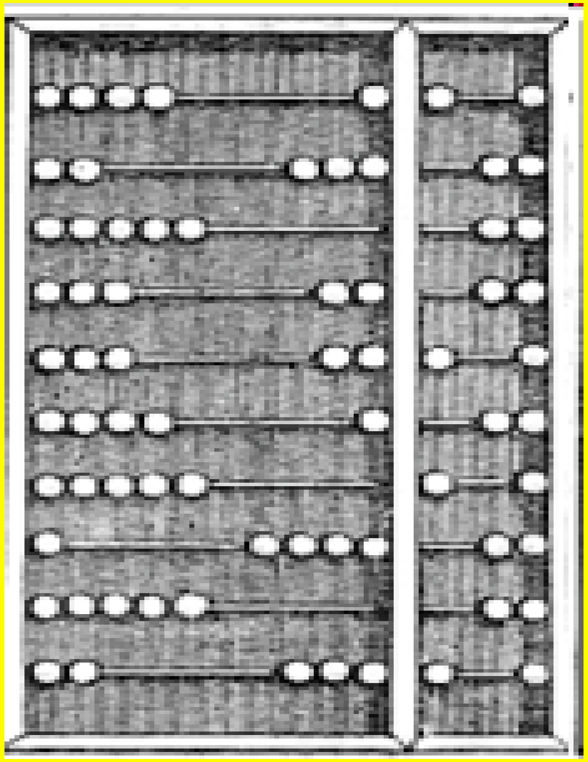
Computing before Computers

R.O. Gould

Sometime Reader in Chemistry

The University of Edinburgh

Notice in Computing Centre



In case of emergency, break glass

The Founders of Numbers in Crystallography

Nicolas Steno: 1638-1686

René Just Haüy: 1743-1822

Defining the Unit Cell 1

- **Steno's Law 1669:**

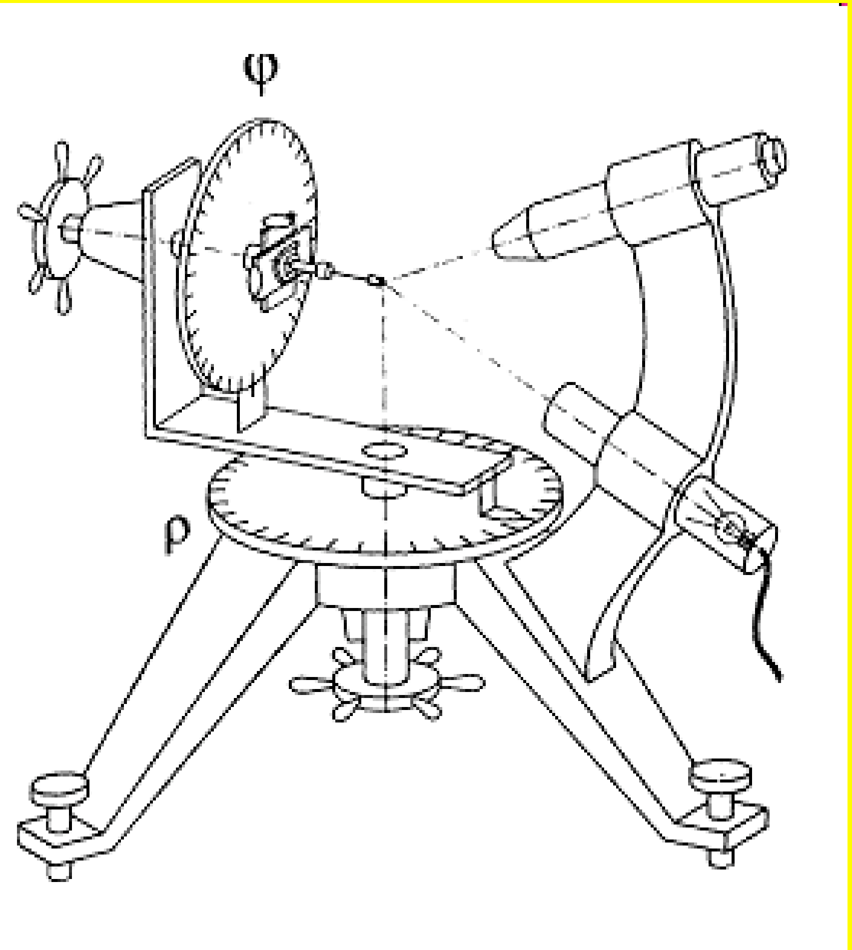
  All crystals of a given substance at a given temperature and pressure have the same angles between corresponding faces, regardless of their size and shape.

Defining the Unit Cell 2

- **Haüy law: 1782**

For a given crystal there is a set of ratios such that the ratios of the intercepts of any crystal plane on the crystal axes are rational fractions of these ratios. Hence all crystals consist of a "masonry of paralellipipedal blocks"

Two Circle Goniometer



- φ: **azimuthal circle**
- ρ: **pole distance circle**

$CuSO_4.5H_2O$

- **Crystals from Groth *Chemische Krystallographie,,* Vol 2, p 419, 1908**

Fig. 667.

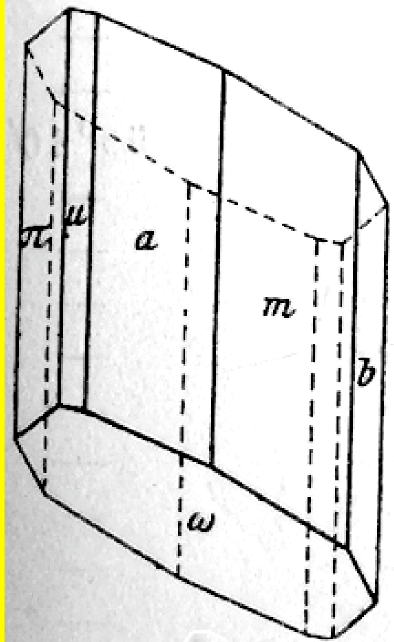


Fig. 668.

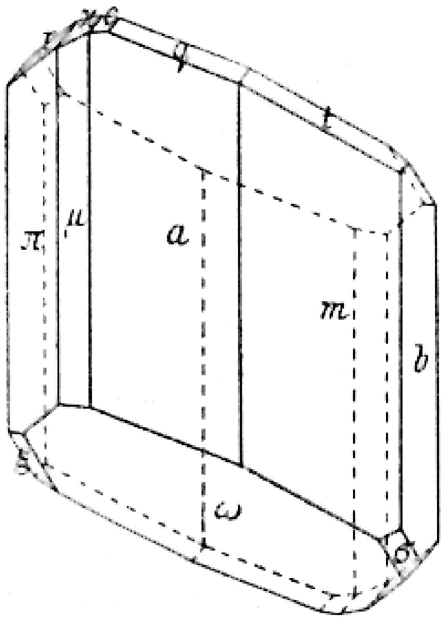
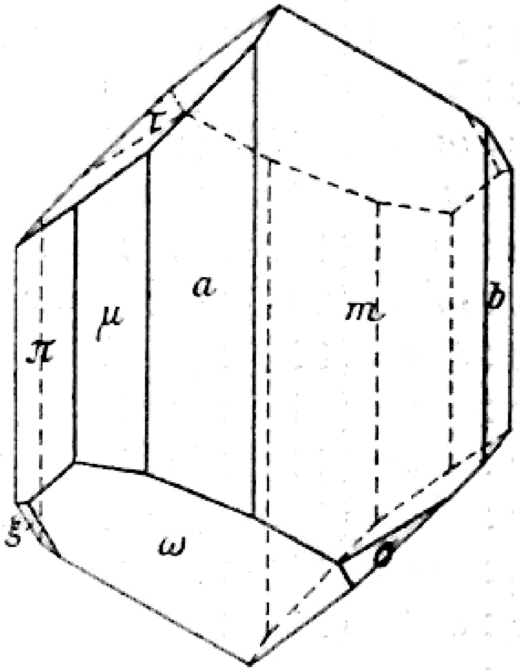


Fig. 669.



