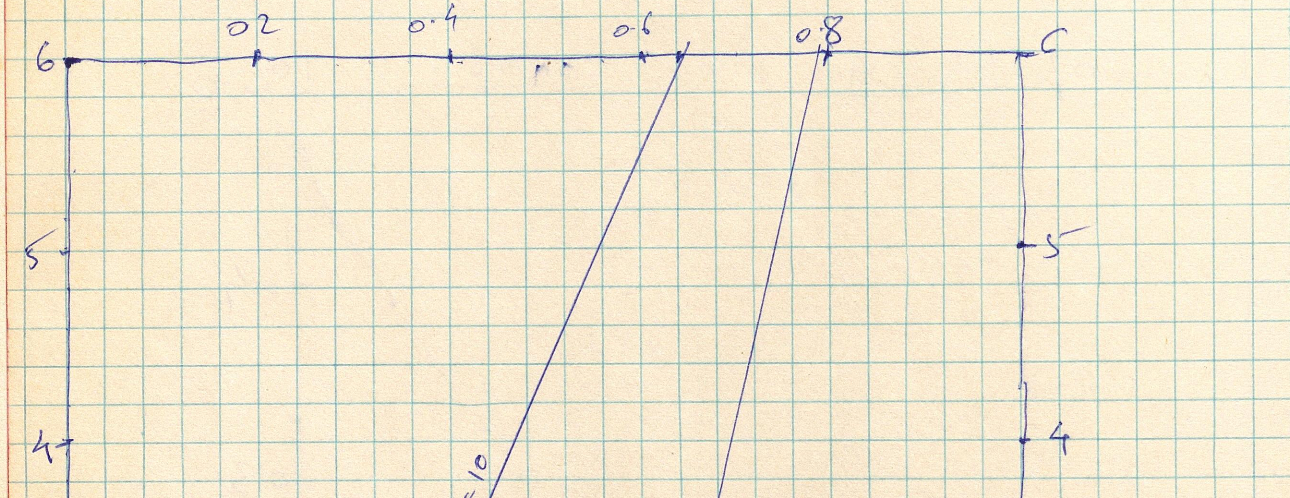
IDM 1154

31/1/85

N=3
M=20



3/2/85
n=4


0.2
0.4
0.6
0.8
6
6
5
4
3
2
1
5
4
3
3
2
1
0
M=10
M=2
ΣC=1, M=10
ΣC=1, M=2
0
M=10
0.2
0.4
M=2
0.6
0.8
1.0

Physical Chemistry of Macromolecules C. Tanford.

ch. 3: Statistics of Linear Polymers.

Molecular wt. averages and Distributions

B. a) degree of polymerization and molecular weight

b) Molecular wt. distributions

c) fractionation of polymers

d) M-wt. average

e)

Average dimensions

a) Average end to end distance

b) Average radius of gyration

c) The completely unrestricted polymer chain

d) The polymethylene chain, assuming free rotation

e) The effect of restricted rotation

f) Other simple flexible polymer chains

g) general ideal expression for dependence of h_{av} on chain length

h) Interaction betw. polymer segments & solvent molecules and its effect on end to end distance

i) completely rigid chain polymers. Stiff chain

j) The radius of gyration

k) Application to heterogeneous polymer mixtures

l) Non-linear polymers

10. Distribution functions for Polymer Configuration

a) The problem of random flight

b) Distribution function for end to end distances

c) Distribution of segments relative to centre of mass

Important relations

$$M_x = x M_0$$

x → no. of repeating units or degree of polymerization

M_0 → residue (unit) molecular wt

no. average DP ~~deg. of~~

$$\bar{x}_n = N_0 / N_0(1-p)$$

p → extent of reaction

$$= \frac{1}{1-p}$$

$$M_n = \sum N_i M_i / \sum N_i = \sum \overset{\text{mole fraction}}{X_i} M_i$$

$$M = M_0 \sum_{x=1}^{\infty} x X_x$$

$$\bar{x}_n = \sum_{x=1}^{\infty} x N_x / \sum_{x=1}^{\infty} N_x = \sum_{x=1}^{\infty} x X_x$$

$$\bar{M}_w = \sum \overset{\text{gms/cc}}{g_i} M_i / \sum g_i = \sum \overset{\text{wt fraction}}{W_i} M_i$$

$$= \sum_i X_i M_i^2 / \sum_i X_i$$

$$\bar{x}_w = \sum_{x=1}^{\infty} x W_x$$

Average end to end distance (~~e.e.d~~).

$$h_{av} = \left(\overline{h^2}\right)^{1/2}$$ distance betn. ends

$$= \left(\overline{\underline{h} \cdot \underline{h}}\right)^{1/2}$$

Ave. radius of gyration: $R^2 = \sum_i m_i r_i^2 \Big/ \sum_i m_i$

(square root of the wt. average r_i^2 for all mass elements)

$$R_G = \left(\overline{R^2}\right)^{1/2} = \left(\overline{\sum_i m_i r_i^2 \Big/ \sum m_i}\right)^{1/2}$$

$$= \left(\sum_i m_i \overline{r_i^2} \Big/ \sum m_i\right)^{1/2}$$

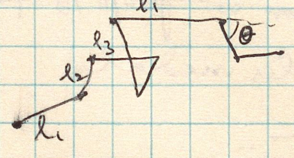
$$= \left(\sum_i \overline{r_i^2} \Big/ \sigma\right)^{1/2}$$

where σ is total no of mass elements per chain

(if mass elements are identical

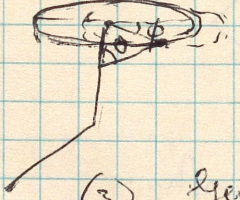
ie $\sigma = \dfrac{\text{total mass } (\sum m_i)}{\text{mass of element } (m_i)}$)

