DILLARD UNIVERSITY
NEW ORLEANS

Branson, Herman

Cincinnati, Ohio
3005 Walter Street
August 7, 1940

	ERE			
Smk				13

Mr. Edwin Embree
4901 Ellis Avenue
Chicago, Illinois

Dear Sir:

I am writing you concerning a fellowship plan which might be of inestimable aid to young men and women holding the Ph.D. degree with research proclivities or others of equivalent training in the small southern college. It is unnecessary to go into the details of the lack of equipment, library facilities and stimulating in-field companionship that may exist in the small school. The instructor often finds it easier to forget his field and to start thinking of a possible administrative position, or he may become a faculty expert on bridge. Since there is little chance of his getting leave of absence for several years and he may not be able to afford it even then, the few competent papers he has produced during his graduate study may well be his total scholarly output. I believe, however, that if there were fellowships available for consecutive summers for research, many of these instructors could turn to problems in their fields which could be pursued during the school year. The stimulation and guidance of the experts during the summers would be enough to get the instructor started on a research path that would effectively combat the sterility of scholarship which otherwise may result.

Mr. Embree- Continued

The fellowships mentioned ahead might be for a total of twelve hundred dollars ($1200) to be used in thirds for any three of four consecutive summers. This arrangement would give the holder actually three years to study with the most stimulating and productive leaders without undue financial strain.

This plan was discussed with Dean J. Max Bond and President William Stuart Nelson of Dillard University who saw great merit in such a venture.

I would appreciate having your reaction to the idea here presented. If you think the plan feasible, I would like to prepare a detailed study of such a plan for presentation to the Rosenwald Board.

Yours very sincerely,

Herman Branson

Herman Branson
Instructor in Physics and Mathematics
Dillard University.

FELLOWSHIPS

August 13, 1940

My dear Mr. Branson: Your letter to Mr. Embree has been referred to me since it involves the fellowship program. I am very much interested in your proposal. This plan has been discussed by the Committee on Fellowships, but so far the Committee is of the opinion that the program should in general be confined to a period of at least six months. Summer work can often be financed by a person; the fellowships which we offer are for the major sort of effort that would, in many cases, be impossible for him to provide for himself.

The Committee has made an exception to the above rule in one or two cases since the fellowship program has been re-established, but in these cases special permission was granted because of unusual persons and unusual proposals. If you would like to apply for a series of periods of study shorter than six months at one time, I will be glad to present your case to the Committee along with any points which you wish to make in favor of such grants.

Very truly yours,

GEORGE M. REYNOLDS

GMR:MLU

Mr. Herman Branson
3005 Walter Street
Cincinnati, Ohio

DILLARD UNIVERSITY
NEW ORLEANS

Branson, H

November 16, 1940

Mr. George M. Reynolds
Director for Scholarships
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Reynolds:

Your letter of August 13th in reply to my request for the granting of fellowships which would enable the recipients to work for three out of four consecutive summers reminds me that the emphasis is upon "the major sort of effort" and "unusual persons and unusual proposals." I cannot say that my own merits such description, but the outlines more fully clothed may assist your appraisal.

A specific request for myself would be a grant of $1,200 to be used as mentioned ahead for work in mathematical biophysics beginning with the group under Professor N. Rashevsky at the University of Chicago. I have done some research and have published five papers in reputable scientific periodicals. The modicum of maturity resulting from this work and my holding the Ph. D. leads me to believe that summer work would be fruitful and would also furnish the necessary impetus for me to carry on more effectively during the school year. In addition, there is the factor of a possible need of contact with other groups of workers, say at Columbia or Woods Hole, after a line of research has been staked out. Were all of a fellowship grant expended in a single year, I would probably find it impossible to make such contact. I believe, too, that the spreading of such research work would assist that natural maturing and ripening of one's insight which I have experienced in working on some other problems.

I wrote to Professor Rashevsky last year about my coming to Chicago. He replied that I would be welcome, although I did not give him the details of this plan at that time. I shall send it on to him shortly.

As for my qualifications, my teachers and colleagues here at Dillard University, the University of Cincinnati, Virginia State College, and the University of Pittsburgh would be able to give you their opinions. I shall send you under separate cover copies of my

papers. I regret that I do not have reprints of my first note published in NATURE, 141, March 26, 1938. My most recent paper has just been accepted by the editor of SCHOOL, SCIENCE, AND MATHEMATICS and will appear soon.

My undergraduate training was received at the University of Pittsburgh and Virginia State College (B.S., 1936). On the recommendations of my instructors at Pittsburgh and Virginia State, I was given the Special Fellowship in Physics (1936-1937) at the University of Cincinnati (Ph. D., 1939). From 1937 to 1939 I held the Laws Fellowship in Physics. During the summer of 1937, I was assistant to Dr. F. F. Heyroth in preparing his book on the chemical effects of the ultraviolet. The following summer I was assistant to Dr. D. A. Wells in working on his book in dynamics. While I was working with Dr. Heyroth, he found it necessary to give up his position as abstractor in biophysics for BIOLOGICAL ABSTRACTS and recommended me for the position. I have held it since 1937 and have contributed some thirty abstracts. Since 1939 I have been instructor in mathematics and physics at Dillard University. I am a full member of Sigma Xi and was made a Fellow of the American Association for the Advancement of Science last summer.

Incidentally, I have been given the use of the Tulane University Physics Department's library, thanks to the generosity of Dr. Elliott, which enables me to carry on some work. At the present time I am working on the Sturm-Liouville problem in mathematical physics, a problem involving difference equations in quantum mechanics, methodology in the sciences, as well as reading and collecting a microfilm library in mathematical biophysics. It seems that the first two of these projects may be drawn upon for results soon.

I was born August 14, 1914. I am married and have an infant daughter. - In spite of this long documentation of my own case, I still believe that such a general plan might be a tremendous boon to many who find the battle against sterility and banality difficult. As I mentioned before, my friends in the sciences here have discussed the idea, and both our late President and Dean, Mr. William Stuart Nelson and Dr. J. Max Bond, seemed favorable.

Thanking you for your kindness in hearing me, I am

Yours very sincerely,

Herman Branson

HB:m

Herman Branson
Instructor in Mathematics & Physics

Plan of Work
Herman Branson
Howard University
Washington, D. C.

Inasmuch as this request for a grant from the Rosenwald Fund is for the continuation of work begun last summer and extending through this school year, a review of the accomplishments and advantages of the grant of last summer is the best introduction to the plan of work for the summer of 1942. Last summer I

1. Began and completed this month the research problem, Diffusion as a Function of Aggregation in Colloidal Media, which will be published in the March, 1942, issue of the "Bulletin of Mathematical Biophysics," University of Chicago Press.
2. Began and have since almost completed a long paper treating the mathematics and physics of aggregation, polymerization and diffusion in colloidal media, which will probably be published in the June, 1942, issue of the "Bulletin of Mathematical Biophysics."
3. Read, collected notes, and discussed research problems in thermodynamics of living systems and the mathematical biophysics of cell injury.
4. Gathered notes, made an outline, and discussed with Dr. Weinberg a paper on "Implications of Semantics in Negro Education," which I may complete this school year.
5. Attended class in modern algebra.
6. Attended occasional lectures by outstanding scholars, for example Prof. Teller.
7. Discussed with Dr. Nedelsky and others the problems of a survey course in the physical sciences. Those discussions have been of inestimable aid this year in planning my work in the physical science survey course at Howard University.
8. Reviewed a paper submitted for publication in the "Bulletin of Mathematical Biophysics."
9. Formed some valuable friendships among scientists and received the stimulus of contact with an excellent research group.

