

GRAPH PAPER FOR TREATMENT OF DIFFUSION EXPERIMENTAL RESULTS

A. A. Shvyrjaev and I. N. Beckman

Vestnik MGU, Chemistry, 1981, v. 22, p.517

The application of functional scales, that is transformations of complex dependencies between the investigated values into linear ones, greatly facilitates the treatment of results of many physical chemical experiments. Thus a logarithm scale is used for calculation of activation energy and pre-exponential factor in Arrhenius relationships; a probability scale is used for verification of statistical distribution law hypotheses and so on. The advantages of linear graphs are the simplicity of the graphical representation, the possibility of applying the linear least-squares method and of testing the agreement with the mathematical model by using the correlation coefficient. This has led to production of special graph papers to save investigators the trouble of converting from the initial scale to the functional one. Thus, logarithmic, square root and inverse (1/x) graph papers, among others, are now available.

It is well known that the phenomenological theory of diffusion leads to rather cumbersome series solutions which preclude the possibility of simple direct calculations of diffusion coefficient from experimental data. Diffusion data are usually treated by using only a fraction of the experimental data in a linearized asymptote to the initial or final part of the curve. Since only a somewhat arbitrary subset of the data is used, difficulties can arise in the interpretation of anomalies since it may be unclear whether these are due to a physical effect or are artefacts of the approximate calculation technique. Furthermore, the initial and final parts of the experimental curve are often distorted by the influence of various side-effects. The object of the present work is the creation of "diffusion" graph paper for treatment of experimental diffusion data. Attention is focussed on the methods used for gas diffusion in solids: permeability method, sorption method and desorption under ramped heating (thermodesorption spectroscopy). The calculations were carried out on a BESM-6 computer. The suggested techniques were verified by using diffusion data of radioactive radon (^{222}Rn) in polypropylene.

The permeability method is based on studying gas diffusion through thin membranes. The flux of penetrant through the membrane is measured as a function of time. The gas flux $Q(t)$ at time t is described by:

$$Q(t)/Q_{\infty} = F(u) = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \pi^2 u) = 4 \sqrt{u} \sum_{n=1}^{\infty} \exp(-(2n-1)^2 / 4u) \quad (1)$$

where $u = Dt/H^2$

D = diffusion coefficient

H = membrane thickness

Q_{∞} = steady state flux of gas

The terms in the series $\sum (-1)^n \exp(-n^2 \pi^2 u)$ decay rapidly with increasing n provided u is large. Jost [1] derived a functional scale with coordinates $\ln(1-Q(t)/Q_{\infty})$ and t on the basis that only the first term of the series is important when $Q(t)/Q_{\infty} > 0.65$. Then the diffusion coefficient can be calculated by using equation (2):

$$D = H^2 \tan \alpha / \pi^2 \quad (2)$$

where $\tan \alpha$ is the slope of the straight line part of the curve.

The terms in the series $\sum \exp(-(2n-1)^2/4u)$ decay rapidly for small u . Thus for $Q(t)/Q_\infty < 0.9$, only the first term need be considered. The functional scale suggested by Pasternak (2) uses the coordinate $\ln(t^{1/2}Q(t)/Q_\infty)$ vs $1/t$. In this case, the diffusion coefficient is given by

$$D = H^2 / 4 \tan \alpha \quad (3)$$

Since both these methods are based on omitting all but the first term in the series, they suffer from the the disadvantages of approximate methods referred to above.

In the present study, equation (1) was used to create graph papers. The transition from the short time solution to the long time solution was realized automatically. We found the u values corresponding to $F(u) = 0, 0.01, 0.02 \dots 0.99$. These values are shown in Table 1. For creation of functional scales, values of u on a linear scale should be put on the right hand side of the y-axis while on the left hand side of the axis the corresponding values of $F(u)$ should be indicated. The resulting scale will be the sought-for functional scale (the abscissa the a linear time scale).

During treatment of results the experimental data are scaled by Q_∞ and the variables are plotted on linear coordinates i.e. $(Q(t)/Q_\infty = F(u))$ vs. t . Each point of the resulting graph has coordinates (t, u) and the linear relationship

$$u = \frac{D}{H^2} (t - t_0) \quad (4)$$

where t_0 is the intercept of the line on the time axis, corresponding to the start of diffusion. This value serves as a measure of the apparatus inertia.