① For completely unrestricted polymer chain



$$\overline{h^2} = \sum_{i=1}^{\sigma} l_i^2 = \sigma \overline{l_i^2} = \sigma l_{av}^2$$

② Free rotation but fixed angle : polymethylene chain



$$\overline{h^2} \simeq \sigma l^2 \frac{1+\cos\theta}{1-\cos\theta} = 2.00\,\sigma l^2$$

for polymethylene ($\cos\theta = 0.333$)

(3) General ideal expression for h_{av}

$$\overline{h^2} = \beta^2 \sigma$$

β ↳ const. characteristic of the nature of polymer

$\beta = 2^{1/2} l_{av}$ for polymethylene

$\approx 3 l_{av}$ for synthetic org. polymers

β / l_{av} is measure of stiffness of polymer chain

4) In the case of interaction with solvent:

$$\overline{h^2} = \alpha^2 \overline{h_0^2} = \alpha^2 \beta^2 \sigma \quad (= \alpha^2 \beta^2 M/M_0)$$

$\alpha > 1$ for good solvent

< 1 for poor "

$= 1$ for ideal solvent

~~α = constant~~

max. variation with M α = (constant) $M^{0.1}$ ie $\overline{h^2} \propto \beta^2 M^{0.6}$

5) Completely rigid chains. Stiff chains.

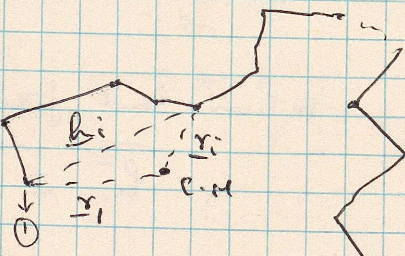
h_{av} = (const) $M^{0.5-0.6}$ for flexible chain

= (const) $M^{1.0}$ for stiff chain

~~α incr is propl to M~~

= (const) $M^{0.6-0.99}$ for intermediates

6) Radius of gyration



$$\underline{R_G^2 = \overline{R^2} = \overline{h^2}/6}$$ for ideal soln.

Distribution functions.

$$W(h)\,dh = 4\pi\left(\frac{3}{2\pi\sigma^2 L^2}\right)^{3/2} e^{-3h^2/2\sigma L^2}\, h^2\,dh$$

$$W(h)\,dh = 4\pi\left(\frac{3}{2\pi\overline{h^2}}\right)^{3/2} e^{-3h^2/2\overline{h^2}}\cdot h^2\,dh$$

Theories of the helix-coil Transitions for Random Copolymers

Poland + Scheraga.

Important Points

— Physical insight into the behavior of a random copolymer in the transition region provided!

— Shown that an important feature detg. the shape of the transition curve is the variation in composition over the correlation length.

Model: Monomers A & B ; overall composition of A is f_A ; Random, unknown occurrence of A + B
only h + c states.

th Temperature of Some Organic Solvents

itical Tables Vol. 3, p 28-30, 1928

ters of the equation

$) + 10^{-6}\beta(t-t_s)^2 + 10^{-9}\gamma$

subscript in

has not been

arrived at

this and

PHYSICO-CHEMICAL
AND
BIOCHEMICAL
DATA

5

to 40

0 to 100

.0002 0 to 74

+10.9 0.001 0 to 136

---

086 J. Ind. Chem Soc 43, 179 (1966)

5 + 0.0009647 (T-25)

etween 30 + 90°C

Equation is VSA's from plot of d vs T.

.0014
[illegible]10

1.2825
.041
1.261
.007

DCB d 25

DCB 70

0.0014×70
.0980

1.283
.098
185

12/12/74

$\boxed{\text{CRC III}}$ Density change with Temperature of Some Organic Solvents

From International Critical Tables Vol. 3, p. 28-30, 1928

Table below gives the parameters of the equation

$$d_t = [d_s + 10^{-3}\alpha(t-t_s) + 10^{-6}\beta(t-t_s)^2 + 10^{-9}\gamma(t-t_s)^3] \pm 10^{-4}\Delta$$

Except when indicated by giving t_s as a subscript in column 3 $t_s = 0°$. Where density at 0°c has not been determined a value has in many cases been arrived at by extrapolation. Such values are given in parenthesis and are given as a basis for calculation only.