Indexing of $CuSO_4.5H_2O$

Final observed and calculated interfacial angles

		Berechnet:	Beobachtet:	
			Barker:	Kupffer:
$a : b$	$= (100) : (010) =$	—	*79° 6′	79° 19′
$a : m$	$= (100) : (110) =$	—	*26 7	—
$m : \mu$	$= (110) : (1\bar{1}0) =$	57° 16′	57 9	—
$a : l$	$= (100) : (120) =$	41 52	41 48	—
$a : \lambda$	$= (100) : (1\bar{2}0) =$	53 50	53 31	—
$a : \pi$	$= (100) : (1\bar{3}0) =$	67 4	—	—
$a : \nu$	$= (100) : (2\bar{1}0) =$	15 56	—	—
$b : q$	$= (010) : (011) =$	—	*64 58	65 4
$b : c$	$= (010) : (001) =$	94 29	—	—
$q : \varkappa$	$= (011) : (0\bar{1}1) =$	—	*56 59	—
$b : t$	$= (010) : (021) =$	44 39	44 41	—
$b' : \tau$	$= (0\bar{1}0) : (0\bar{2}1) =$	40 33	40 33	40 17
$b : \omega'$	$= (010) : (\bar{1}11) =$	76 32½	76 23	76 33
$b : \sigma$	$= (010) : (12\bar{1}) =$	40 49	40 52	40 47
$b : \zeta'$	$= (010) : (\bar{1}31) =$	40 31	40 56	—
$b : \xi'$	$= (010) : (\bar{1}21) =$	54 49	54 44	—

Indexing of $CuSO_4.5H_2O$

- The idea of the reciprocal cell was not current, so calculations were complex.

- Obs: (100):(010) = 79.10º; γ^* = 79.12º

- Obs: (010):(001) = 94.48º; α^* = 94.54º

Unit Cell for $CuSO_4.5H_2O$

- **1: From indexing crystals: (Groth)**

  a:b:c: 0.5721, 1, 0.5554

  $\alpha = 82.08^o$; $\beta = 107.13^o$; $\gamma = 102.68^o$

- **2: From X-ray :(Varghese and Marslen, Acta Cryst B41,184-190, 1985)**

  a:b:c: 0.5710, 1, 0.5566

  $\alpha = 82.35^o$; $\beta = 107.33^o$; $\gamma = 102.60^o$

Value of Blue Sky Research

- Compare the invaluable and obviously useful work done by Groth to identify crystalline substances by careful measurement of painstakingly grown crystals with
- The totally academic work done by Fedorov and Schoenflies in identifying the 230 space groups which were of purely theoretical interest.

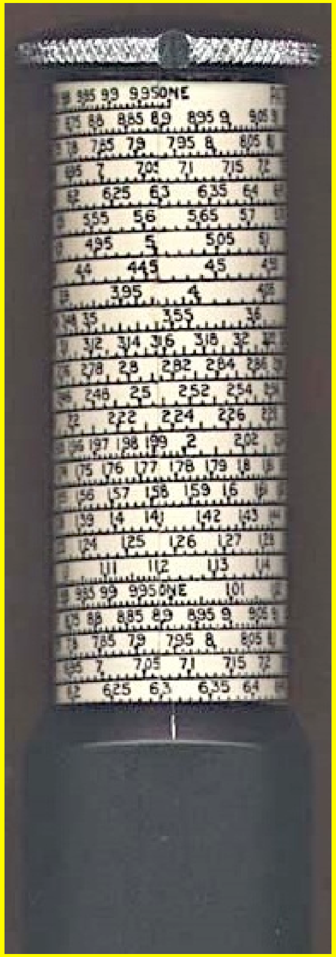
Calculation in early 20th Century

Addition – the BrunsViga as rescued from Scapa Flow

Calculation in early 20th Century

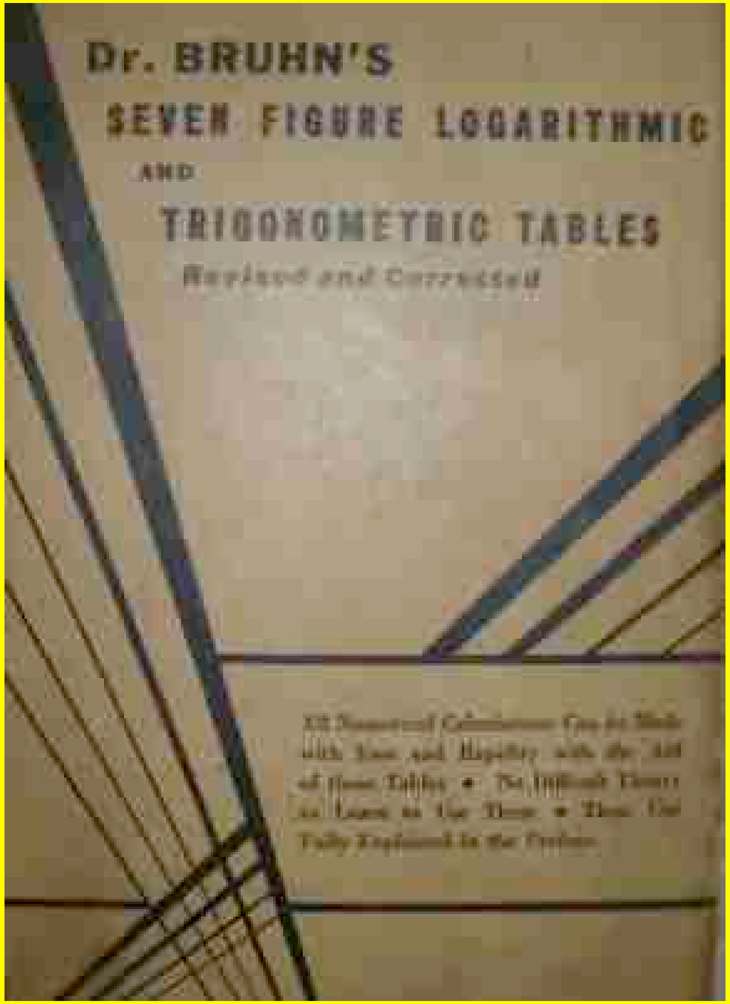
- **Multiplication**

- **Slide rules – here the Otis King cylindrical rule for 4-figure accuracy.**



Calculation in early 20th Century

- **Seven figure(!) tables for “ease and rapidity …. No difficult theory”**



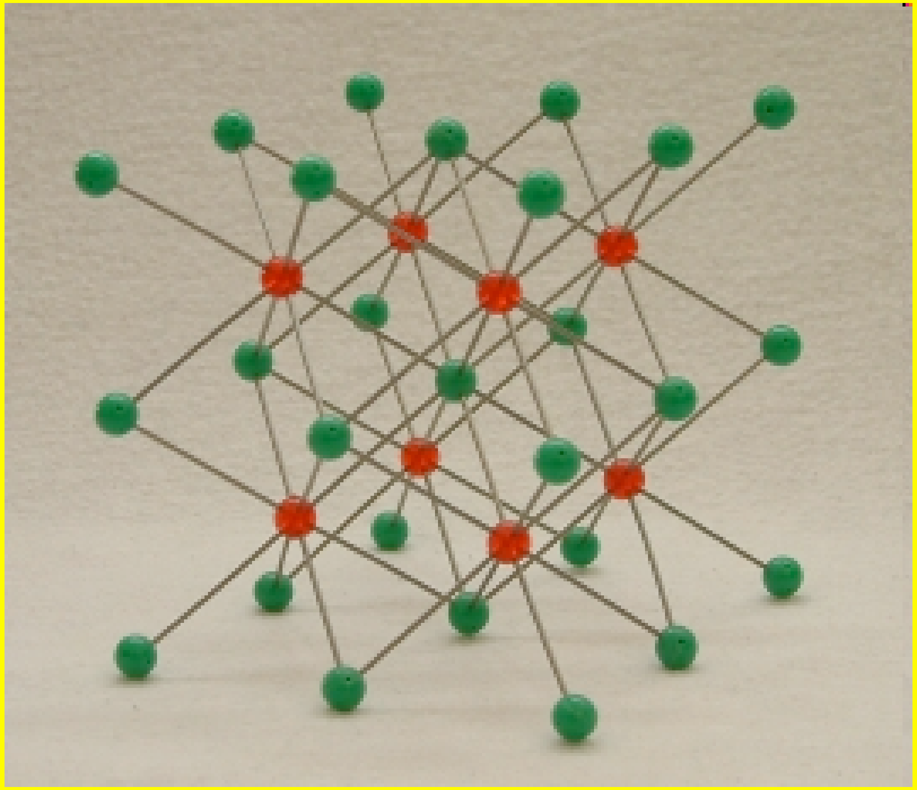
Preface to one of these

The opinions expressed in this book are those of the author, and do not necessarily represent the policy of the United States Department of Defense.