The diffusivity is calculated from equation (5):

$$D = H^2 \tan \alpha \quad (5)$$

Fig. 1a shows an experimental curve and Fig. 1b the linearized analogue.

All points on the experimental curve are used in this linearization method and there is a unique t_0 . (In the ideal case the line must pass through the origin).

The Sorption Method is based on investigation of gas diffusion into the sample from a gas phase. The quantity of gas taken up by a sheet of thickness H up to time t is described by equation (6) (3):

$$M(t)/M_\infty = F(u) = 1 - 8/\pi^2 \sum_{n=1}^{\infty} 1/(2n-1)^2 \exp(-(2n-1)^2 \pi^2 u) \quad (6)$$

The functional scale is shown in table 2. In Fig. 2a a typical experimental curve is plotted on ordinary axes while the linearized plot is shown in Fig. 2b. The diffusion coefficient can be calculated from eqn. (5).

The Method of Thermodesorption Spectroscopy is based on

programmed heating. Under conditions of linearly increasing heating [4], the dependence of the gas release flux on time is given by eqn. (7):

$$Q(t) = C_0 k_0 \exp(-E/RT) \exp(-k_0/B (RT/E \exp(-E/RT) - E_1(-E/RT))) \quad (7)$$

where $T = Bt$

or, for reduced flux (scaled by its maximum value):

$$Q(T)/Q(T_m) = F(u) = F(E/RT - E/RT_m) \quad (8)$$

where $u = E(1/T - 1/T_m)$, T = temperature, T_m = temperature of peak flux, C_0 = starting concentration of gas; R = Gas constant; E = activation energy; k_0 = pre-exponential factor, E_1 = the integral power function, B = the heating rate.

The functional scale is shown in Table 3. Figure 3 shows the experimental data plotted on both ordinary axes and functional axes. The activation energy can be determined from equation (9):

$$E = R \tan \alpha \quad (9)$$

The pre-exponential factor k_0 can be obtained from the intercept of the straight line on the u -axis from

$$k_0 = \frac{\exp(-A) \cdot E \cdot \beta}{R \cdot T_m^2} \quad (10)$$

The suggested method of treatment of diffusion data was tested on a gas-polymer system. The method allows reliable values of diffusion parameters to be calculated quickly.

The authors thank U. R. Dzelme for submission of "DIFAS" program.

Literature Cited

1. Jost, W. *Diffusion in Solids, Liquids and Gases*, Acad. Press, New York, 1966, p. 137.
2. Pasternak, K. A., Schimschumer, I. E., Hebler, I., *J Polym. Sci.*, 1970, A2, 8, p.467.
3. Crank, J., Henry, M. E., *Trans Faraday Soc*, 1949, 45, 636.
4. Inthoff, W. Zimen, K. E., *Trans Chalmers Univ. Techn. Gothoburg*, 1956, 175, p 23.

Titles of Figures

- Fig. 1 Kinetic curve from permeability method
 - (a) ordinary scale
 - (b) functional scale

- Fig. 2 Kinetic curve from Sorption method
 - (a) ordinary scale
 - (b) functional scale

- Fig. 3 The kinetic curve of thermodesorption spectroscopy method.
 - (a) ordinary scale
 - (b) functional scale