Formula	Name	d_s	α	β	γ	Limit of error	Range °c
CCl_4	Carbon tetrachloride	1.63255 ~~1.435~~	-1.9110	-0.690	-	0.0002	0 to 40
$CHCl_3$	Chloroform	1.52643	-1.8563	-0.5309	-8.81	0.0001	-53 to +55
CH_2O_2	Formic acid	1.2441	-1.221	+0.126	-	0.002	0 to 40
$C_2H_2Cl_2O_2$	Dichloroacetic acid	(1.5919)	-1.375	-	-	0.002	0 to 100
$C_2H_4Cl_2$	Ethylene chloride	1.28248	-1.4217	-0.933	+2.29	0.0002	0 to 74
$C_2H_6O_2$	ethylene Glycol	1.1257	-0.5713	-2.766	+10.9	0.001	0 to 136

~~DMF~~

DMF : Data of Gopal + Rizvi J. Ind. Chem Soc 43, 179 (1966)

$$d_t = 0.9445 + 0.0009647\,(T-25)$$

~~[illegible]~~ between 30 + 90°c

Check → Authors give only d at diff. T's.

~~E th mult of To~~

Equation is VSA's from plot of d vs T.

From Glasstone 'Text book of Physical chemistry'

p.524

Electric moment $m = \alpha F$, α - polarizability F - Electric field strength

$I = m n$ $n \rightarrow$ no of molecules/cc

From Electrostatics $E_0 = E + 4\pi I$ or $(\epsilon - 1)E = 4\pi I$

(ϵ is dielectric const $= \mathbf{E}/E$)

$F = E_0 + \frac{4}{3}\pi I - 4\pi I$ for moles in spherical cavity

$= \left(\frac{\epsilon+2}{3}\right)E$

$\therefore \frac{\epsilon-1}{\epsilon+2} = 4/3\pi n \alpha$

$n = \frac{N\rho}{M}$ ρ is density

$\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha = P$

or $P = \frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho}$ molar polarization

$P_E \cancel{=} = \frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_E = R$ $(\epsilon = n_\infty^2)$

$P_E \rightarrow$ Electron poln R in the visible region, away from absorption band

p.519 Lorentz & Lorenz formula:

$[R] = \frac{n^2-1}{n^2+2}\frac{M}{\rho}$ from electromag. & wave theories of light

where R is molecular refraction. (or molar refraction)
R is both additive & constitutive

Sample calculation for H_2O: ~~n 1.334~~ Data: $n_D^{0°} = 1.3340$ $n_D^{70°} = 1.3252$

$\frac{[R]^{0°}}{M} = \frac{(1.334)^2-1}{(1.334)^2+2}\cdot\frac{1}{0.99987}$ $\rho^{0°} = 0.99987$ $\rho^{70} = 0.97781$

R.I. - density relation for CsCl solns given by

$\rho^{25°C} = (10.8601 \times R.I.^{D\text{ line }25°}) - 13.4974$, J. Phys chem 65, 1138 (1961)

12/12/74

Refractive Index Data

CRC Handbook ^{1968} gives R.I. dispersion $^{\text{p. J-240}}$ for CCl_4, Chloroethanol, $CHCl_3$, Cyclohexane, DCA, DMF, p-dioxane, EDC, Ethylene glycol, glycol-water (1:1), formamide, formic acid, furan, hydrazine, methylene chloride, 8M urea.

Concn dependence of R.I. for, LiBr, NaCl, urea solns. J238, 239 GuHCl, J241

CRC II Refractive Index Change with Temperature

Check c orig. ref.

Ethanol: Data of Hall & Payne, Phys Rev 1922, 20, 249.
given by J.R. Partington, An Adv. Treatise on Physical chem, IV, p.30, 1953 (Longmans)

$$\cancel{n_{EtOH}} = n = 1.3625 - 10^{-6}\left[404(t-15) + 0.22(t-15)^2 + 0.0075(t-15)^3\right]$$

12/12/74 → (Also see Hawkes & Astheimer J Opt Soc. Amer. 1948 38, 617, 804)
(~~Seen:~~ not for EtOH but H_2O

CRC XV

Chemical Resistance and other properties

(a) Millipore filter Copy pp. 1A050 & 6A010, 6A011 of Catalog of Millipore

(b) Ultracentrifuge centerpieces.

[Three types of center pieces materials are available use with for ~~the~~ Beckman Model E ultracentrifuge.

~~The~~ For use with the Beckman Model E ultracentrifuge, the Centrepieces are offered in three materials – Epon (Regd. trade mark of Shell Chemical Corp.), Kel-F (Registered trade mark of 3M Company) and aluminium. The materials vary in chemical resistance, temperature tolerance and strength. Configuration also affects the strength of the Centrepiece as reflected in the maximum speeds of recommended in the chart given below]

~~Chemical Resistance and other properties of~~ ~~analytical ultracentrifuge centrepieces~~
~~Centrepiece materials~~

~~(registered trademark of 3M Company)~~

Kel-F : Kel-F is a trifluorochloroethylene polymer. It has a durometer hardness of 80 (D scale), does not absorb water and is not affected by sunlight. The chlorine constitutes exceptional rigidity of the material, while the fluorine is responsible for its chemical inertness and zero moisture absorption. Because Kel-F is chemically inert, it will withstand exposures to strong acids and alkalies and to most organic solvents.

Kel-F centrepieces are recommended for biological materials — when non-aqueous solvents are to be used or when the pH of the solution falls outside the range tolerated by the Epon centrepiece (see below). Notable exceptions are highly halogenated and aromatic compounds.