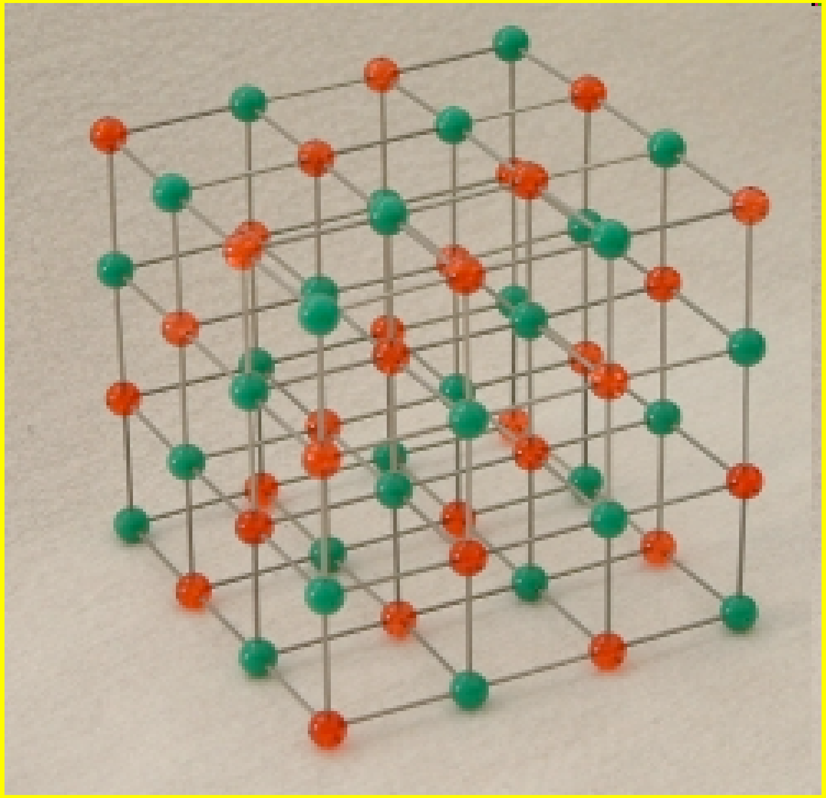
Determining a Structure

- ***Obtaining a crystal***
- ***Collecting Data***
- ***Solving Structure***
- ***Refining Structure***
- ***Presenting Data***

Early Crystal Structures



CsCl



NaCl

Pictures from Miramodus Molecular Models

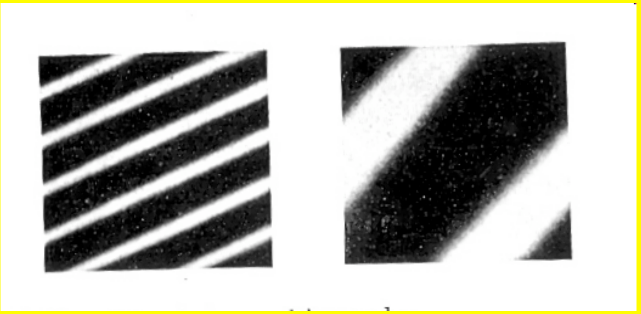
Fourier Summations

- **Consider projection of 10 atoms, 200 data, 1000 points in map.**

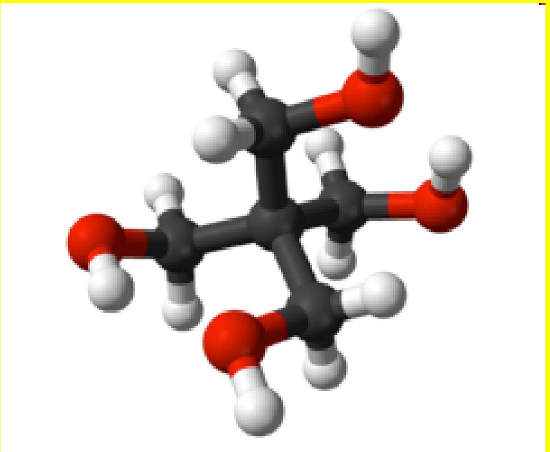
- **Structure Factors – 2000 calculations**

- **Electron density – 200 000 calculations**

Optical Methods – Huggins Masks



Masks: 4,2 and 1,1



**pentaerythrito
l**

Optically generated structure

1-d Fourier Summations

- **In line group p2: ρx = 2Σ$_h$ F(h) cos 2πhx**
- **"Strip" showing values of function for specific values of F (76) and h (7):**

76	C	7	76	56	8	$\overline{45}$	$\overline{74}$	$\overline{66}$	$\overline{23}$	31	69	72	38	$\overline{16}$	$\overline{61}$	$\overline{76}$	$\overline{51}$	0

- **For even h, cos 2πh(½-x) = cos 2πhx**

F h 60x: 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

2-d Fourier Summations

- **In plane group *p*2:**

- $\rho x,y = 2\Sigma_h \Sigma_k F(h,k) \cos 2\pi hx+ky)$

$$= 2\Sigma_h \cos 2\pi hx \, \Sigma_k F(h,k) \cos 2\pi ky$$

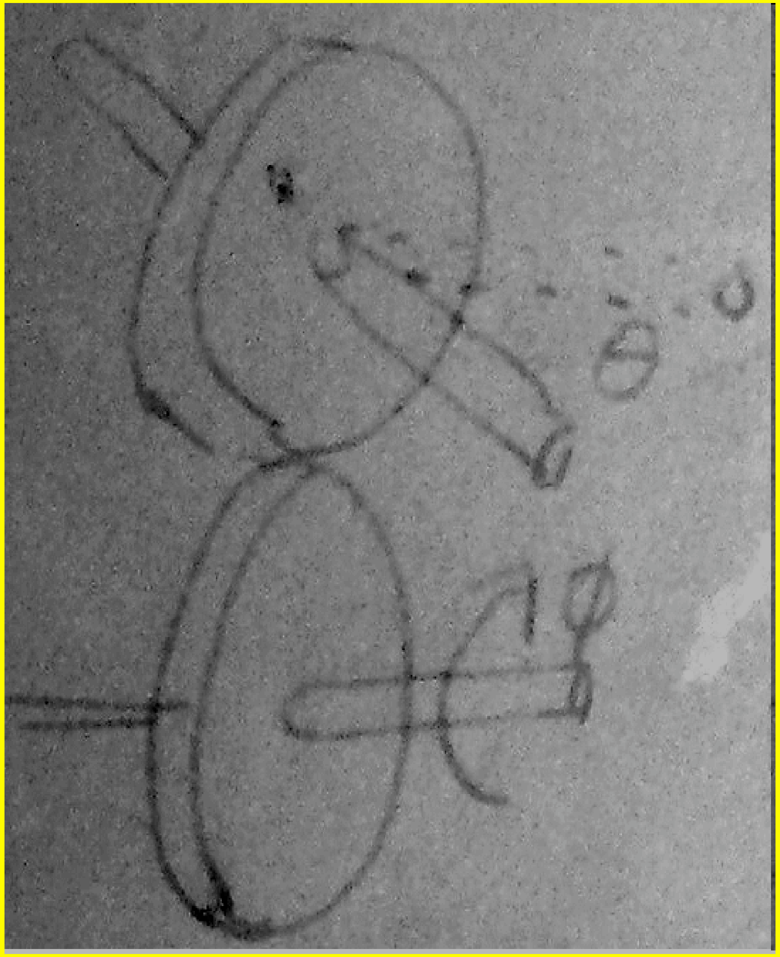
$$-2\Sigma_h \sin 2\pi hx \, \Sigma_k F(h,k) \sin 2\pi ky$$

Beevers-Lipson Strips

Dr C.A. Beevers

Arnold Beevers, 1908-2001, scientist, humourist, and inventor.