TABLE 1
Functional scale for permeability method

F(u)	u	F(u)	u	F(u)	u	F(u)	u
0.01	0.0394	0.26	0.0944	0.51	0.1409	0.76	0.2147
0.02	0.0447	0.27	0.0961	0.52	0.1431	0.76	0.2190
0.03	0.0486	0.28	0.0978	0.53	0.1454	0.78	0.2235
0.04	0.0519	0.29	0.0995	0.54	0.1476	0.79	0.2282
0.05	0.0547	0.30	0.1012	0.55	0.1499	0.80	0.2332
0.06	0.0573	0.31	0.1029	0.56	0.1523	0.81	0.2384
0.07	0.0597	0.32	0.1047	0.57	0.1547	0.82	0.2434
0.08	0.0619	0.33	0.1064	0.58	0.1572	0.83	0.2497
0.09	0.0641	0.34	0.1081	0.59	0.1597	0.84	0.2559
0.10	0.0661	0.35	0.1099	0.60	0.1622	0.85	0.2624
0.11	0.0681	0.36	0.1117	0.61	0.1649	0.86	0.2694
0.12	0.0700	0.37	0.1135	0.62	0.1676	0.87	0.2769
0.13	0.0719	0.38	0.1153	0.63	0.1703	0.88	0.2850
0.14	0.0737	0.39	0.1171	0.64	0.1731	0.89	0.2939
0.15	0.0755	0.40	0.1190	0.65	0.1760	0.90	0.3035
0.16	0.0773	0.41	0.1208	0.66	0.1790	0.91	0.3142
0.17	0.0791	0.42	0.1227	0.67	0.1821	0.92	0.3261
0.18	0.0808	0.43	0.1246	0.68	0.1853	0.93	0.3397
0.19	0.0825	0.44	0.1266	0.69	0.1886	0.94	0.3553
0.20	0.0843	0.45	0.1285	0.70	0.1919	0.95	0.3738
0.21	0.0860	0.46	0.1305	0.71	0.1953	0.96	0.3964
0.22	0.0877	0.47	0.1325	0.72	0.1989	0.97	0.4255
0.23	0.0893	0.48	0.1346	0.73	0.2026	0.98	0.4666
0.24	0.0910	0.49	0.1366	0.74	0.2065	0.99	0.5368
0.25	0.0927	0.50	0.1388	0.75	0.2105		

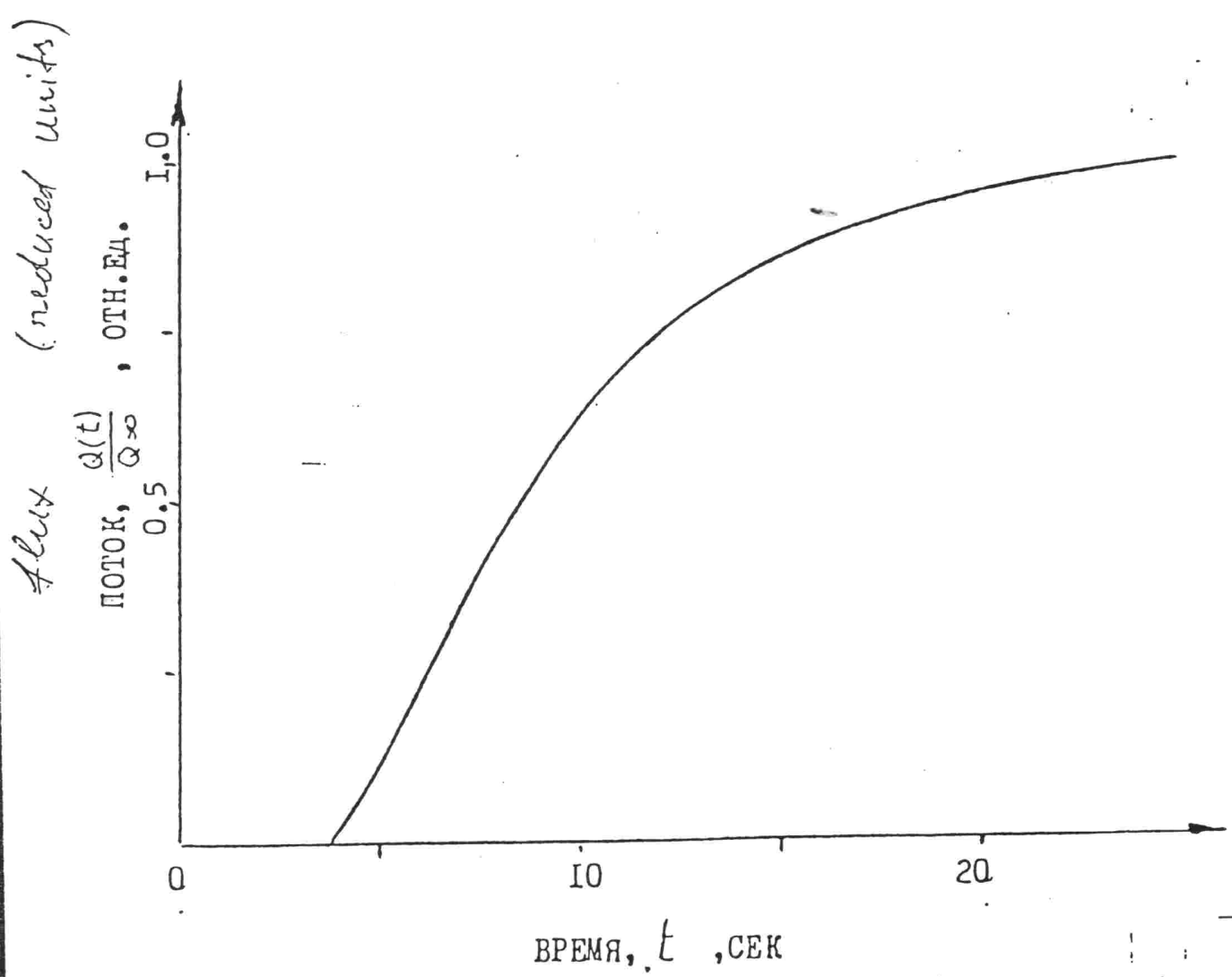
TABLE 2
Functional scale for sorption method