The work of the summer of 1942 will be a continuation of the research listed ahead and on the mathematical biophysics of hearing. This last topic seems to be full of good problems and has hardly been touched. My work at Howard University suggests two additional emphases for the summer: spectroscopy and the physical science survey course. The first arises from my need for an experimental research program. We have some excellent equipment in spectroscopy which is at my disposal. I have been giving some attention to it this year and I am giving a course now covering the elementary aspects. From the physical science survey course I have problems of presentation, of demonstrations, of evaluation and of aims and objectives which I would like to discuss with the University of Chicago group.

My estimate, however, is that I shall give no more than 10 or 15 hours each week to the secondary topics leaving at least 45 hours each week for the main work of research in mathematical biophysics.

It is my belief that the work of the summer of 1942 should give more results than that of 1941. I know more about the field now; I know the people at the University of Chicago; and I have the excellent library facilities of Washington to draw on in the continuation of the work.

Plan of Work
Herman Branson
Howard University
Washington, D. C.

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3. Read, collected notes, and discussed research problems in thermodynamics of living systems and the mathematical biophysics of cell injury.
4. Gathered notes, made an outline, and discussed with Dr. Weinberg a paper on "Implications of Semantics in Negro Education," which I may complete this school year.
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My estimate, however, is that I shall give no more than 10 or 15 hours each week to the secondary topics leaving at least 45 hours each week for the main work of research in mathematical biophysics.

It is my belief that the work of the summer of 1942 should give more results than that of 1941. I know more about the field now; I know the people at the University of Chicago; and I have the excellent library facilities of Washington to draw on in the continuation of the work.

1941 JW

Name Herman Russell Branson **Field:** Physics

Instructor in Physics and Mathematics
Dillard University, New Orleans

Plan of Work

Research work with the University of Chicago group of mathematical biophysicists in the application of the methods of theoretical physics to sociological problems or to physical and mathematical problems relevant to biology.

Seeks no degree. Asks grant for three months - June to September, 1941.

Will return to present position.

Personal Data Born Pocahontas, Virginia, August, 1914. **Age:** 26
Married, one child. Parents partially dependent.

Undergraduate Work Virginia State College, B. S., 1936.

Graduate Work University of Cincinnati, Ph.D., 1939.

Experience Instructor, Dillard University, 1939 -, $1800-$2000.

Accomplishments Member of Sigma Xi.

Has had articles in Nature, Radiology, The Physical Review, School, Science and Mathematics, Science; between 20 and 30 abstracts have appeared in Biological Abstracts since 1937.

Fellowships: University of Cincinnati, 1936-37, tuition, fees, $250; 1937-38, tuition, fees, $400; 1938-39, tuition, fees, $450.

References

N. Rashevsky, University of Chicago
H. Kersten, University of Cincinnati
D. A. Wells, University of Cincinnati
J. Max Bond, Tuskegee Institute
William Stuart Nelson, Howard University

Budget Summary

Total Amount Needed	$ 855
From Applicant	455
From Fund	$ 400

AMOUNT GRANTED

Herman Branson
Dillard Univ.
New Orleans, La.

Statement of project:

The three months will be a more intensive period of research and study on a group of problems to which I have given attention for some time. My work in the past in biophysics has resulted in two papers, one in NATURE and the other in RADIOLOGY. Since coming to Dillard I have contributed only abstracts to BIOLOGICAL ABSTRACTS in this field, altho I have continued to study. I feel now that a period with the Chicago group will prime my own productivity. My goal is a research program that I can carry on from year to year within the small college framework. I shall work specifically on problems such as the mathematical biophysics of cell injury, of cell aggregates and others. Prof. N. Rashevsky of the Univ. of Chicago agrees that contact is a most important factor now and that I should be able to carry this work thru the year.

I keep a rather detailed time schedule and find that I can give from 15 to 20 hours to research each week during the school year. The time this year and last has been given to

1. Mathematical biophysics - background material and current research, including abstracts.
2. The Sturm-Liouville problem in mathematical physics - I have completed a 30 page paper but have not considered it sufficiently significant.
3. Difference equations in physics - I have a small paper that I shall soon send to a mathematics journal.
4. Methodology in the sciences - background material.
5. Microfilm and research methods - Three published notes have come from this work, one in SCHOOL, SCIENCE and MATHEMATICS, May, 1940, the other two have been accepted by the editors of SCHOOL, SCIENCE and MATHEMATICS and SCIENCE. I have prepared two additional papers relating to these topics, one "Microfilm in the Negro College" will soon be submitted, the other "Microfilm and Science Teaching" has just been completed in a first draft.

Prof. Daniel S. Elliott, head of the Physics Dept. at Tulane Univ., has most generously allowed me the use of the Tulane Physics Library. I spend each Wednesday afternoon there, gathering material to be microfilmed, reading current developments and searching out references.

My plan is to work intensively during the period of the grant with the Univ. of Chicago group of biophysicists and to bring back topics for continued research thru the school year, 1941-1942. Several research papers could - and I hope will - grow out of this work. If the contact proves stimulating, I may find myself carrying on research for the next few years - research which will lend zest and tang to one's teaching.

Letters included in this application will document the statements made ahead.

Publications of
Herman Branson
Dillard University
New Orleans, La.

1. Effects of soft x-rays on chaetopods, NATURE, 141, 554-555, March 26, 1938.

2. The differential action of soft x-rays on the anterior and posterior regions of Tubifex Tubifex, RADIOLOGY, 34, 200-204, Feb. 1940.

3. On the quantization of mass, THE PHYSICAL REVIEW, 57, 495 - 500, March 15, 1940.

4. A reader for microfilm, SCHOOL, SCIENCE and MATHEMATICS, 40, 411-412, May, 1940.

5. Microfilm equipment for the individual worker, accepted by the editor of SCHOOL, SCIENCE and Mathematics, November 10, 1940.

6. A microfilm camera, soon to appear in SCIENCE.

7. Between 20 and 30 abstracts in BIOLOGICAL ABSTRACTS since 1937.

Virginia State College
Petersburgh, Va.

Office of the Registrar
Official transcript of the record of Branson, Herman Russell.
Admitted: Sept. 21, 1934. Graduated: June 2, 1936.
Degree: B.S. (With Distinction). Major: Physics .

Record

	Weeks	Hours Rec.	Hours Lab.	Grade	Credit qr.hrs.
Fall Quarter 1934:					
Chem. 203, Qual. Anal.	12	2	8	A	5
Math. 206, Calculus	12	5		A	5
Biol. 203, Comp. Anat.	12	2	6	A	5
Phys. 206, Adv. Mech.	12	5		A	5
Winter Quarter 1935:	12				
Math. 207, Calculus	12	5		A	5
Biol. 204, Comp. Anat.	12	2	6	A	5
Chem. 204, Quant. Anal.	12	2	6	A	5
Phys. 210, Prop. of Matter	12	3		A	3
Spring Quarter 1935:					
Ed. 311, Dir. Obs. in H.S.	12	1	4	A	3
Ed. 315, High Sch. Methods	12	5		A	5
Math. 208, Calculus	12	3		A	3
Chem. 205, Quan. Anal.	12	2	8	A	5
Phys. 211, Mod. Phys.	12	3		A	3
P.E. 203, Fl.Wk.&Calis.	12	3		B	1½
Fall Quarter 1935:					
Ed. 212, Phil of Ed.	12	5		A	5
Ed. 421, Dir. Tchg.	12	6		B	5
Ger. 206, Sci. Ger. Prose	12	5		A	5
Eco. 200, Prin. of Eco.	12	3		A	3
Math. 213, Diff. Equations	12	3		A	3
Phys. 207, Elec. & Mag.	12	3		A	3
Winter Quarter 1936:					
Eco. 201, Prin. of Eco.	12	3		A	3
Eng. 208A, Shakespeare,	12	3		A	3
Phys. 207, Elec.& Mag.	12	3		A	3
Phys. 212, Adv. Phys. Lab.	12		6	A	2
Hyg. 201, School Hygiene	12	3		B	3
P.E. 202, Fl.Wk.& Calis.	12	3		B	1½
Spring Quarter 1936:					
Ed.328, Sci. in Sec. Schs.	12	3		A	3
Ed. 331, Dir. Tchg.	12	5		A	3
Eng. 208B, Shakespeare	12	3		A	3
P.E. 203, Fl.Wk.&Calis.	12	3		A	1½
Phys. 208, Elec.& Mag.	12	3		A	3

Date: Dec. 19, 1940.