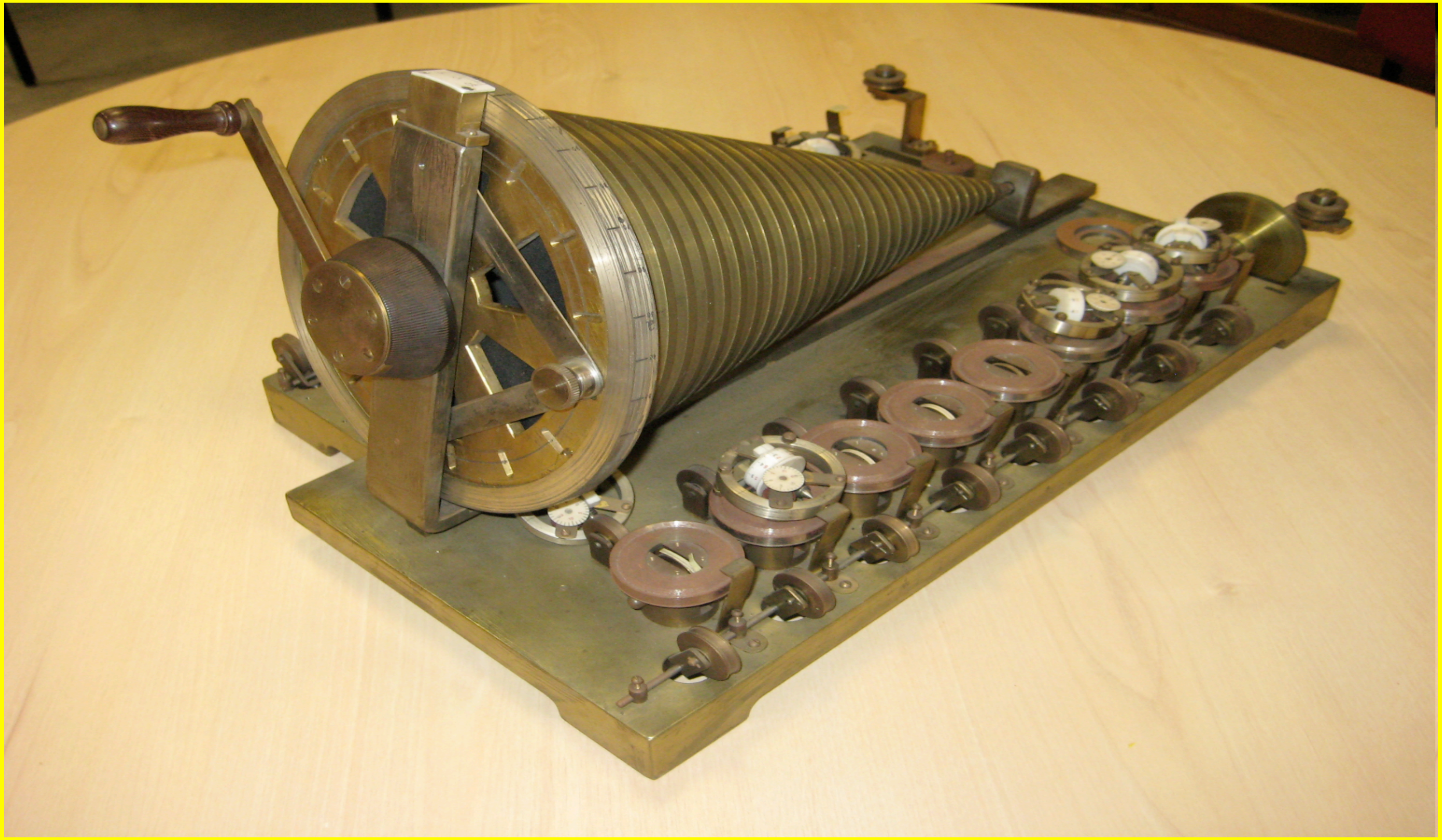
A Fourier Machine



- One of many attempts by Dr C.A. Beevers to effect the rapid calculation of electron Density maps in crystals (1946-1950). This one was never brought to a successful use, but it had an excellent principle – that of the planimeter: If the lower wheel went through φ, the upper wheel would be driven through an angle of cos θ. Successive turns would give $\Sigma\varphi_i \cos\theta\, xn$. n goes 0 – 15)

- C.A. Beevers

A Fourier Machine



Engineering Problems

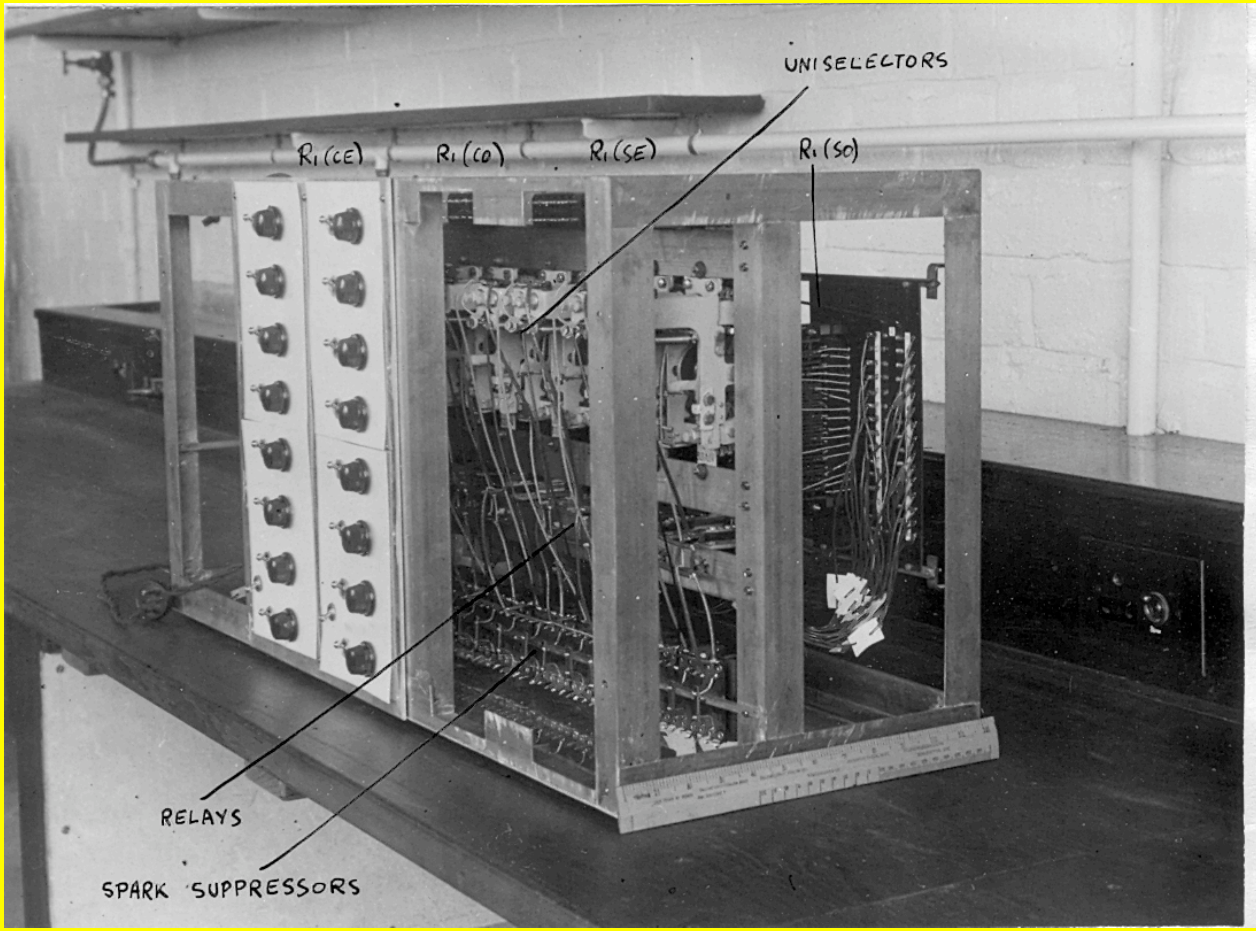
I've a brake which I make
With a string sort of thing.
It's a good sort of brake,
But it hasn't worked yet.