F(u)	u	F(u)	u	F(u)	u	F(u)	u
0.01	0.00002	0.26	0.0133	0.51	0.0512	0.76	0.1233
0.02	0.00008	0.27	0.0143	0.52	0.0533	0.77	0.1276
0.03	0.00018	0.28	0.0154	0.53	0.0554	0.78	0.1321
0.04	0.00031	0.29	0.0165	0.54	0.0575	0.79	0.1369
0.05	0.00049	0.30	0.0177	0.55	0.0597	0.80	0.1418
0.06	0.00071	0.31	0.0189	0.56	0.0620	0.81	0.1470
0.07	0.00096	0.32	0.0201	0.57	0.0643	0.82	0.1525
0.08	0.00125	0.33	0.0214	0.58	0.0667	0.83	0.1583
0.09	0.00159	0.34	0.0227	0.59	0.0691	0.84	0.1644
0.10	0.00196	0.35	0.0241	0.60	0.0716	0.85	0.1709
0.11	0.0024	0.36	0.0255	0.61	0.0742	0.86	0.1779
0.12	0.0029	0.37	0.0269	0.62	0.0768	0.87	0.1854
0.13	0.0034	0.38	0.0284	0.63	0.0795	0.88	0.1936
0.14	0.0038	0.39	0.0299	0.64	0.0823	0.89	0.2024
0.15	0.0044	0.40	0.0314	0.65	0.0851	0.90	0.2120
0.16	0.0051	0.41	0.0330	0.66	0.0880	0.91	0.2227
0.17	0.0057	0.42	0.0346	0.67	0.0911	0.92	0.2346
0.18	0.0063	0.43	0.0363	0.68	0.0942	0.93	0.2482
0.19	0.0071	0.44	0.0380	0.69	0.0974	0.94	0.2638
0.20	0.0079	0.45	0.0398	0.70	0.1007	0.95	0.2823
0.21	0.0087	0.46	0.0416	0.71	0.1041	0.96	0.3049
0.22	0.0095	0.47	0.0434	0.72	0.1077	0.97	0.3340
0.23	0.0104	0.48	0.0452	0.73	0.1114	0.98	0.3751
0.24	0.0113	0.49	0.0472	0.74	0.1152	0.99	0.4453
0.25	0.0123	0.50	0.0492	0.75	0.1192		