If Kel-F absorbs certain highly halogenated and aromatic compounds, it will swell slightly. Consequently, when using a Kel-F centrepiece with these materials, rinse it immediately after run with distilled water. The following is a partial list of materials that will cause a weight change in Kel-F of 1% or more in seven days at 25°C.

Chlorine ---	12.3%
Diethylamine ---	1.9%
Ethyl acetate ---	1.2%
Ethyl ether ---	3.8%
Ethyl propionate -	1.0%
Freon 113	1.3
Furan	2.4
Methyl acetate	1.0
Methylal	1.3
Methyl ether	6.4
Methyl propionate	1.4
Trichloroethylene	2.3

High speeds may cause a slight distortion in Kel-F centre pieces; the distortion may lead to convection in the cell. Generally, this distortion is negligible but becomes permanent and significant after the centrepiece has been used in about 100 runs at maximum speed.

The maximum operating speed of Kel-F centrepiece varies as follows; for single sectors - maximum speed of rotor, for double sectors - 60,000 rpm, ~~in except~~ for 6-channel equilibrium ~~centrepiece~~ - 20,000 rpm and for fixed position — 30,000 rpm. The maximum operating temperature for Kel-F centrepiece is 40°C.

ALUMINUM

Filled-Epon ~~centrepiece~~. Filled-Epon (registered trademark of Shell Chemical Corporation) centrepieces are made from an ~~exp~~ epoxy resin with a filler consisting of either a powdered alumin~~ium~~ (or powdered charcoal). The ~~filler~~ aluminium filler ~~[illegible]~~ increases the strength and thermal conductivity of the Epon, while the powdered charcoal simply makes the epoxy opaque. ~~The filler increases the strength and thermal conductivity of~~ After machining, the alumin~~ium~~-filled Epon ~~the~~ centrepieces are subjected to a passivation process in which they are soaked in a 20% solution of sodium hydroxide. This process removes aluminium particles from the centrepiece surfaces. However, there is still a possibility of ~~the~~ alumini~~um~~ ions contaminating the sample—particularly after repeated use of the centrepieces, ~~To avoid this,~~

If this possibility can affect the results of an experiment, or if results suggest that it is having an effect, charcoal-filled Epon centrepieces should be used.

Filled-Epon centrepieces are used for aqueous solutions in the pH range of 3 to 10. They are the most widely used and recommended for biological materials. ~~The Epon is mixed with either powdered aluminium~~ or powder

The water absorption of filled-Epon is negligible. Some reagents, however, may penetrate the centrepiece and soften it slightly. Generally, any softening effect can be eliminated by rinsing the centrepiece with distilled water after run, regardless of what material was run. The following chemicals cause excess softening of filled-Epon and should not be used with this centrepiece:

Acetic acid, glacial
Ammonium hydroxide (27%)
Chloroform
Diethylene triamine
Dimethyl. ~~sulfo~~ sulphoxide
Ethylene diamine
Formaldehyde (40%)
M-Cresol
N,N-dimethyl)formamide
Nitric acid (10%)
Phosphoric acid (85%)
Sulphuric acid (70%)
Tetrahydrofuran

The maximum operating speeds are: for single ~~sngle~~ sectors — maximum speed of rotor, for double sectors — 50,000 rpm, for single-sector capillary — 60,000 rpm, for 6-channel equilibrium — 48,000 rpm and for interference wedges — 44,000 rpm. The maximum operating temperature is 40°C.

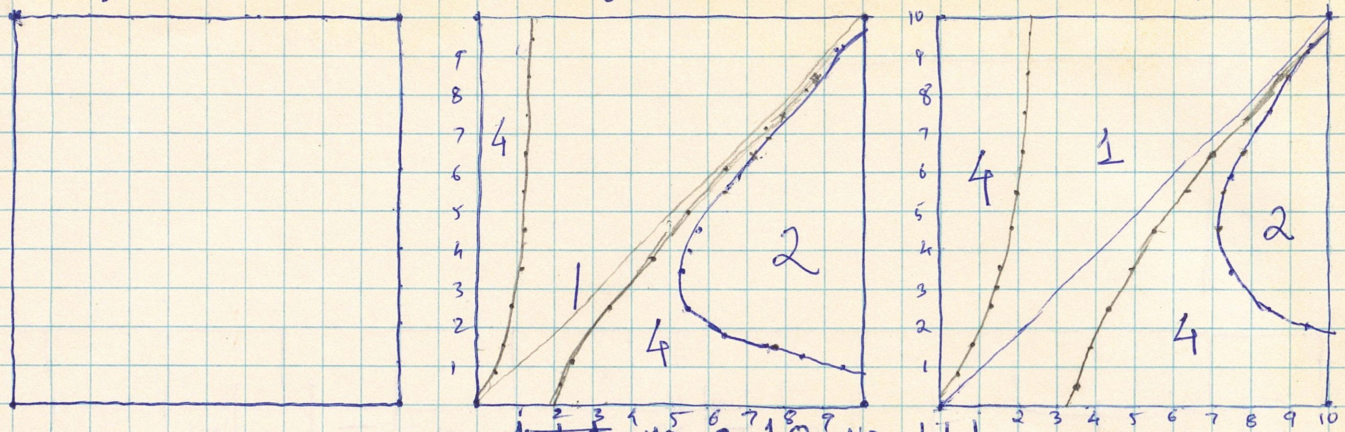
Aluminum Aluminum ~~of~~ is the strongest of the centrepiece materials, has the best resistance to temperature and has the longest life expectancy. Aluminum centrepieces are recommended primarily for non-biological materials and for high temperature work. ~~Standard single~~ Solutions in aluminum centrepieces must be kept at ~~the~~ neutral pH range, and some of the organic solvents that plastics do not tolerate can be used. For protection against corrosion, each aluminum centrepiece is anodized. The hard, anodized surface permits ~~the~~ use of aluminum centrepieces with a wide variety of materials. When handling these centrepieces, care must be taken not to scratch the anodized surface, for corrosion can begin in the ~~scratches~~ ~~scat~~ scratches on the finish.