"The Engineer", from *Now we are Six* by A.A. Milne

An Electric Analogue Machine

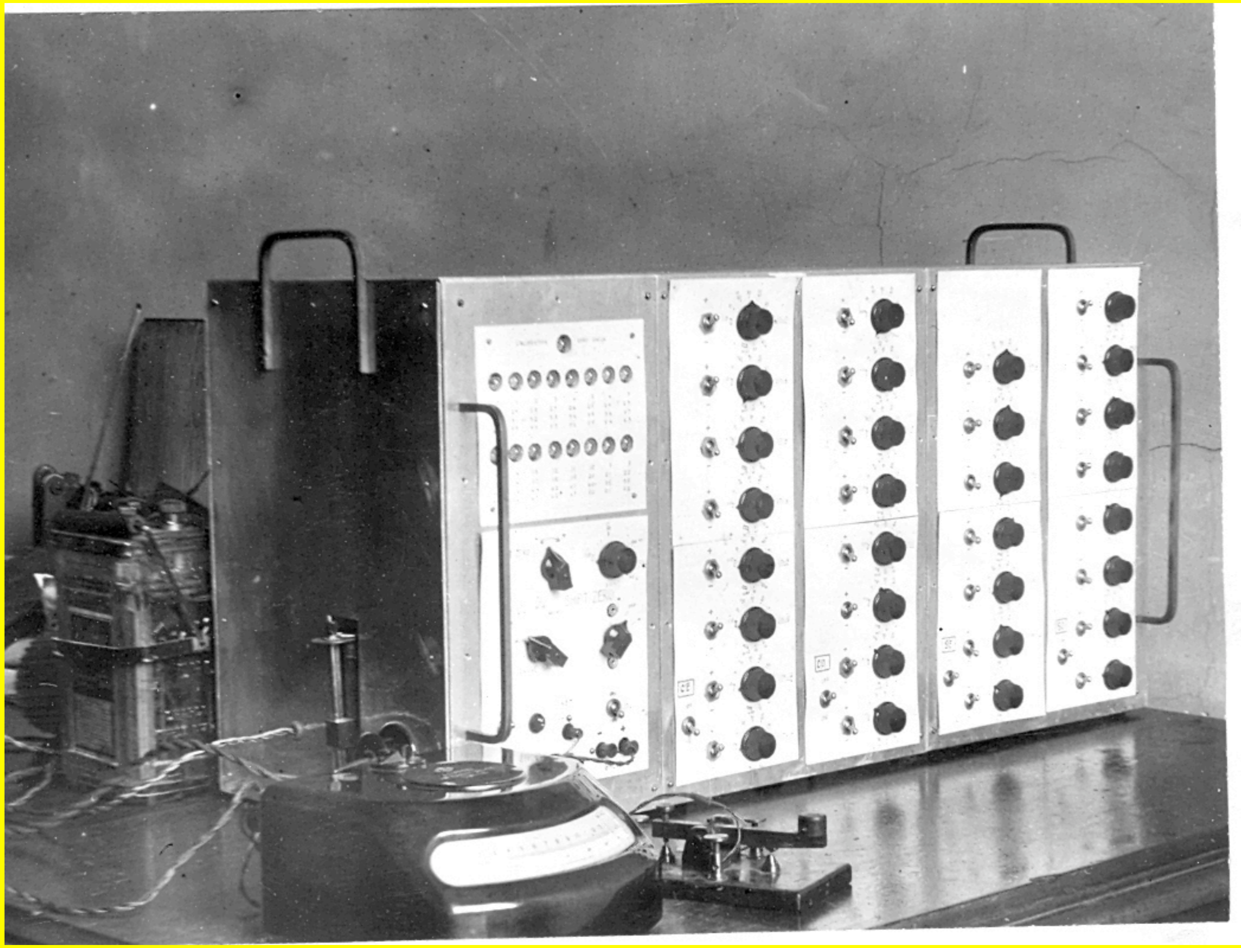
- Designed by Beevers and Stern in 1950
- Electrical generation of terms to be summed
- Sums read from a galvanometer with adjustable zero.
- Approximately 6 times faster than strips with error about 1%.
- Used until the "advent of other machines"