J. Louise Barrett, Registrar.

UNIVERSITY OF PITTSBURGH
OFFICE OF THE REGISTRAR

Scholastic Record of Branson, Herman Russell (Mr.)

Record IN COURSE

Courses	No.	CR.	GR.	Q.P.	COURSES	NO.	CR.	GR.	Q.P.
1st. Sem. 1932-33					1st. Sem.1933-34				
Chem.	3	4	A	12	Chem.	31	4	A	12
Col. Or.	1	1	A	3	Eng.	21	3	B	6
Eng.	1	4	B	8	Germ.	1	3	A	9
Math.	9	3	A	9	Psych.	3	3	A	9
Zool.	1	4	A	12	Physics	1	4	B	8
Ph. Ed.		1	P	-					
2nd Sem. 1932-33					2nd Sem. 1933-34				
Chem.	4	4	A	12	Chem.	32	4	A	12
Col. Or.	2	1	A	3	Eng.	22	3	A	9
Eng.	2	4	A	12	Germ.	2	3	A	9
Phil.	9	3	A	9	Psych.	6	1	A	3
Zool.	2	4	A	12	Psych.	4	3	A	9
Ph. Ed.		1	P	-	Physics	2	4	A	12
	Totals 34			92		Totals 35			98

UNIVERSITY OF CINCINNATI
THE GRADUATE SCHOOL OF ARTS AND SCIENCES

Official Transcript of the Record of ...Herman Russell Branson...

Bachelor's Degree from ...B.Sc.,.Virginia.State.College,.1936...

Attendance: Admitted September,.1936...to.the.Graduate.School.of.Arts and Sciences

Attended from September, 1936 to June, 1939

Graduated June, 1939 Degree Doctor of Philosophy

One Credit-- one lecture period of 50 minutes, or one laboratory period of three hours.

Course Number	Descriptive Title of Course	1st Semester Credits	2nd Semester Credits
	1936-1937		
127	Physics----Heat and Thermodynamics	3	-
150	Physics----Advanced Experimental Physics	4	2
152	Physics----Introduction to Theoretical Physics	3	3
167	Physics----X-ray and Crystal Structure	2	-
109	Mathematics-Differential Equations	-	3
170	Physics ---- Research	-	2
	1937-1938		
155	Physics----Thermodynamics	2	-
108	Basic Science-Theory and Functions of a Complex Variab le	3	3
168	Physics----Electrodynamics	3	3
107	Basic Science----Quantum Mechanics	3	-
170	Physics----Research for the Doctorate	2	1
106	Basic Science----Physical Chemistry	-	3
129	Physics----Physical Optics	-	3
169	Physics----Quantum Electrodynamics	-	2
	1938-1939		
163	Physics----Quantum Mechanics	3	3
170	Physics----Research	1	3
106	Mathematics-Tensor Analysis and Relativity	2	-
145	Mathematics-Integral Equations	2	-
160	Physics----The Position	2	2

This transcript issued December 9, 1940

LETTERS OF REFERENCE

Herman Branson

Mr. N. Rashevsky, Department of Physiology, University of Chicago

While I do not know much about Dr. Branson, and have never met him personally, I am very much in favor of his plan, provided he turns out to be a good research worker. The reprints of his publications, which he sent me, do indicate that such is the case. I am making inquiries from the different persons which he gave as references concerning his general character. I suppose that in connection with his application, you have already made similar inquiries and have all the data concerning him available in your files.

If, as I said above, the result of those inquiries indicate that Dr. Branson is the right kind of person, I would be very much pleased to have him come during the next summer, and start on some research problem in Mathematical Biophysics. It is quite true that generally speaking a longer stay would be more desirable. In as much, however, as Dr. Branson has already had experience in original research work, even a connection for only three months with our research group would be beneficial to him, and would help him carry on alone the research work during the remainder of the year. I have had some correspondence with Dr. Branson during the past year or two. From this correspondence I understand that he has already familiarized himself pretty thoroughly with the subject of Mathematical Biophysics by studying all available publications. Under those circumstances, even a relatively short contact with our research group here would be rather useful. Personally, of course, I am anxious to have as many young research workers enter that field as possible. Therefore, I am heartily backing Dr. Branson's propositions subject to the provisions mentioned at the beginning of this letter.

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Mr. H. Kersten, Associate Professor of Biophysics, University of Cincinnati, O.

Mr. Branson did part of his doctor's research work under my direction and was a student in one of my classes. He presents a polished appearance and has the manners of a gentleman. His ability is above the average and he is a hard worker.

My only objection to him is that his optomism often leads him to rate his ability too highly, and his desire to put his "best foot forward" leads him to approach slightly the realm of dishonesty. For example, the list of publications attached leads one to suppose that these are his creations, exclusively. If you will look them up you will find that he is co-author on the three most important publications.

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Mr. D. A. Wells, Associate Professor of Physics and Chairman of Graduate Work in Physics, University of Cincinnati, Ohio

I have known Dr. Branson for over four years and, in all sincerity, I cannot speak too highly of him.

As a student of science and mathematics, he is outstanding by any basis of comparison. His graduate work here at the University of Cincinnati was excellent in every respect and he showed far better than average creative ability. He is an indefatigable worker.

As to personality, Dr. Branson is also outstanding. I have never known a student, colored or white, with a more pleasing unaffected manner. His dignity and personality take him completely above any feeling of racial distinction.

Dr. Branson is well prepared to carry on research in mathematical biophysics. I believe his contacts with Dr. Rashevsky and others would be of inestimable value to future contributions which he will make.

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Dr. J. Max Bond, School of Education, Tuskegee Institute, Alabama

Mr. Branson of Dillard University is, in my opinion, the best informed man that I have had the pleasure to know. His scholarly attainment as a teacher at Dillard University made me feel that this was a man who was deserving of any opportunity that might be made available for study.

He is such an exceptional and promising young person that I feel I cannot adequately describe his many qualifications.

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Mr. William Stuart Nelson, Dean of the School of Religion, Howard University, Washington, D. C.

During the year of my association with Dr. Herman Branson at Dillard University, I was most favorably impressed with his teaching ability, his research interest, and his personal qualities. I feel that any assistance which may be provided to make possible continued research with him will be most fruitfully spent. To me, as a layman, the plan which Dr. Branson presents to the Rosenwald Fund appears to have merit.

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JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. H. Kersten

University of Cincinnati, Ohio

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

Director for Fellowships

REPORT

Mr. Branson did part of his doctor's research work under my direction and was a student in one of my classes.

He presents a polished appearance and has the manners of a gentleman.

His ability is above the average and he is a hard worker.

My only objection to him is that

OVER

his optomism often leads him to rate his ability too highly, and his desire to put his his "best foot forward" leads him to approach slightly the realm of dishonesty. For example the list of publications attached leads one to suppose that these are his creations, exclusively. If you will look them up you will find that he is co-author on the three most important publications.

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

He has no personal handicaps.

Signed Harold J. Jensen

Position or Title Assoc. Prof. of Biophysics

Address Univ. Cincinnati.

Date Jan 14 '41.

Please return to the Director for Fellowships, Julius Rosenwald Fund, 4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

JULIUS ROSENWALD FUND

GR 1941

4901 ELLIS AVENUE

CHICAGO

Application and accompanying documents should be filed as early as possible for the convenience of the Fellowship Committee, preferably during the early autumn. No application can be considered by the Committee unless the completely filled-out blank and all of the materials requested reach the Director for Fellowships by January 5, 1942.