Table I A classifies the groups of chemicals according to their effect on aluminum centrepieces while Table IB is a partial list of individual chemicals corrosive to aluminum centrepiece,

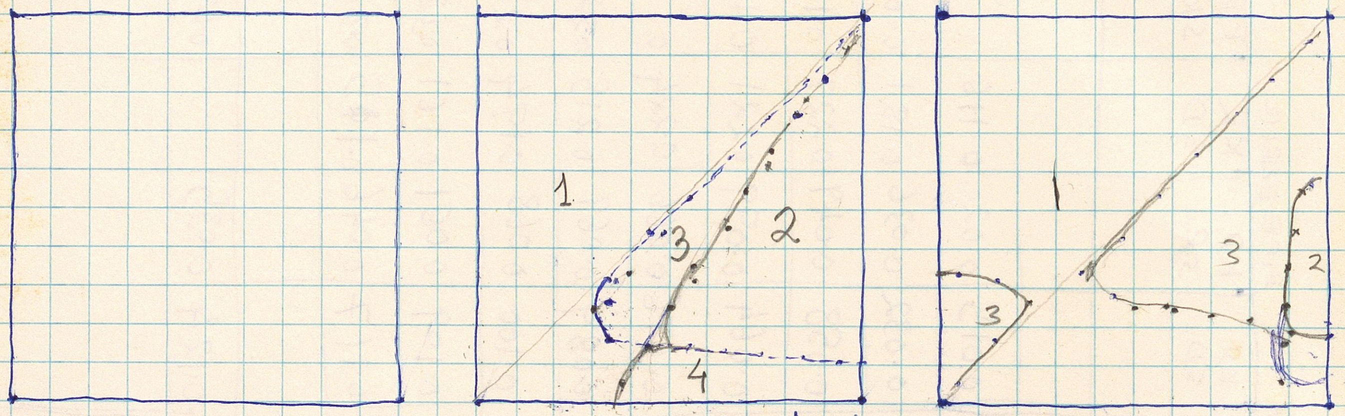
(Copy Tables 2D & 2E from Beckman booklet p. 29.)

	~~UPPER~~ LOWER LIMIT				UPPER LIMIT				DIFFERENCE			
d	KD SD	KD SR	KR SD	KR SR	KD SD	KD SR	KR SD	KR SR	KD SD	KD SR	KR SD	KR SR
0.10	0.0271	0.02	0	0.019	0.042	0.046	0.116	0.055	0.015	0.02	0.116	
0.20	0.0538	0.047	0	0.019	0.086	0.083	0.181	0.089	0.032	0.036	0.181	0.07
0.30	0.0802	0.069	0	0.026	0.138	0.118	0.227	0.132	0.058	0.049	0.227	0.106
0.40	0.1061	0.092	0.039	0.033	0.170	0.151	0.262	0.177	0.064	0.059	0.221	0.144
0.50	0.1315	0.114	0.065	0.039	0.208	0.180	0.289	0.225	0.076	0.066	0.224	0.186
0.60	0.1564	0.136	0.098	0.045	0.245	0.205	0.313	0.274	0.089	0.069	0.215	0.229
0.70	0.1809	0.159	0.137	0.050	0.281	0.227	0.331	0.327	0.100	0.068	0.194	0.277
0.80	0.2047	0.183	0.185	0.055	0.314	0.244	0.346	0.382	0.109	0.061	0.161	0.327
0.90	0.2278	0.209	0.242	0.059	0.345	0.255	0.357	0.440	0.117	0.046	0.115	0.381
0.99	0.2478	0.230		0.062	0.372	0.265		0.495	0.124	0.035		0.433