An Electric Analogue Machine



The machine during construction

An Electric Analogue Machine

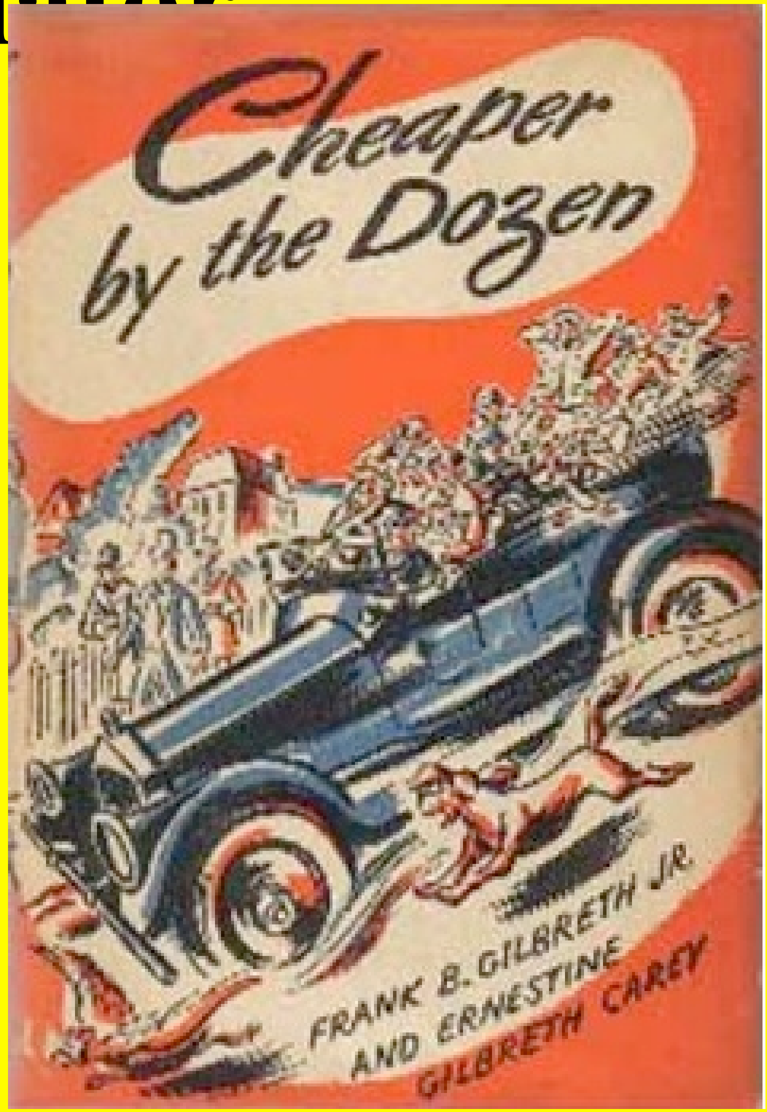


The Completed Machine

Competition for the Calculator

- **Frank Gilbreth:**

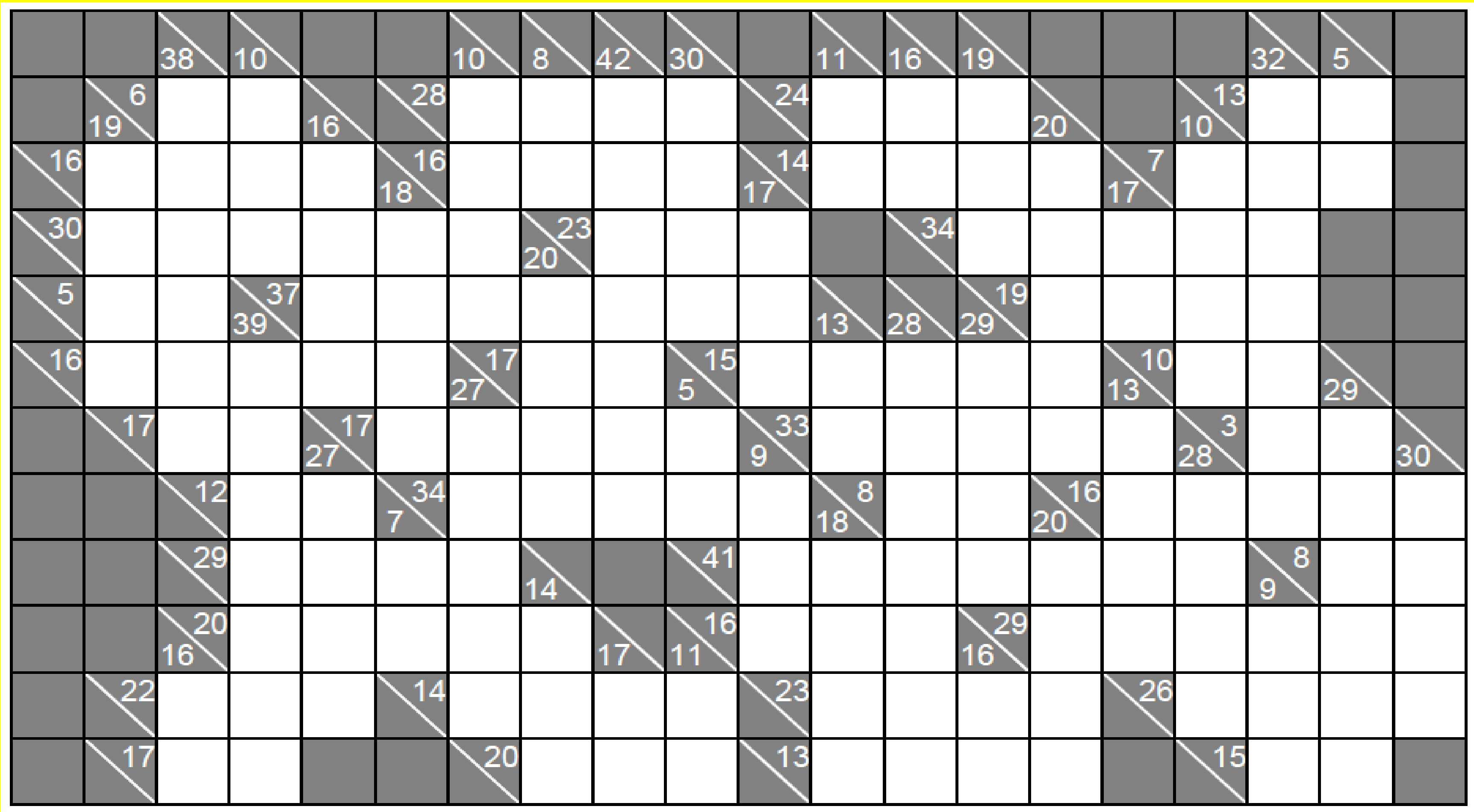
- **Proper upbringing of children to compete with dehumanising machinery.**



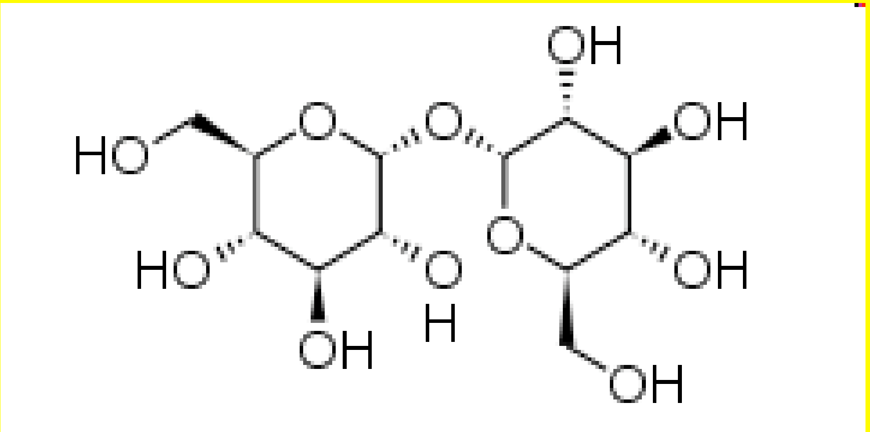
Rosalind Franklin Adding?

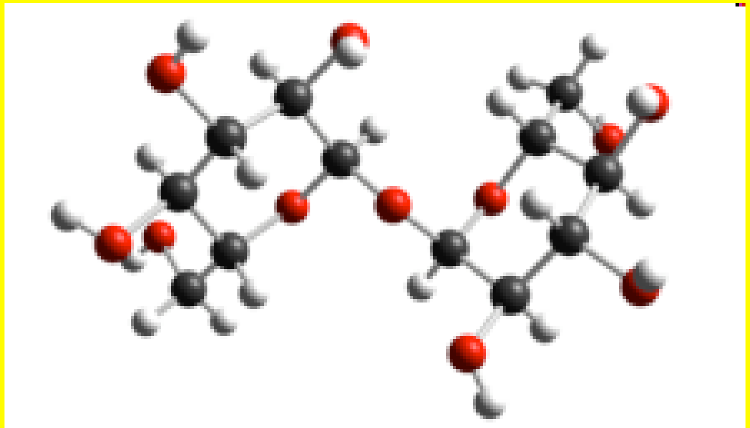
Juliet Stevenson as Rosalind Franklin : BBC Horizon Programme

Kakuro – for the additionally unchallenged!



α,α-Trehalose dihydrate: unit cell





$P2_12_12_1$ a = 12.233(9), b = 17.889(13), c = 7.596(6)

Spherical crystals ground (r ≈ 0.35 mm)

Work by Robert Simpson, -1971

α,α-Trehalose dihydrate: data

Photographs: 0kl - 9kl, h0l - h,14,l, hk0 – hk5

6 films per layer (186 total), intensities by eye

5500 data → 2097 independent, 52 too weak

$\sigma(I) \approx 0.09I$ – All data used for solution

α,*α*-Trehalose dihydrate: solution

(much of this carried out on VSO in Nigeria)

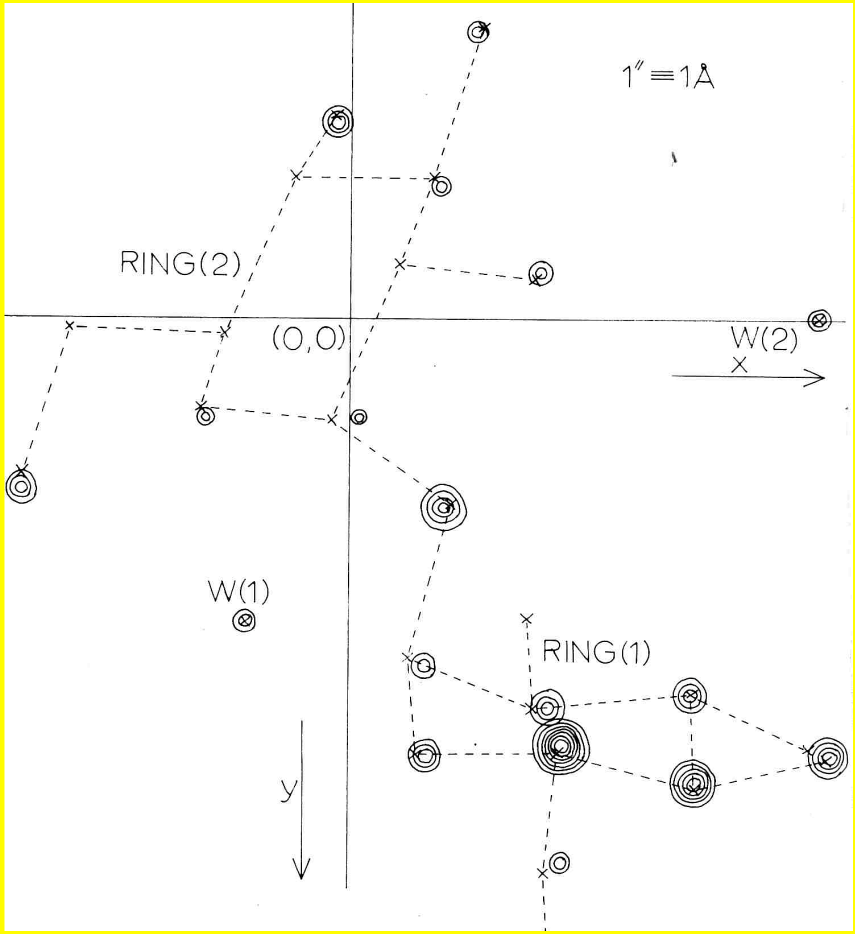
Four centric reflections fix origin and enantiomorph

Two symbols chosen for symbolic addition.