Negro ☒ White Southerner ☐

Name in full Herman Russell Branson

Present address Chemistry Building, Howard University, Washington, D.C.
(City) (State)

Permanent address Box 32, Pocahontas, Virginia
(City) (State)

Present position (be specific) Assistant Prof. of Physics and Chemistry

Institution or organization Howard University Annual salary $2300.

Address Washington, D.C.
(City) (State)

Specific Field ~~Mathematical Biophysics~~ Biology

Concise statement of plan of work Research on mathematical physical problems arising in diffusion, thermodynamics, sensory perception, etc. with the University of Chicago group of mathematical biophysicists.

Dates of period for which grant is desired June 5 to September 5, 1942.

What is your estimate of the total duration of the proposed project? Continuous

Will you return to your present position? Yes If not, for what position do you seek further training?

If you contemplate graduate study, please fill in the following:

What institution do you wish to attend? University of Chicago

Have you been admitted? Yes For what degree will you work? None

Under whose supervision? Prof. N. Rashevsky Department of Math. Biophysics

Personal History

Place of birth Pocahontas, Virginia Date of birth August 14, 1914

Single, married, widowed, divorced Married

Name and address of wife or husband Corolynne Gray Branson, 1623 S St., N.W., Wash., D.C

Occupation and salary of wife or husband Housewife

Number and ages of children One; eighteen months.

Dependents 3 To what extent? $10 per month Relationship Parents and Grandp.

Have you any constitutional disorder or physical disability? None.

(The Committee on Fellowships reserves the right to require a full physical examination.)

Education

One official transcript of your college and university records together with *five copies* must be submitted with your application. (Copies may be typed by the applicant.)

	Name of Institution	Period of Study (Give dates)	Degrees, Diplomas, Certificates (Give dates)
College	Univ. of Pittsburgh	1932 - 1934	
	Virginia State College	1934 - 1936	B.S. (1936)
University	Univ. of Cincinnati	1936- 1939	Ph.D. (1939)
Professional or technical			
Special study	Univ. of Cincinnati	Summer, 1940	
	Univ. of Chicago	Summer, 1941	

Significant extra-curricular activities Newspaper, sceicne club, student government, camera club, etc.

Experience

Give record chronologically.

Institution or Organization	Address	Position	Inclusive Dates	Annual Salary
Basic Sci. Research	Dr. F. F. Heyroth Univ. of Cincinnati	Research Assistant	Summer, '37	.50 hour
Physics Dept.	Prof. D. A. Wells Univ. of Cincinnati	"	Summer, '38	.50 hour
Dillard Univ.	New Orleans, La.	Instructor	1939-1940	$1800.
Dillard Univ.	New Orleans, La,	"	1940-1941	$2000.
Howard University	Washington, D.C.	Asst. Prof.	1941 -	$2300.

Accomplishments

1. Of what learned, scientific, or artistic societies are you a member? American Math. Society, Fellow American Physical Society, American Association for the Advancement of Science, and Sigma Xi.

2. What research or creative work have you done? (If in business or a profession, give evidence of standing and achievements.)

1. Research in electronics
2. " " x-rays
3. " " Biophysics
4. Research in theoretical physics.
5. " " mathematics.
6. " on microfilm.

3. Publications (Books and articles. Give title, date, and publisher.)

See appended list carrying nine articles.

4. List scholarships or fellowships you have previously held or now hold, stating in each case the places and periods of tenure, the studies pursued during your incumbency, and the amounts of the stipends.

Special Fellow in Physics, U. of Cincinnati, 1936-1937, $250 plus tuition
Laws, 1937-1938, $400 "
Laws, 1938-1939, $450 "
Alpha Phi Alpha Fraternity Fellowship, 1938-1939, $250.
Rosenwald Fellowship, Summer 1941, $400.

Budget Estimate

Room and board	$ 400.00
Clothing	100.00
Insurance	20.00
Tuition including wife's	200.00
Transportation	100.00
Miscellaneous books, publications	100.00
Maintenance of home in Washington, care of baby, etc.	$ 100.00
Total amount needed	$ 1020.00
Amount applicant can provide	$ 420.00
Amount requested from Fund	$ 600.00

Clip (do not paste) photograph here

If you have applied or expect to apply elsewhere for any fellowship for the same period (which is, of course, permissable) state the facts regarding such application.

I have not applied elsewhere.

References

List references from whom confidential information may be obtained concerning your professional qualifications and from whom expert opinion may be obtained as to the value and practicability of your proposed plan of work.

Name of Reference	Position	Address
Dr. N. Rashevsky	Assoc. Prof. of Math. Biophysics	Univ. of Chicago, Chicago, Illinois
Dr. D. A. Wells	Assoc. Prof. of Physics	Univ. of Cincinnati, Cincinnati, Ohio
Dr. H. Kersten	Assoc. Prof. of Biophysics	Univ. of Cincinnati, Cincinnati, Ohio
Dr. J. Max Bond	Prof. of Education	Tuskegee Institute, Tuskegee, Alabama
Dr. Charles H. Thompson	Dean of the College of Liberal Arts	Howard University, Washington, D.C.

Statement of Plan of Work

Submit a statement giving detailed plans for your work during the tenure of your fellowship. This statement should include: (1) a full description of the project, including its character, scope, and significance; (2) the present state of the project (time of commencement, progress to date, etc.) and expectation as to completion; (3) the proposed university, institution of similar grade, or other place where work would be carried on, and the authorities with whom it would be done; (4) your expectation as to publication or use of the results of your study; (5) subsequent plans for your career.

Your plan of work should be carefully prepared. Submit *seven copies* typed on 8½"x11" paper. Your name should be on each sheet.

SIGNATURE Herman Branson

Publications of
Herman Branson
Howard University
Washington, D.C.

1. NATURE, March 22, 1938.

2. RADIOLOGY, 34, February, 1940.

3. THE PHYSICAL REVIEW, 57, March 15, 1940.

4. SCHOOL, SCIENCE AND MATHEMATICS, 40, May, 1940.

5. SCHOOL SCIENCE AND MATHEMATICS, 41, Feb., 1941.

6. SCIENCE, 93, March 28, 1941.

7. "Diffusion as a Function of Aggregation in Colloidal Media," BULLETIN OF MATHEMATICAL BIOPHYSICS, Univ. of Chicago Press, Jan. 1942. Accepted for publication.

8. "Microfilm in the Negro College," JOURNAL OF NEGRO EDUCATION, in press for Jan., 1942 issue.

9. About 30 abstracts for BIOLOGICAL ABSTRACTS since 1937.

10. Paper in mathematical biophysics which may be submitted before the grants are made. Otherwise planned for the June, 1942 issue of the BULLETIN OF MATHEMATICAL BIOPHYSICS.

You have reprints of all the articles which are available. Reprints of the others will be sent you as soon as they are received.

Anyone who can
even talk with
Rachmaninoff is way
beyond me. He should
have a fellowship,
but I urge that it
be for more than
summer quarter

WH

A

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. D. A. Wells

University of Cincinnati, Ohio

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

Director for Fellowships

REPORT

I have known Dr. Branson for over four years and, in all sincerity, I cannot speak too highly of him.

As a student of science and mathematics he is outstanding by any basis of comparison. His graduate work here at the University of Cincinnati was excellent in every respect and he showed far better than average creative ability. He is an indefatigable worker.

As to personality, Dr. Branson is also outstanding. I have never

OVER

known a student, colored or white, with a more pleasing unaffected manner. His dignity and personality take him completely above any feeling of racial distinction.

Dr. Branson is well prepared to carry on research in mathematical biophysics. I believe his contacts with Dr. Rashevsky and others would be of inestimable value to future contributions which he will make.

If you have specific questions regarding Dr. Branson I shall be glad to answer any and all that I can.