TABLE 3

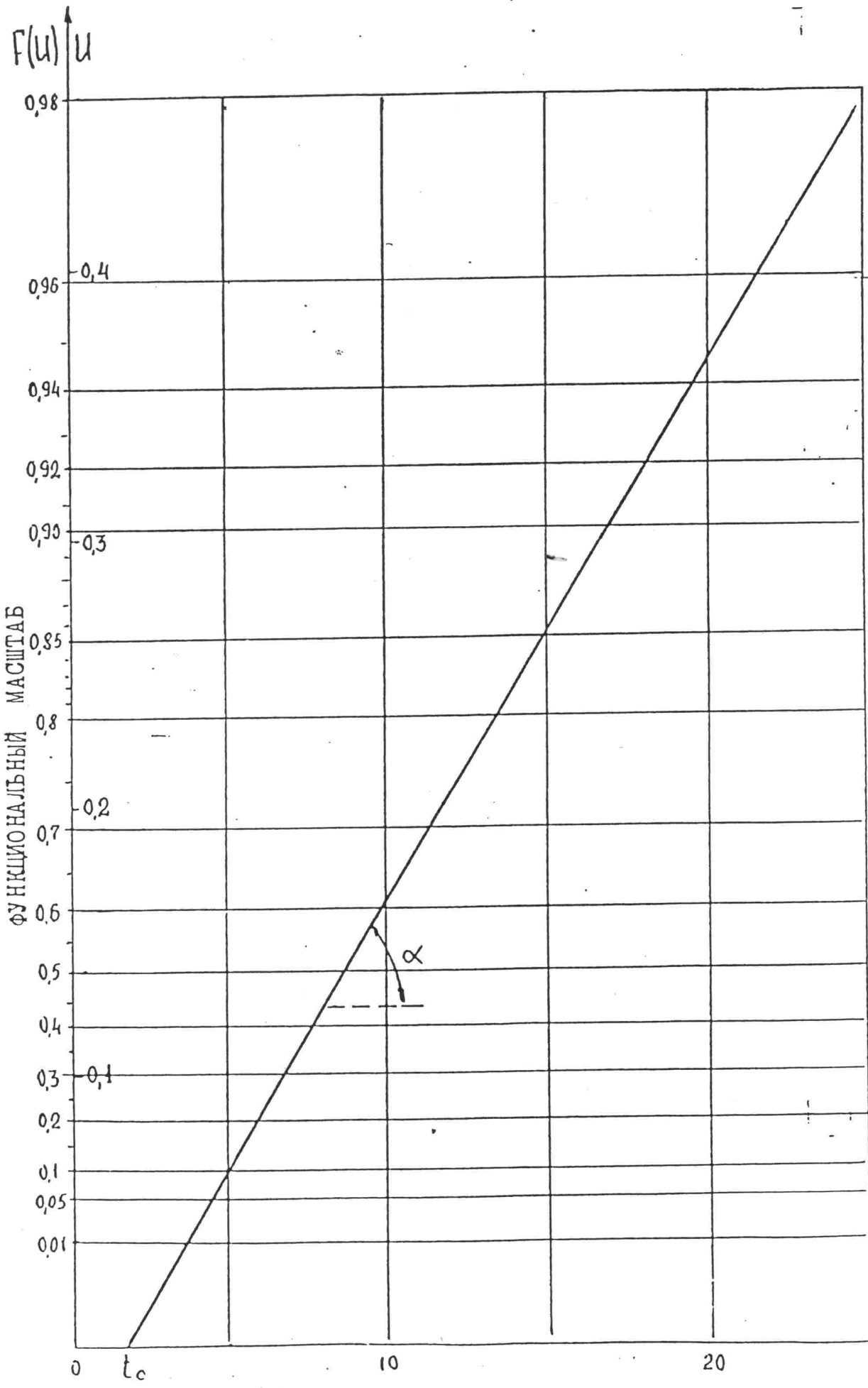
Functional scale for thermodesorption spectroscopy method

$\frac{Q(T)}{Q(T_m)}$	upward part $\times 10^2$ of curve	downward part $\times 10^2$ of curve	$\frac{Q(T)}{Q(T_m)}$	upward part $\times 10^2$ of curve	downward part $\times 10^2$ of curve
0.02	4.8376	-1.8277	0.52	1.3709	-0.9195
0.04	4.1386	-1.7072	0.54	1.3216	-0.8969
0.06	3.7270	-1.6270	0.56	1.2733	-0.8742
0.08	3.4329	-1.5645	0.58	1.2258	-0.8514
0.10	3.2033	-1.5122	0.60	1.1790	-0.8284
0.12	3.0142	-1.4666	0.62	1.1323	-0.8052
0.14	2.8531	-1.4258	0.64	1.0874	-0.7818
0.16	2.7125	-1.3884	0.66	1.0423	-0.7580
0.18	2.5875	-1.3537	0.68	0.9974	-0.7339
0.20	2.4746	-1.3212	0.70	0.9528	-0.7093
0.22	2.3717	-1.2904	0.72	0.9083	-0.6842
0.24	2.2769	-1.2611	0.74	0.8637	-0.6585
0.26	2.1888	-1.2329	0.76	0.8189	-0.6320
0.28	2.1065	-1.2057	0.78	0.7737	-0.6046
0.30	2.0291	-1.1795	0.80	0.7280	-0.5762
0.32	1.9560	-1.1540	0.82	0.6816	-0.5466
0.34	1.8865	-1.1290	0.84	0.6341	-0.5155
0.36	1.8203	-1.1046	0.86	0.5851	-0.4825
0.38	1.7570	-1.0806	0.88	0.5343	-0.4472
0.40	1.6962	-1.0570	0.90	0.4808	-0.4091
0.42	1.6376	-1.0336	0.92	0.4237	-0.3667
0.44	1.5811	-1.0105	0.94	0.3613	-0.3187
0.46	1.5263	-0.9876	0.96	0.2899	-0.2616
0.48	1.4732	-0.9649	0.98	0.2003	-0.1933