α,α-Trehalose dihydrate: solution

hkl	Φ	E
043	0	2.58
092	π/2	2.45
502	0	3.44
950	π/2	3.25
683	a	2.86
4,13,4	b	2.53

α,α-Trehalose dihydrate: solution



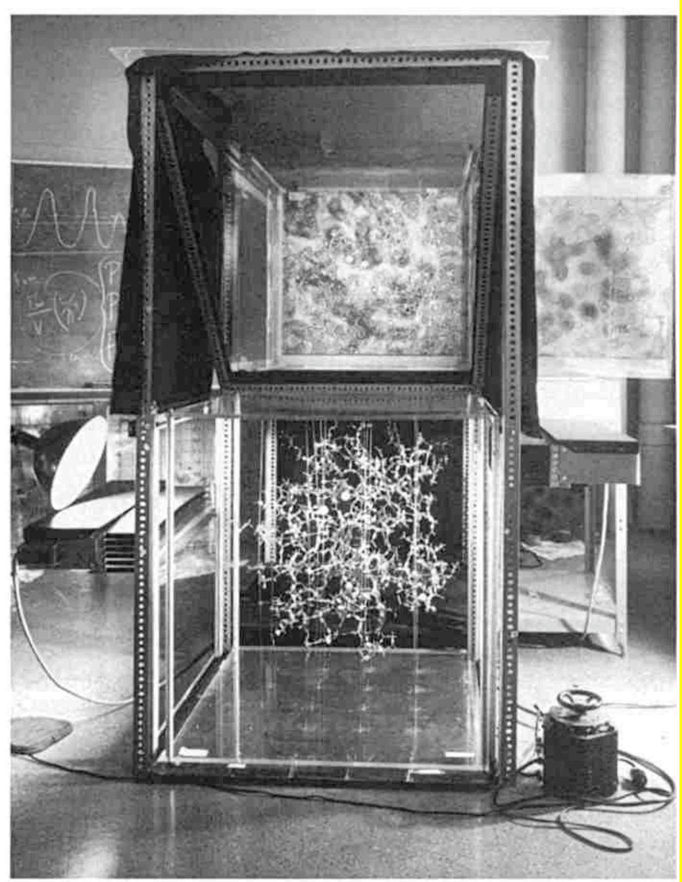
- **E-map along [001].**
- **Essentially correct although not used!**

The contoured map

"There is little future in peak-search methods; crystallographers enjoy contouring maps so much"

Anon. ca 1980

Richards Box



← **Half-silvered mirror**

← **Contoured map behind**

← **Model being built**

From Dickerson, “Present at the Flood”

Refinement

- **Early structures were refined by Fourier methods – shift until difference map indicates best fit**

- **R-factors of 20% considered very good.**

α-D-Glucose

- $P2_12_12_1$: a = 10.38, b = 14.84, c = 4.93Å
- Suitable for solution in hk0 projection, difficulty with z-coordinates.

T.R.R. Macdonald, 1950

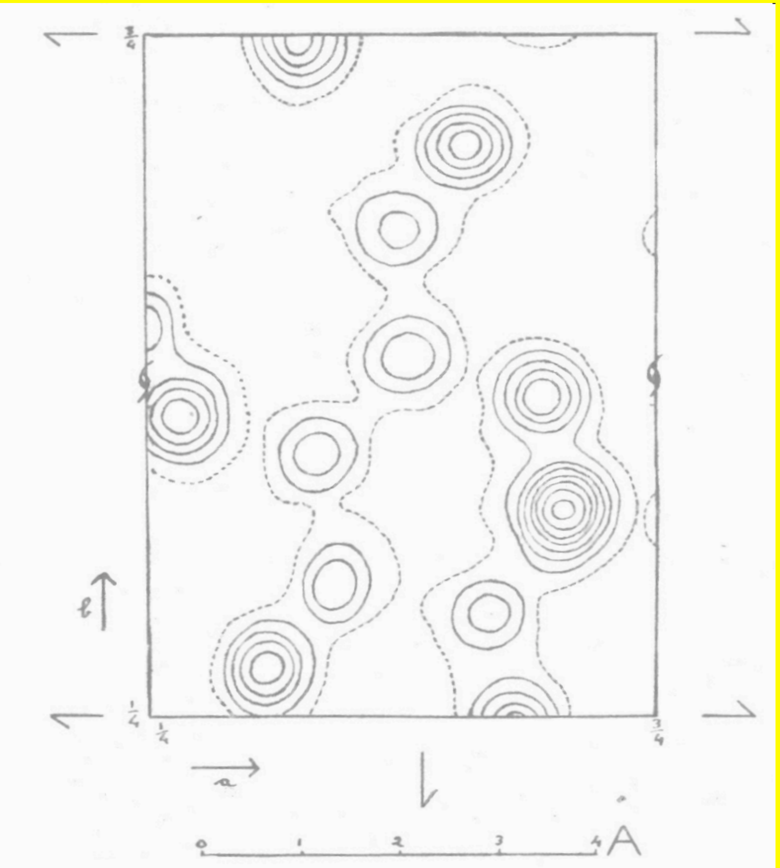
Refinement – early attempts at least squares

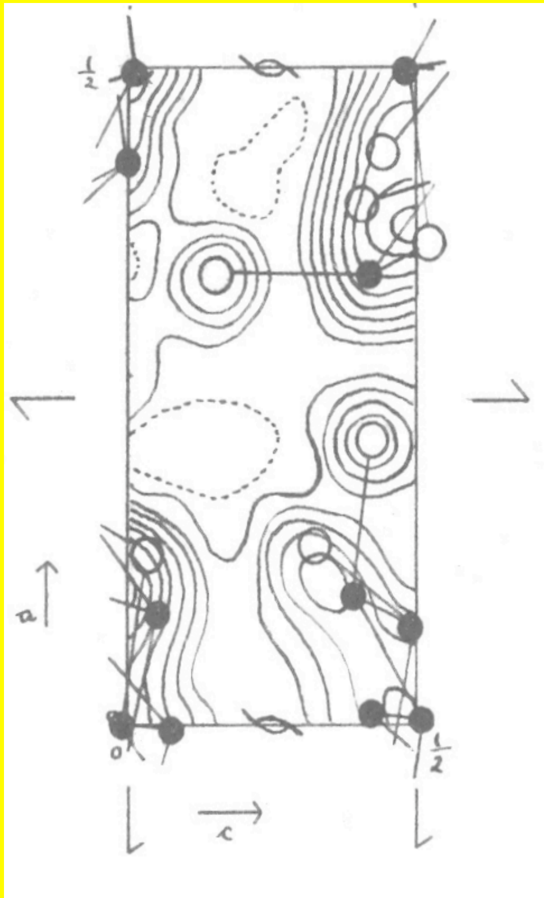
- **Even in projection, least squares gives a huge matrix for inversion.**

- **"block diagonal" least squares is only a series of 2x2 matrices.**

- **Considered useful with 0.3Å resolution Fourier requiring 0.7Å resolution (Hughes, 1941)**