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities? (yes - see remarks above)

Signed D. A. Wells

Position or Title Associate Prof. of physics and

Address Chairman of Graduate Work in Physics

University of Cincinnati, Cincin. O Date Jan 14, 1941

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

A

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Dr. J. Max Bond

Tuskegee Institute, Alabama

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

Director for Fellowships

REPORT

Mr. Herman Branson of Dillard University is, in my opinion, the best informed man that I have had the pleasure to know. His scholarly attainment as a teacher at Dillard University made me feel that this was a man who was deserving of any opportunity that might be made available for study.

He is such an exceptional and promising young person that I feel I cannot adequately describe his many qualifications.

J. Max Bond, Director
School of Education -
Tuskegee Institute, Alabama

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

Signed _____

Position or Title _____

Address _____

_____ Date _____

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

A

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. William Stuart Nelson

Howard University, Washington, D. C.

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

Director for Fellowships

REPORT

During the year of my association with Dr. Herman Branson at Dillard University, I was most favorably impressed with his teaching ability, his research interest, and his personal qualities. I feel that any assistance which may be provided to make possible continued research with him will be most fruitfully spent. To me, as a layman, the plan which Dr. Branson presents to the Rosenwald Fund appears to have merit.

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

Signed C. Stuart Nelson

Position or Title Dean of the School of Religion

Address Howard University

Washington, D. C. Date January 27, 1941.

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

The University of Chicago
Department of Physiology

MATHEMATICAL BIOPHYSICS
5822 DREXEL AVENUE

January 2, 1941

Mr. George M. Reynolds
Director for Scholarships
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

Dear Mr. Reynolds:

Dr. Herman Branson of Dillard University has written to me recently concerning his desire to join the Mathematical Biophysics research group here during the coming summer. He also writes me that he is applying to the Rosenwald Fund for a grant which would enable him to realize his plan, and he asks me to write to you, giving my point of view of the whole question.

While I do not know much about Dr. Branson, and have never met him personally, I am very much in favor of his plan, provided he turns out to be a good research worker. The reprints of his publications, which he sent me, do indicate that such is the case. I am making inquiries from the different persons which he gave as references concerning his general character. I suppose that in connection with his application, you have already made similar inquiries, and have all the data concerning him available in your files.

If, as I said above, the result of those inquiries indicate that Dr. Branson is the right kind of person, I would be very much pleased to have him come during the next summer, and start on some research problem in Mathematical Biophysics. It is quite true that generally speaking a longer stay would be more desirable. In as much, however, as Dr. Branson has already had experience in original research work, even a connection for only three months with our research group would be beneficial to him, and would help him carry on alone the research work during the remainder of the year. I have had some correspondence with Dr. Branson during the past year or two. From this correspondence I understand that he has already familiarized himself pretty thoroughly with the subject of Mathematical Biophysics by studying all available publications. Under those circumstances, even a relatively short contact with our research group here would, I believe, be rather useful.

Personally, of course, I am anxious to have as many young research workers enter that field as possible. Therefore, I am heartily backing Dr. Branson's propositions subject to the provisions mentioned at the beginning of this letter.

Yours very truly,

N. Rashevsky

NR:Hdy

FELLOWSHIPS

April 12, 1941

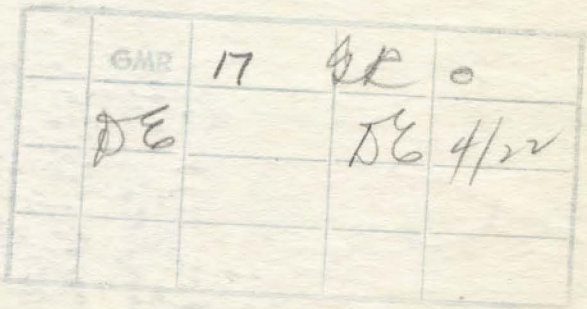
My dear Mr. Branson: I am enclosing an announcement of your award of $400 for special work at the University of Chicago during the coming summer. This grant is being made contrary to our usual policy, since our usual minimum period of continuous study is six months. We hope that the results obtained under this grant will be satisfactory to you and to us. We will be glad to receive a general report of progress after you have finished your work here.

Very truly yours,

GMR:MLU

Mr. Herman Russell Branson
Dillard University
New Orleans, Louisiana

Dillard University
New Orleans, La.
April 16, 1941



Mr. George M. Reynolds
The Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Reynolds:

Please accept my thanks for the Scholarship Committee for granting me a fellowship of $400 to be used in research in mathematical biophysics this summer. I am more than eager to accept. In the meantime, I shall go ahead with my plan of work with the biophysics group under Professor Rashevsky. I, too, hope that this deviation from your usual program will be happy.

Yours very sincerely,

Herman Branson

Herman Branson.

ACCOUNT Negro Fellowships APPROPRIATION No. 40-11

NAME OF STUDENT Herman Russell Branson

ADDRESS

Institution Attending - University of Chicago

INSTITUTION al Position - Instructor in Physics and Mathematics, Dillard

Specific Field - Physics

RECOMMENDED BY

STATEMENT OF OFFER

GMR to Mr. Branson - 4/11/41

"It is a pleasure to inform you that you have been selected by the Committee on Fellowships of the Julius Rosenwald Fund to receive a grant of four hundred dollars ($400) to assist you in carrying forward your studies in mathematical biophysics at the University of Chicago for a three-month period beginning June 1, 1941."

AMOUNT OF OFFER $400 PAYMENT DATES

CHECKS PAYABLE TO

TIME PERIOD OF OFFER Three months

APPROVED BY AUTHORIZED BY

PAYMENTS

DATE	EXPLANATION	AMOUNT	DATE	EXPLANATION	AMOUNT

April 11, 1941

My dear Mr. Branson: It is a pleasure to inform you that you have been selected by the Committee on Fellowships of the Julius Rosenwald Fund to receive a grant of four hundred dollars ($400) to assist you in carrying forward your studies in mathematical biophysics at the University of Chicago for a three-month period beginning June 1, 1941.

Will you please let us know at once whether or not you can accept this grant? An official announcement of the Committee's selections will be made soon and it can include only those from whom acceptances have been received.

Very truly yours,

GMR:MLU

GEORGE M. REYNOLDS

Mr. Herman Russell Branson
Dillard University
New Orleans, Louisiana

April 22, 1941

Dear Mr. Branson: I have seen your recent letter to Mr. Reynolds accepting the fellowship of $400 awarded to you for study at the University of Chicago this summer. When you are ready to begin work under this grant, please let me know whether you would prefer to receive it in monthly installments or to receive the full amount at the beginning of the summer quarter.

Very truly yours,

DOROTHY A. ELVIDGE

DAE:AM

Mr. Herman Branson
Dillard University
New Orleans, Louisiana

May 6, 1941

Dear Mr. Branson: I am returning to you under separate cover the publications which you submitted with your application for a fellowship. With this I am enclosing some extra copies of your transcripts and a a group of letters addressed to you regarding your publications.

Very truly yours,

WILLIAM C. HAYGOOD
Acting-Director
for Fellowships

WCH*MLU

Mr. Herman Branson
Dillard University
New Orleans, Louisiana

Box 27

New Orleans, La.
Dillard University
June 1, 1941

Miss Dorothy A. Elvidge, Comptroller
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Miss Elvidge:

I shall arrive in Chicago June 7th and shall begin work immediately. Inasmuch as I shall not have to pay any fees until the beginning of the Summer Quarter I shall not need my Rosenwald grant before the 15th of June. I prefer that you make payment in a single sum.

My address in Chicago is not certain. I hope to stay at International House until the quarter closes at which time a University apartment may be available.

Yours very sincerely,

Herman Branson

Herman Branson.

MLK - Mss

FELLOWSHIPS

June 5, 1941

Dear Mr. Branson: Your suggestion of payment of your fellowship grant in a single sum on June 15 is entirely agreeable to us. When you are settled in the City, please call me, Drexel 7100, letting me know to what address the check should be sent.