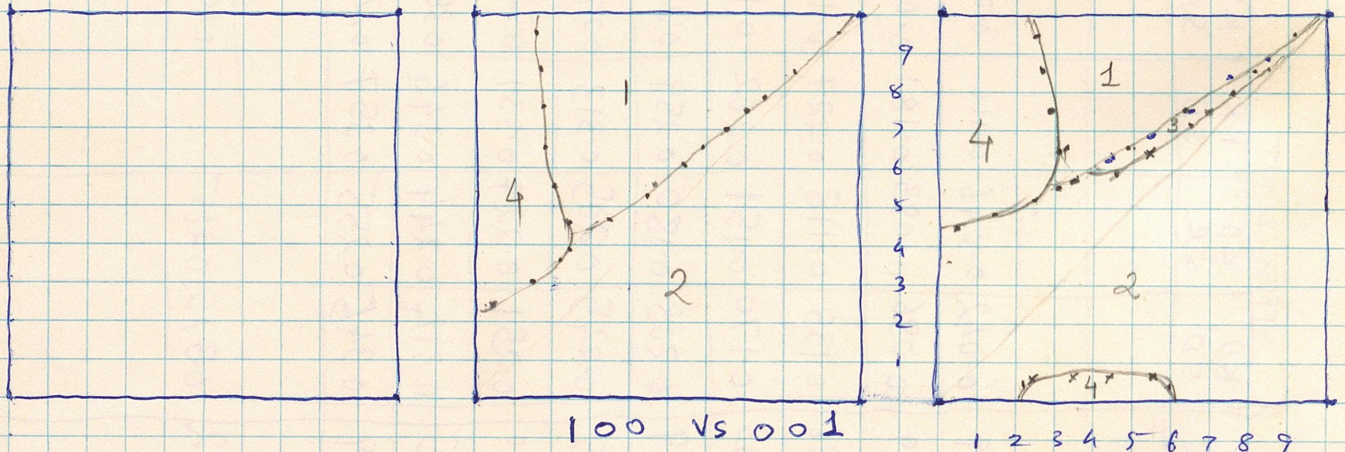
d=0·10 d=0·50 d=0·90



~~111 vs~~ 010 vs 111

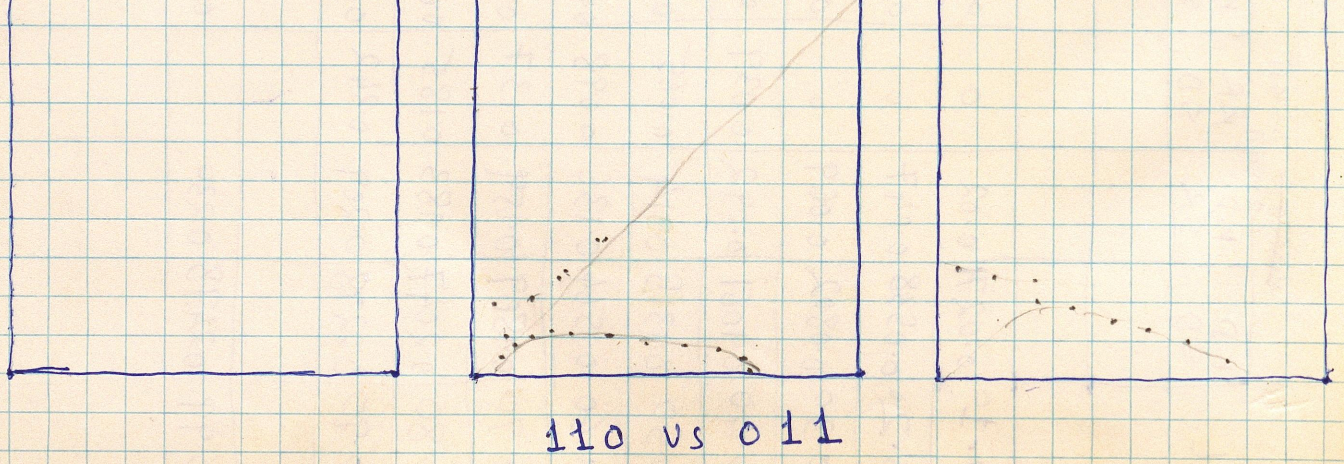


000 vs 101



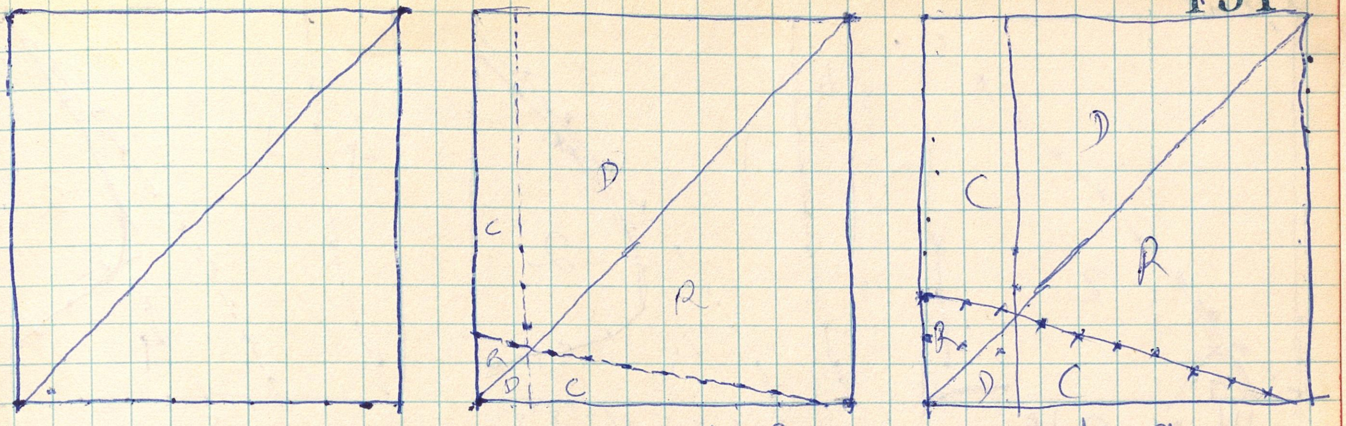
100 vs 001

1 2 3 4 5 6 7 8 9