α-D-Glucose





[001] projection

[010] projection

α-D-Glucose

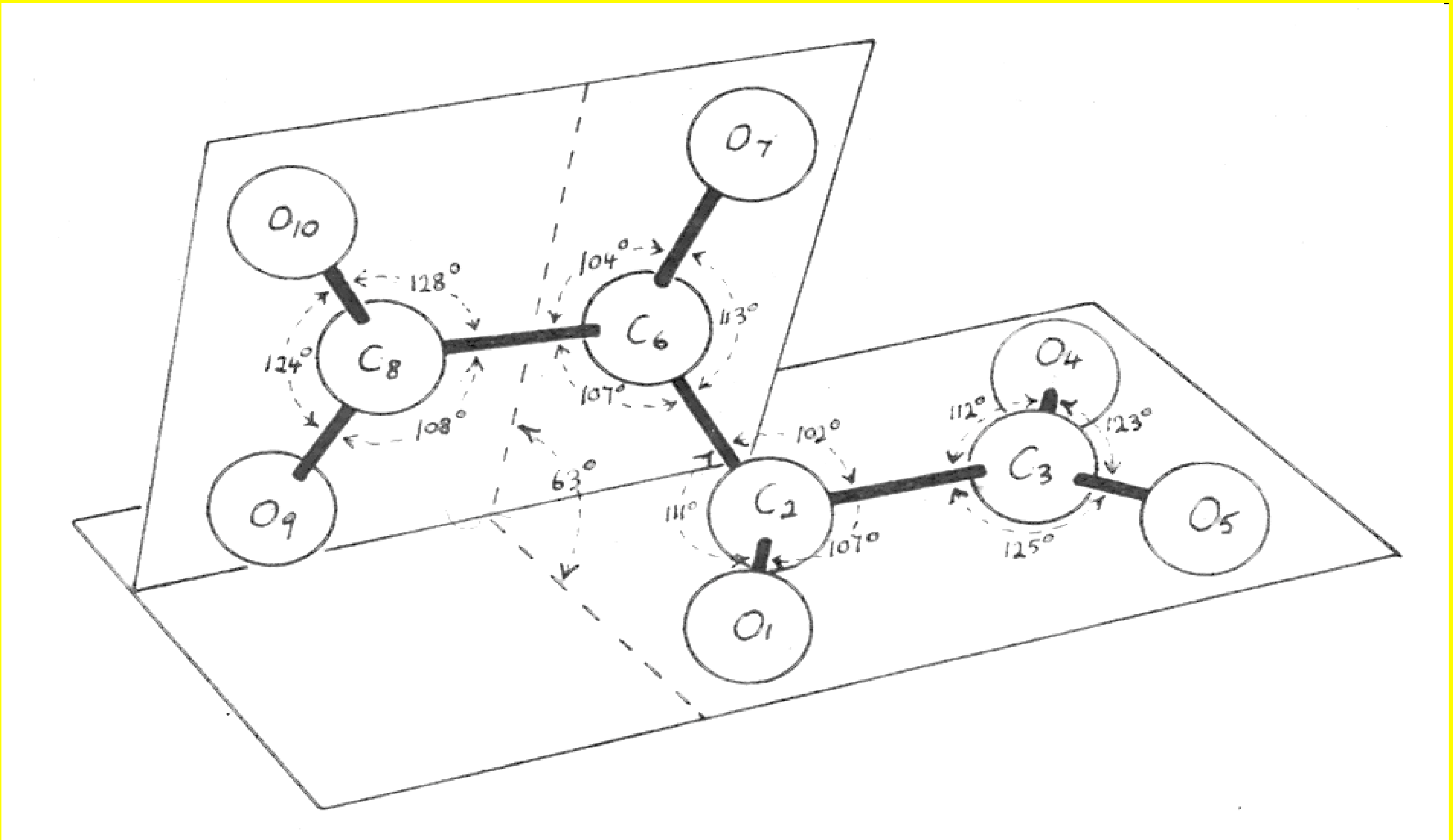
- **Least squares used to refine z-coordinates in h0l and 0kl projections.**

Final R-factors:

R_{hk0}: 18.4% R_{h0l}: 20.4% R_{0kl}: 14.7%

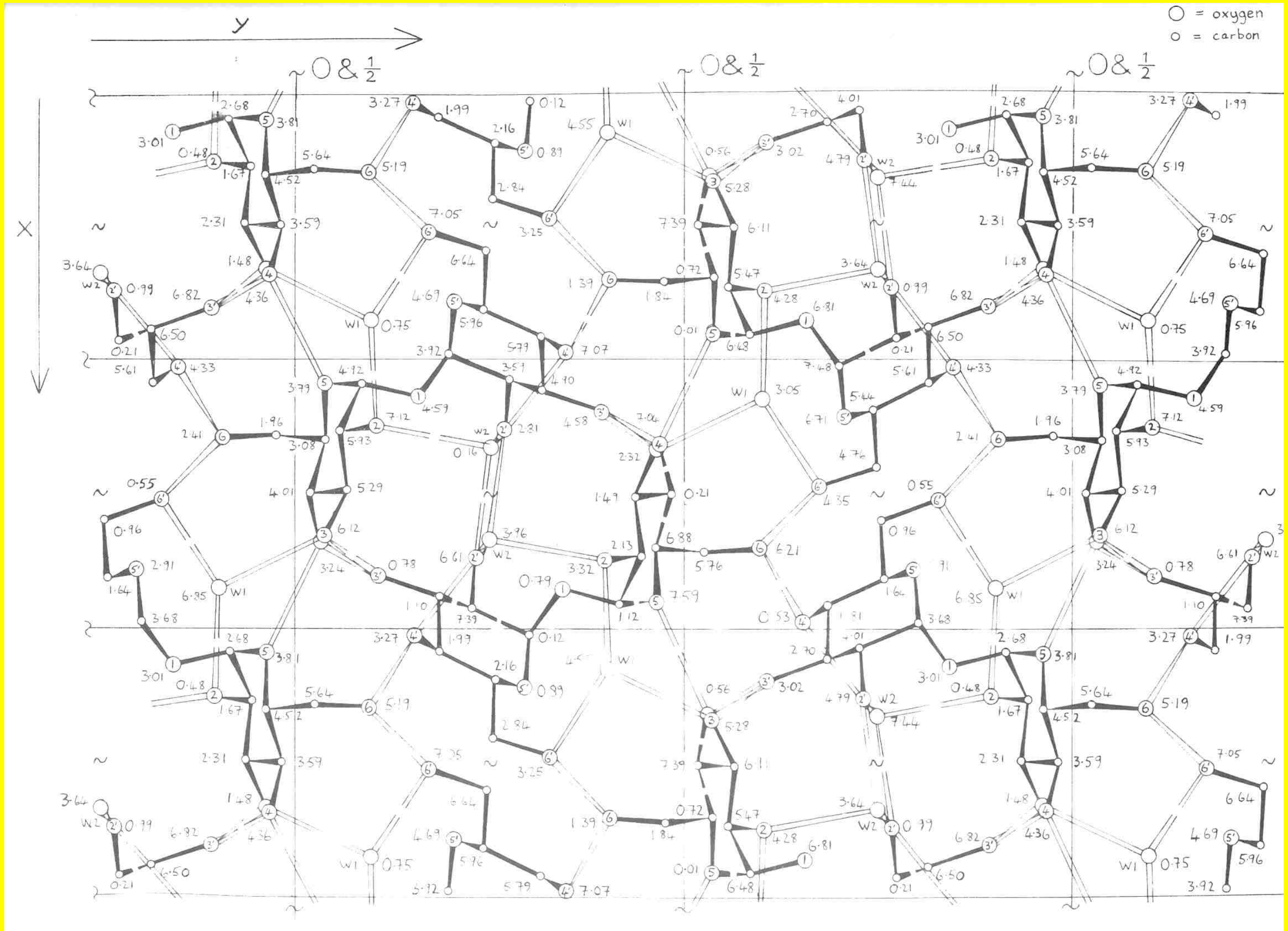
(cf trehalose: R= 5.7% on all data)

Diagrams – presenting the results – a molecule – d-tartaric acid



F. Stern, 1950

Diagrams – presenting the results – trehalose dihydrate packing



R. Simpson, 1971

Facing up to a complex future

The opposite of faith is not doubt, it is certainty.

R. Holloway

How much are we prepared to accept that we need not understand?