Very truly yours,

DOROTHY A. ELVIDGE

DAE:AM

Mr. Herman Branson
Box 27, Dillard University
New Orleans, Louisiana

	WCH	13	WCH	13
	DE		DE	0

June 11, 1941
5822 Drexel Avenue
Chicago, Illinois

Mr. George M. Reynolds
Director for Scholarships
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Reynolds:

I have been working with the Univ. of Chicago group of Mathematical Biophysicists since June 6th. The work is interesting and I believe that the results will be satisfactory to the Fund. I have been given office space, the necessary keys to the building and the other items too trivial for mention. The work so far is a over-view of certain problems. One of which I have singled out for thorough investigation.
Some time back I asked that my fellowship check be mailed to me about the 15th of June. I would appreciate your directing the comptroller to mail it to me at the Mathematical Biophysics building, 5822 Drexel. We are living at 4627 Champlain, OAKland 6763.

LDE
6/13/41

Yours very sincerely,

Herman Branson

Herman Branson.

FELLOWSHIPS

June 13, 1941

Dear Mr. Branson: Mr. Reynolds has resigned his position with the Julius Rosenwald Fund to accept a post in Washington, and your letter of June 11 has come to me for answer.

I am indeed glad to hear that you are comfortably settled in Chicago and that you have begun your work. If you are over in this neighborhood I hope you will drop in for a talk.

Miss Elvidge will mail your check to you in accordance with your instructions.

Sincerely yours,

WILLIAM C. HAYGOOD

WCH:MLU

Director for Fellowships

Mr. Herman Branson
5822 Drexel Avenue
Chicago, Illinois

Julius Rosenwald Fund

4901 Ellis Avenue
CHICAGO

FELLOWSHIPS

To

Mr. Herman R. Branson
Mathematical Biophysics Building

5822 Drexel Boulevard
Chicago, Illinois

Payment Voucher No. 3079

Date June 15, 1941

Payment in full of award of $400 to assist in carrying forward studies in mathematical biophysics at the University of Chicago for a three-month period beginning June 1, 1941 - - - $400.00

Ck.#25162

Accounts	Appropriation No.	Debit	Credit
Negro Fellowships	40-11	$400.00	

Prepared by	Checked by	Posted by	
AM			Comptroller

BIOLOGICAL ABSTRACTS
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA

ISSUED, BEGINNING WITH THE LITERATURE OF 1926, WITH THE COOPERATION OF BIOLOGISTS GENERALLY

PUBLISHED UNDER THE AUSPICES OF THE UNION OF AMERICAN BIOLOGICAL SOCIETIES

September 23, 1941

Dr. Herman Branson
Department of Physics
Dillard University
New Orleans, Louisiana

Dear Doctor Branson:

We shall greatly appreciate if you will let us have some abstracts for the JOURNAL OF PHYSICAL CHEMISTRY within the next two weeks. We are assembling an issue for the press and we are very anxious to include your abstracts.

Sincerely,

H. R. Rehill

HRR:ca

H. R. Rehill

HOWARD UNIVERSITY
WASHINGTON, D. C.

October 28, 1941

DEPARTMENT OF CHEMISTRY

	WCH	31	WCA	6

Dr. William Haygood
The Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

Dear Dr. Haygood:

Soon after I was in to see you this summer, I received an offer to come to Howard University as Assistant Professor of Physics and Chemistry. The problems of moving, planning programs and getting adjusted have kept me from sending you a report of the summer until now.

I think the two letters from Professor Rashevsky are probably more adequate summaries of the work than anything I may say. I am sending you the original letters and copies for your files, for I would like the return of the originals. In addition to the work in biophysics, the fellowship enabled me to discuss with Drs. Weinberg and Nedelsky the physical science survey course. These men have had wide experience in such courses and their conversations have been of great assistance to me this year at Howard where I have such a course.

I should like to continue with my original plan of applying for a grant for work next summer, 1942. I wonder if it will be necessary to submit all the records that I have in the past or will these letters of Professor Rashevsky and his recommendations mailed directly to you be sufficient.

The work at Howard is opening up several interesting research avenues where assistance from the Rosenwald Fund could be of inestimable worth and the returns in the form of publications, outfitting research units, and training of graduate students very satisfactory. I should like to discuss this with you if you are in Washington this year.

Yours very sincerely,

Herman Branson

Herman Branson

HB:J
Enclosures

THE BULLETIN OF
MATHEMATICAL BIOPHYSICS
Editorial Office: 5822 Drexel Avenue, Chicago, Ill.
Business Office, 5750 Ellis, University of Chicago Press

Editor:
N. RASHEVSKY
The University of Chicago

September 29, 1941

Dr. Herman Branson
Chemistry Building
Howard University
Washington, D. C.

Dear Dr. Branson:

I have your letter of September 25, and accordingly, I am substituting another paper into the space that was reserved for yours in the next December issue. I hope, however, to get your paper very soon, so as to make sure to get it into the March issue. In your previous letter, you said you intended to send us two papers, one for the December, and one for the March issue. I wonder to what extent your original schedule has been changed in that respect. Of course, I cannot promise anything definite about the March issue at present, but in principle I am not opposed to having two papers by one author in the same issue. In any case, I hope that we'll have one paper in the March, and one paper in the June issue from you.

I am very glad to learn of your opportunities at Howard. What I think you should do, amongst other things, is to organize a seminar in Mathematical Biophysics. Such things are being done already in one or two universities in this country, and even in a couple of places abroad. Of all the persons outside Chicago, you are at present, unquestionably the best qualified to run such a seminar, and I think it would be very desirable for you to do that. You would, of course, have to confine yourself, for the first year at least, to mere reviews of the subject. But if you will continue your own research work in this field, you will unquestionably have, before very long, some students helping you along in your work.

Dr. Householder and Dr. Weinberg are still on their vacation. Mr. Landahl joins me in sending you our best regards,

Yours very cordially,

(signed) N. Rashevsky
dy.

N. Rashevsky

NR:Hdy

THE BULLETIN OF
MATHEMATICAL BIOPHYSICS
Editorial Office: 5822 Drexel Avenue, Chicago, Ill.
Business Office, 5750 Ellis, University of Chicago Press

Editor:
N. RASHEVSKY
The University of Chicago

September 4, 1941

Dr. Herman Branson
Department of Physics
Howard University
Washington, D. C.

Dear Dr. Branson:

I was very sorry not to have seen you before you left Chicago. I was happy, however, to learn from Dr. Householder that on one hand, you had a very productive summer, and on the other hand, which is still better, you landed a job at Howard University. This should give you now plenty of opportunity for a very successful scientific career.

I understand from Dr. Householder that you have a short note practically ready, and a larger paper, which you plan to submit later on. I wonder whether you would like to have that short note published in the next December issue of the Bulletin? This could be done, provided the size of that note does not exceed ten typewritten pages, and provided I have the complete manuscript ready for publication not later than the 5th of October.

As you know, there will, of course, be a charge for publication, which will amount to approximately $20 for a paper of this size. The exact amount will be given to you a few days after receipt of the manuscript.

Since I must plan the December issue right now, I would appreciate your letting me know immediately whether you plan to send in that paper before October 5 or not, so that I can make my arrangements accordingly. I would like to have your reply within a week.

Hoping to see you sometime in the future, I remain, with best regards to Mrs. Branson and yourself,

Yours very cordially,

(signed) N. Rashevsky

N. Rashevsky

NR:Hdy

November 6, 1941

Dear Mr. Branson: In response to your letter of October 28 I am enclosing an application blank. As you know, your application is a bit unusual in that it contemplates summer work only. Since it will have to be in competition with all requests for the full period it would be well for you to submit a complete set of records just as if you were applying for a full fellowship for the first time.

I am returning the original copies of Professor Rashevsky's letters since I will have to write directly to him in the usual course of obtaining recommendations.

I am still sorry to know that Dillard lost you, but glad to know that you are so happily situated at Howard University. I look forward to seeing you on my next visit to the campus.