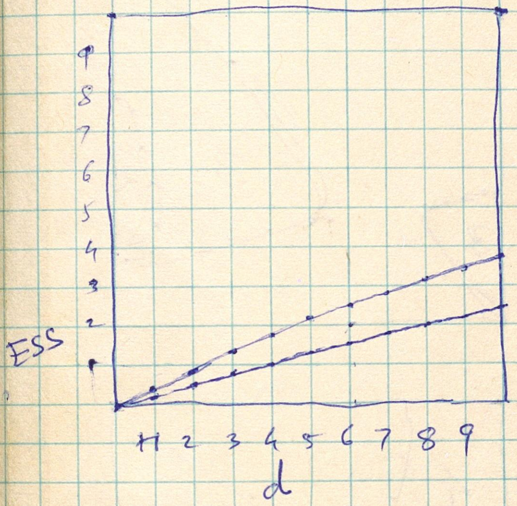
110 vs 011

20.2.84

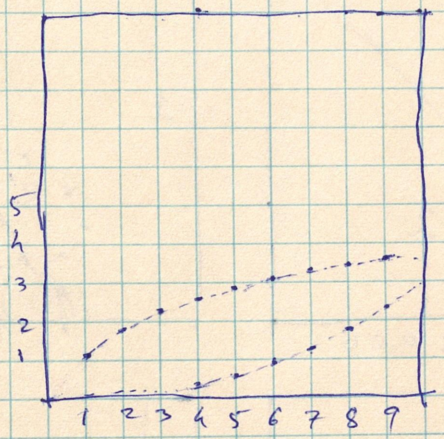


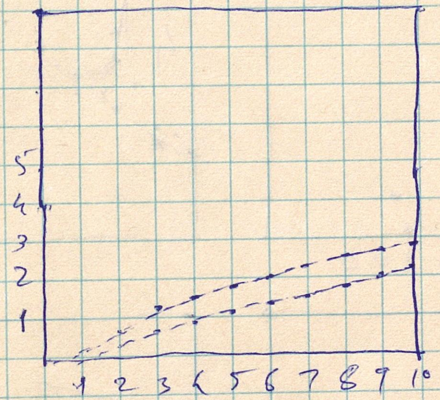
d=0.1 2,1,1 vs 2,1,0 d=0.5 d=0.9

010 vs 111



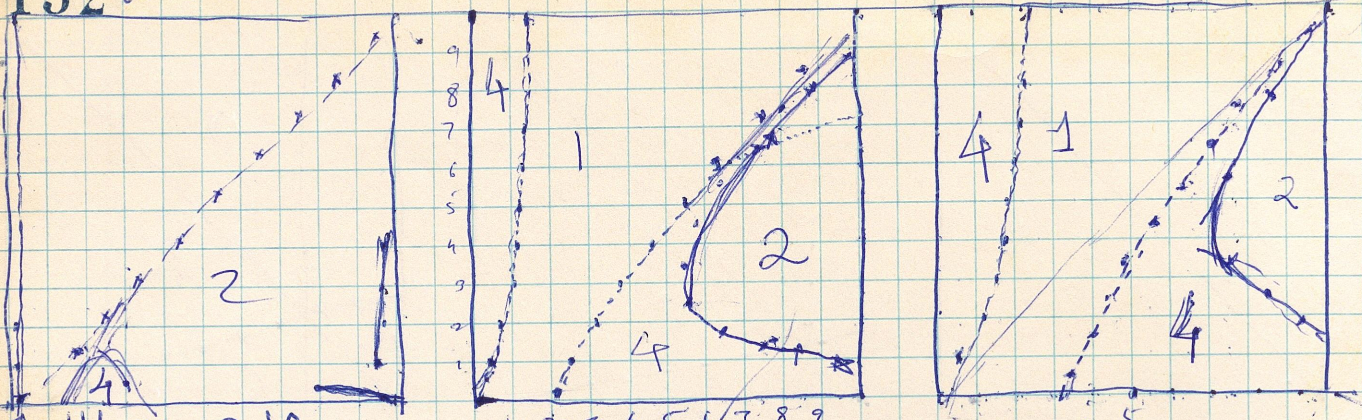