time, sec
Fig. 1a

Функциональный масштаб



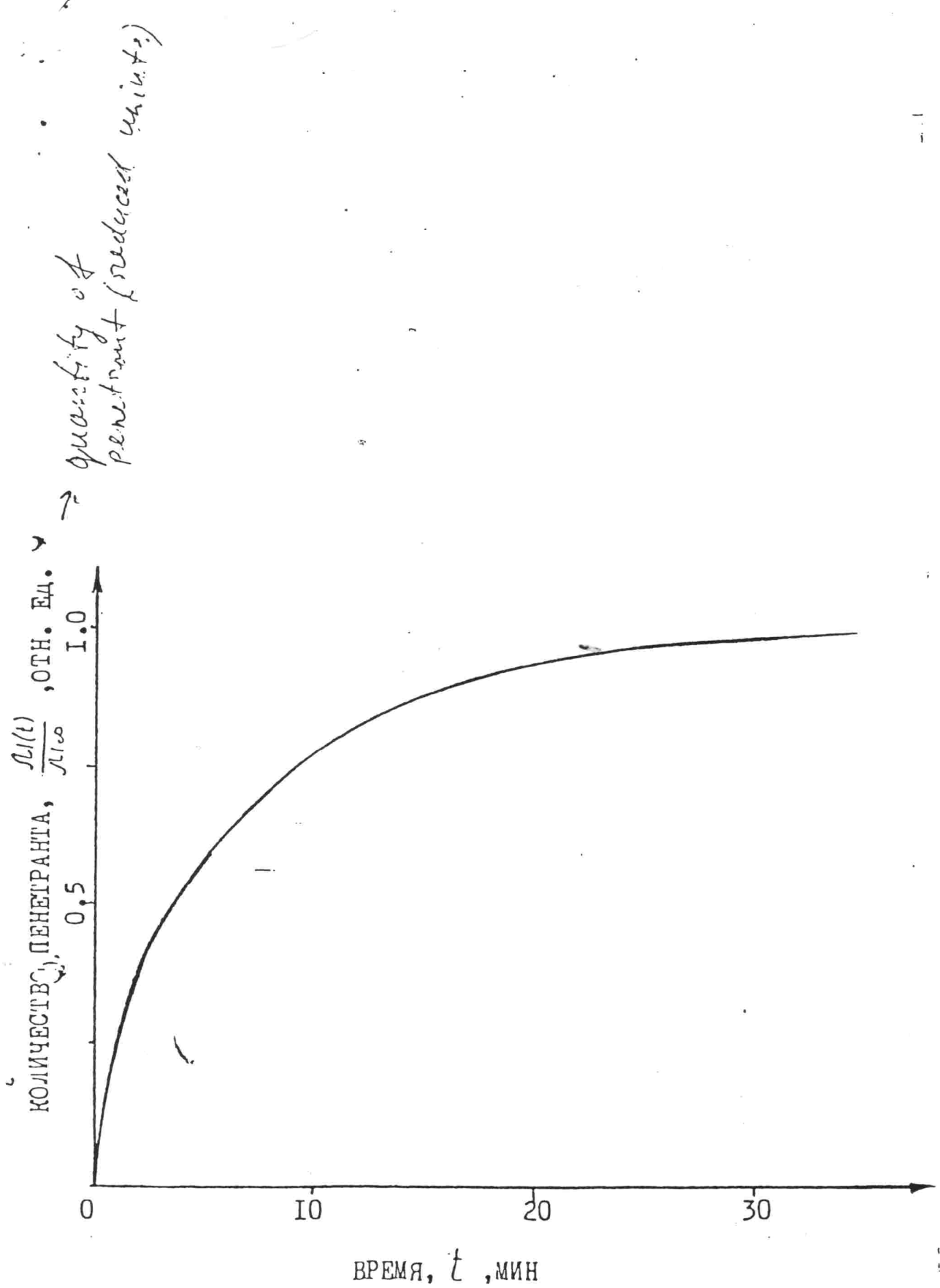