Sincerely yours,

WILLIAM C. HAYGOOD

WCH:MLU
Enc.

Mr. Herman Branson
Department of Chemistry
Howard University
Washington, D. C.

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. N. Rashevsky

University of Chicago

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

William C. Haygood

Director for Fellowships

REPORT

Dr. Herman Branson has spent the summer quarter of 1941 with the Mathematical Biophysics group of the University of Chicago, and has proved to be a man of outstanding abilities. ~~The attached~~ plan of work ~~prepared by Dr. Branson~~ meets entirely with my approval. Personally I would like very much to see Dr. Branson working here not only for the short period of a summer, but for a considerably longer time, and I hope that sometime in the future it will be possible to make some arrangements for a Fellowship of a longer duration. I quite agree with Dr. Branson that his work in the summer of 1942 should give more results than that in 1941, because he is now rather thoroughly acquainted with the field, and will not have to spend any time in preparatory work.

I strongly recommend that the Rosenwald Fund make a favorable decision on Dr. Branson's application.

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities? Yes

Signed N. Rashevsky

Position or Title Associate Professor of Mathematical Biophysics

Address University of Chicago

Chicago, Illinois Date January 9, 1942

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

a.

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. J. Max Bond

Tuskegee Institute, Alabama

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

William C. Haygood

Director for Fellowships

REPORT

January 14, 1942

Last year I reported to the Fund that I thought Mr. Herman Branson was about the best person that I had met. I still hold to that view. He is a man of good intellect, high scholarship, good insight, and training. He is worthy for consideration for a Fellowship and will make good use of his time in the event that a scholarship award is made available to him. Again may I say that Mr. Branson is an outstanding candidate for any scholarship award.

J. Max Bond

J. Max Bond, Director
School of Education

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

Signed _____

Position or Title _____

Address _____

_____ Date _____

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

a

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. Charles H. Thompson

Howard University, Washington, D. C.

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

William C. Haygood

Director for Fellowships

REPORT January 21, 1942

I am very happy to be able to give the following reaction concerning the plan of work of Dr. Herman Branson. In the first place may I state that I consider him one of the most promising of the younger Negro scientists. He is highly intelligent and has already demonstrated his "flair" for research. He happens to be in the field of Physics and Physical Science where equipment is very costly and necessary intelligent contact is scarce in such a situation as we have at Howard University. I am hoping that it will be possible to renew his grant for the summer so as to enable him to carry on his research while his enthusiasm is at its peak.

While I am not an expert in the field of Physics, nevertheless, I have been able to keep up with Dr. Branson's career for the past two years; particularly with reference to his research publications. The papers which have been accepted to date seem to me to indicate that there is no question about his ability nor about the importance of the work which he wishes to continue. I think the Fund could not invest its finances in a more profitable venture than in Dr. Branson.

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

He has no such handicaps that I know of

Signed Thos. H. Thompson

Position or Title Editor, Journal of Negro Education,

Address Howard University, Washington, D.C.

Date January 21, 1942

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

a

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. D. A. Wells

University of Cincinnati, Ohio

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

William C. Haygood

Director for Fellowships

REPORT

I cannot speak too highly of Dr Branson in every respect. I am confident that the Rosenwald foundation cannot find a better or more worthy applicant for aid. He is, in my opinion, sure to produce worthwhile or even outstanding results.

D. A. Wells

Associate Prof of Physics

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

Signed _____

Position or Title _____

Address _____

_____ Date _____

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

a

JULIUS ROSENWALD FUND

4901 ELLIS AVENUE

CHICAGO

Confidential Report on Candidate for Fellowship

Name of Candidate Mr. Herman Branson

Report Requested of Mr. H. Kersten

University of Cincinnati, Ohio

The above-named candidate has applied to this Fund for a fellowship and has given your name as a reference. The candidate's plan of work is attached. Please return it with your statement.

We shall appreciate your frank opinion of this applicant's qualifications, and an appraisal of his plan of work and of his ability to make a noteworthy contribution in his field. *An early reply will be of great assistance in allowing the Fellowship Committee sufficient time for adequate consideration of the large number of candidates.*

We request candid and critical comment. Your reply will be held in strict confidence.

William C. Haygood

Director for Fellowships

REPORT

I filled out this form last year. Since that time I have not seen the candidate nor have had any correspondence with him so must refer you to my report of a year ago, to which I can add nothing.

Harold J. Kersten

OVER

Is the candidate free from personality handicaps which would make it difficult to obtain and hold a position giving him opportunity to utilize his abilities?

Signed _____

Position or Title _____

Address _____

_____ Date _____

Please return to the Director for Fellowships, Julius Rosenwald Fund,
4901 Ellis Avenue, Chicago, Illinois. Addressed, stamped envelope is enclosed.

WCH 19

HOWARD UNIVERSITY
WASHINGTON, D. C.
DEPARTMENT OF CHEMISTRY

December 15, 1941

Mr. William Haygood
Director for Fellowships
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Haygood:

I am submitting herewith my application for a grant of $600 for the summer of 1942. Because you already have copies of my academic record and since my references have examined my record, I have not included official transcripts and five copies of each. If you require them, however, I would be very pleased either to copy the official transcripts you hold or gather transcripts from my schools if your copies are not available.

There are two other points which should be mentioned. As last summer, my wife plans to attend the graduate school at the University of Chicago. (Her field is botany.) I have included her tuition in my budget estimate. The second point is my request for $600. The increased cost of living and the greater expense of maintaining our apartment over the summer in Washington are to blame.

In looking over the work of the past nine months, I am convinced of the validity of my original contention that a grant such as the one I held gives one problems which can be completed during the school year even with a fairly heavy schedule of classes.

This request was formulated before the declaration of war. Just what effect that will have upon our scholastic program is not certain. I suppose the best procedure is to continue as though next summer can be given to the quiet pursuit of work and permit the emergency to enact any changes.

Yours very sincerely,

Herman Branson

Herman Branson

HOWARD UNIVERSITY
WASHINGTON, D. C.

DEPARTMENT OF CHEMISTRY

WCH 30 WCH 30

FELLOWSHIPS

December 29, 1941

Mr. William Haygood
The Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Haygood:

About two weeks ago, I mailed through our department secretary my application for a Rosenwald grant for next summer. I have received no acknowledgment of your receiving the packet. If you have not received it, please send me another application blank as soon as possible in order that I may meet the January 5th schedule.

Thanking you in advance, I am

Yours very sincerely,

Herman Branson

Herman Branson.

December 30, 1941

Dear Mr. Branson: Your letter of December 15 and your application for another grant has not been acknowledged sooner owing to my absence on a field trip and the long Christmas week end.

Official transcripts will not be required in your case at this time. The request for tuition for Mrs. Branson is not in order since this would virtually amount to subsidizing study for two people on one fellowship. Mrs. Branson may, of course, apply for a regular grant - one involving more than summers of work - if she wishes to do so, and I am enclosing a set of blanks for this purpose.

Sincerely yours,

WILLIAM O. HAYWOOD

WCH:MLU

Mr. Herman Branson
Department of Chemistry
Howard University
Washington, D. C.

WCH 5- WCH

HOWARD UNIVERSITY
WASHINGTON, D. C.

DEPARTMENT OF CHEMISTRY

January 2, 1942

Mr. William C. Haygood
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Haygood:

Many thanks for your letter of December 30th acknowledging my request for another grant. I did not wish Mrs. Branson's tuition to be considered as part of the grant. But wishing to be as accurate as possible, I included it in my budget. If there are no objections, you can consider it in the expenses under "Amount applicant can provide."

With best wishes for the New Year, I am

Yours very sincerely,

Herman Branson

Herman Branson.

HOWARD UNIVERSITY
WASHINGTON, D. C.