000 vs 101



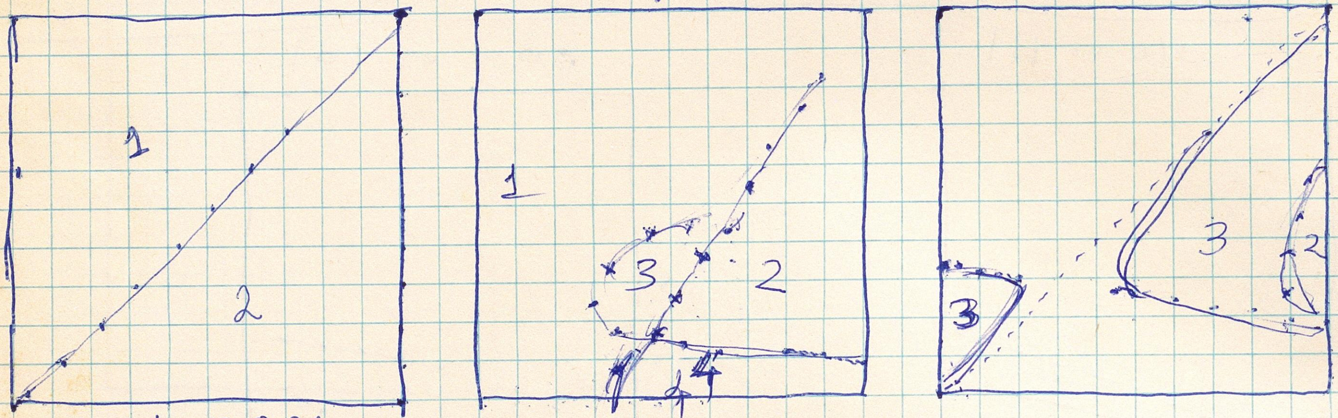


011 vs 110

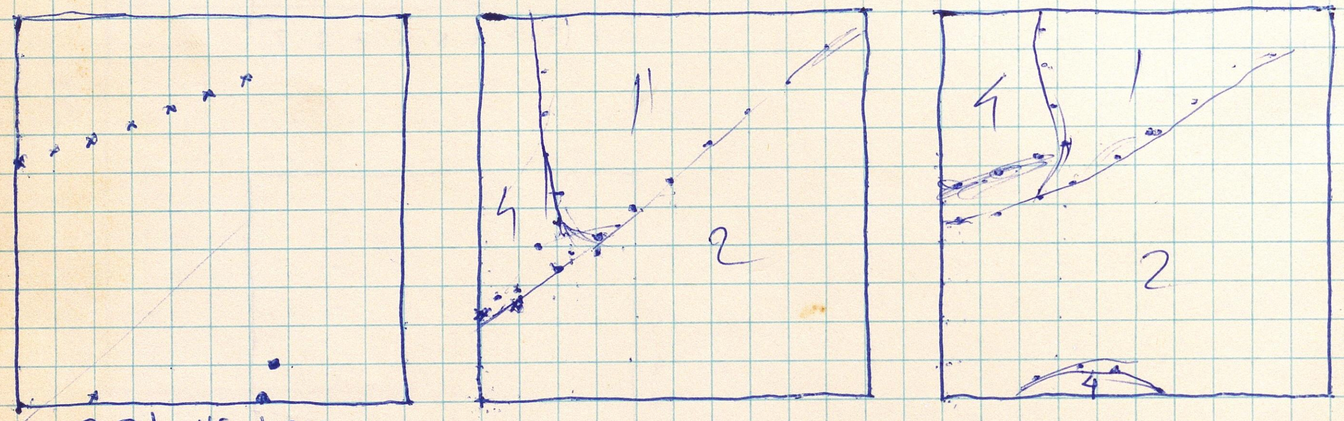
d=0.1 d=0.5 d=0.9



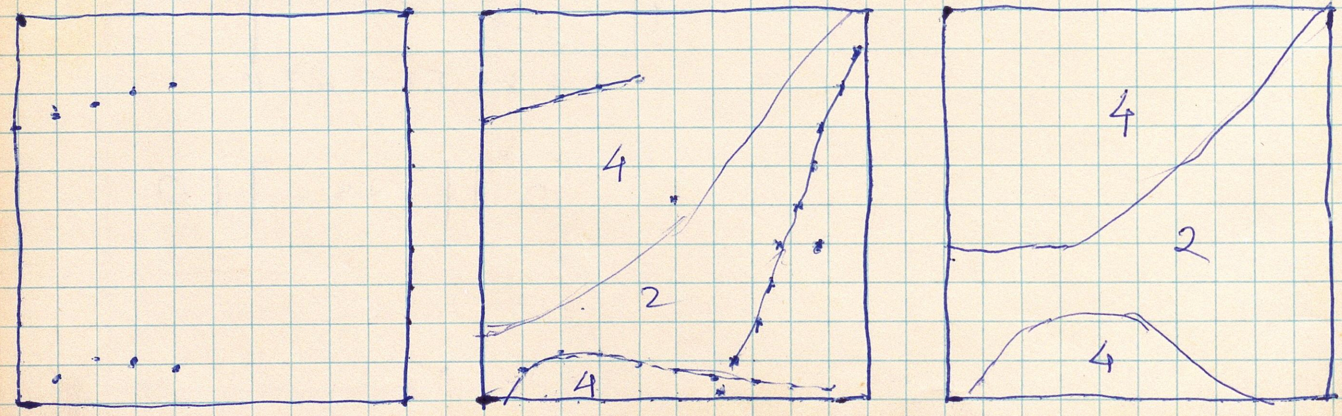
111 vs 010



1,0,1 vs 000



001 vs 100



011 vs 110