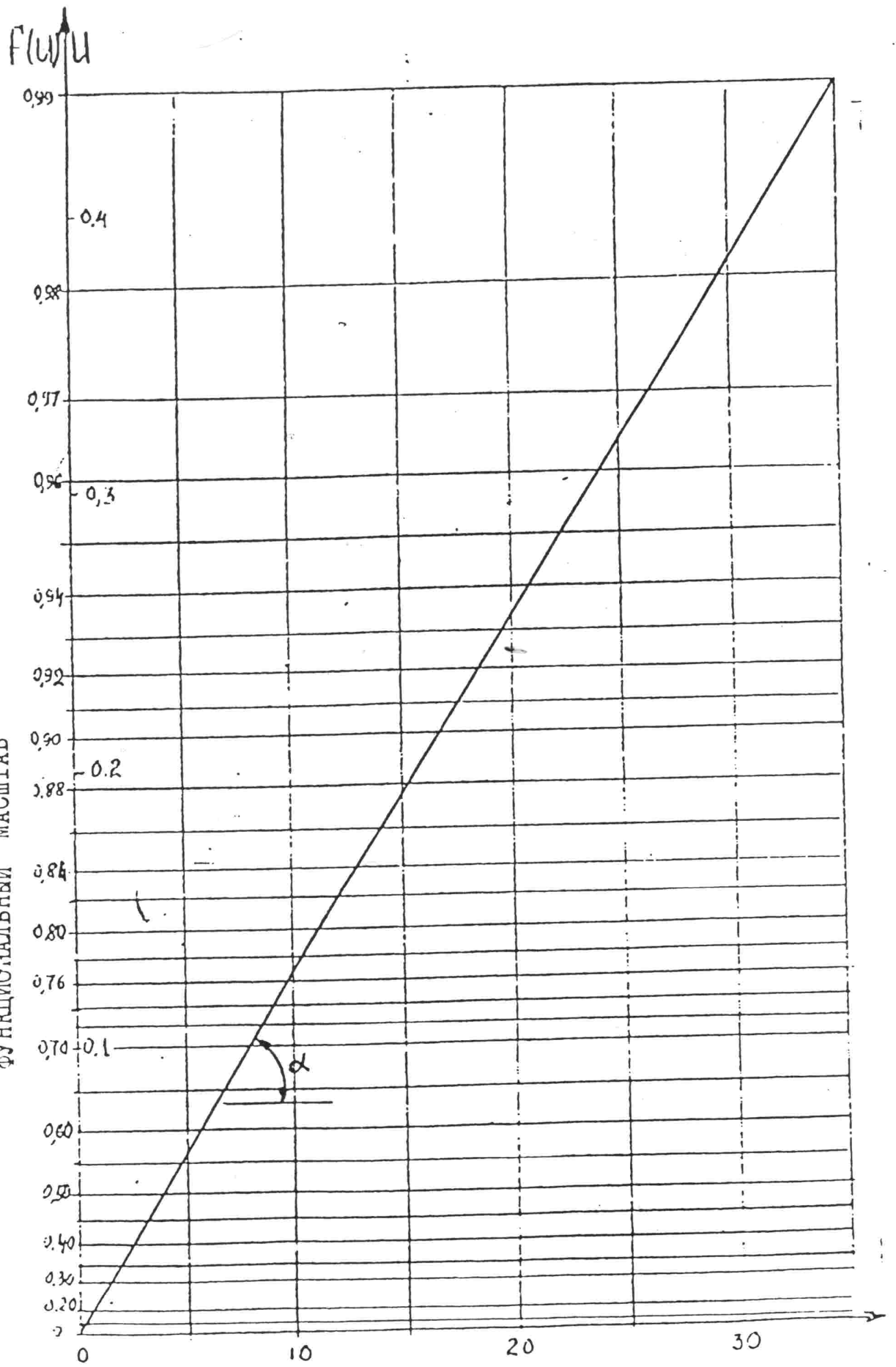


Fig. 2a

Functional scale
ФУНКЦИОНАЛЬНЫЙ МАСШТАБ



ВРЕМЯ t , МИН

time, min