DEPARTMENT OF CHEMISTRY

March 3, 1942

	WCH	5	WCH	0

Mr. William C. Haygood
Director for Fellowships
Julius Rosenwald Fund
4901 Ellis Avenue
Chicago, Illinois

Committee folder

My dear Mr. Haygood:

I am enclosing with this letter the manuscript of a paper just completed and the proofs of an earlier one which is to appear in the March issue of the BULLETIN OF MATHEMATICAL BIOPHYSICS. The other will probably be in the September issue. It was my wish to have reprints of the March paper for you by now, but they have not come off yet. You will observe that both papers have statements of thanks to the Fund for its assistance.

Under separate cover, I am sending three copies of the January, 1942 issue of the JOURNAL OF NEGRO EDUCATION which has an article of mine on microfilm. I hope that these will not be too late for the consideration of the fellowship committee.

I have other work in progress which may be submitted before June, but it will be better to tell you of that when it is completed.

Yours very sincerely,

Herman Branson

Herman Branson

BULLETIN OF
MATHEMATICAL BIOPHYSICS
VOLUME, 4, 1942

DIFFUSION AS A FUNCTION OF AGGREGATION IN COLLOIDAL MEDIA

HERMAN BRANSON
HOWARD UNIVERSITY, WASHINGTON, D. C.

With the assumption that adsorption is a simple function of surface area, an analytical treatment is given for the dependence of the diffusion coefficient of an adsorbable solute upon the degree of aggregation of the adsorbing colloid. A simple relation is deduced after introducing some approximations. Some implications of the final diffusion equation are given.

The effects which colloids may have upon diffusion have been discussed qualitatively by N. Rashevsky (1938) and the specific problem of the adsorption of a diffusing solute by a single type of colloid has been treated by J. M. Reiner (1939). This note reports an investigation of a general phenomenon in a colloidal medium: with the assumption that adsorption is a simple function of surface area what could we expect to be the effect upon the diffusion coefficient of an adsorbable solute of the continued aggregation of the adsorbing colloid. This discussion proceeds under some plausible assumptions which simplify the analysis. The results are finally related to certain membrane phenomena of the cell.

The system we consider has initially simple, colloid particles and solute particles. The primordial colloid particles coalesce giving larger particles of uniform surface, uniformly distributed. If the initial number of simple colloid particles is designated by N_c and the initial number of neutral solute by N_s, the relationships which must always be met are

$$\begin{aligned} N_s &= n_s + \sum_{l=1}^{r} \sum_{k=1}^{n} l n(l, a, k) \\ N_c &= \sum_{l=1}^{r} \sum_{k=1}^{n} k[n(c, k) + n(l, a, k)] , \end{aligned} \tag{1}$$

where $n(l, a, k)$ designates the number of k-th-aggregated colloid particles with 1 adsorbed solute particles, $n(c, k)$ is the k-th-aggregated colloid particles having no adsorbed solute particles, and n_s is the number of solute particles not adsorbed. The types of possible re-

actions taking place in the system may be written

$$\begin{aligned} &n(c, a) + n_s \rightarrow n(1, a, 1) \\ &n(1, a, 1) + n(c, 1) \rightarrow n(1, a, 2) \\ &\cdots\cdots\cdots\cdots\cdots \\ &n(c, i) + n(c, j) \rightarrow n(c, i + j) \\ &n(i, a, r) + n_s \rightarrow n(i + 1, a, r) \end{aligned} \qquad (2)$$

provided $i + 1 \leqq r^{2/3}$. This condition is explained below. The first three reactions express the general assumption that a solute particle may be adsorbed by a single colloid particle but that the aggregate cannot adsorb another solute particle until the surface is at least twice the surface of the single colloid particle. Any other reaction of agglomeration is possible in the system so long as it does not violate this principle.

Nevertheless two particles having such a number of adsorbed particles that the complex formed by their agglomeration would have more than the allowed number of adsorbed solute particles were they all retained, can still agglomerate with the release of solute particles. This is expressed by adding to (2)

$$\begin{aligned} &n(1, a, 1) + n(1, a, 1) \rightarrow n(1,a, 2) + n_s \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ &n(k, a, m) + n(j, a, r) \rightarrow n(q, a, m + r) + ln_s \end{aligned} \qquad (3)$$

where $(m + r)^{2/3} - 1 < q \leqq (m + r)^{2/3}$, $k + j = q + l$.

For simplicity the reactions are assumed to be irreversible. With these assumptions the maximum number of adsorbed particles is easily deduced. If we let v_1 , r_1 , and s_1 represent the volume, radius and surface of a single colloid particle and v_k , r_k , and s_k the same for an aggregate of k particles, we have

$$V_k = \frac{4}{3}\pi r_k^3 \; ; \quad s_k = 4\pi r_k^2$$

$$v_k = kv_1$$

since the k aggregate to form a spherical cluster, $kr_1^3 = r_k^3$ thereupon $s_k = 4\pi k^{2/3} r_1^2 = k^{2/3} s_1$. The maximum number of adsorbed solute particles on an aggregate of k colloid particles is

$$l = k^{2/3} \qquad \text{if } k \text{ is an integer,}$$

$$k^{2/3} - 1 < l < k^{2/3} \qquad \text{if } k \text{ is not an integer,}$$

which we have already used in (2) and (3).

Some hint as to possible numerical values for the maximum number of colloidal particles which may aggregate before flocculation can be taken from the specification of the range of colloidal particle size, the diameters ranging from 10^{-7} to 10^{-5} cm. Assuming that our primoridal colloid particle has the smaller diameter and the largest the larger, we have the maximum for $m \sim 10^6$ and the maximum for $r \sim 10^4$.

The solute particles are taken as uncharged so Fick's law for the transport of solute is

$$J = J_s + \sum_{l=1}^{r} \sum_{k=1}^{m} J(l, a, k), \tag{4}$$

in which J is the number of solute particles passing through unit surface in unit time whether as simple solute or in aggregate. The l, k, r, and m are the same as in (1). The $J(l, a, k)$ may be written

$$J(l, a, k) = -D(l, a, k) \text{ grad } n(l, a, k). \tag{5}$$

Introducing (5) into (4) with the corresponding forms for J_s and $J(l, a, k)$ and with the dependence of n_s and $n(l, a, k)$ on the positional coordinates expressed through N_s, we have

$$-D \text{ grad } N_s = -D_s \text{ grad } n_s - \sum_{l=1}^{r} \sum_{k=1}^{m} D(l, a, k) \text{ grad } n(l, a, k)$$

or

$$D = D_s \frac{\partial n_s}{\partial N_s} + \sum_{l=1}^{r} \sum_{k=1}^{m} D(l, a, k) \frac{\partial n(l, a, k)}{\partial N_s}. \tag{6}$$

D is the effective diffusion coefficient of the solute. Using (1) this becomes

$$D = D_s \left[1 - \sum_{l=1}^{r} \sum_{k=1}^{m} l \frac{\partial n(l, a, k)}{\partial N_s} \right] + \sum_{l=1}^{r} \sum_{k=1}^{m} D(l, a, k) \frac{\partial n(l, a, k)}{\partial N_s}. \tag{7}$$

Inasmuch as the adsorbed solute particles do not appreciably affect the bulk of the colloid aggregates we may take $D(l, a, k) = D(c, k)$ for all values of k. Furthermore on the basis of Einstein's law of diffusion the diffusion coefficient of an aggregate of h colloid particles is related to that of an aggregate of one solute particle and one solute particle by

$$D(c, h) = \frac{D(c, 1)}{h^{2/3}}; \tag{8}$$

These substitutions simplify (6). There remains, however, the rather complex double summations. We can approximate them through

$$\sum_{l=1}^{r}\sum_{k=1}^{m} l\, n(l, a, k) \sim \beta(p) n(r, a, p) \tag{9}$$

$$\sum_{l=1}^{r}\sum_{k=1}^{m} n(l, a, k) \sim \alpha(p) n(r, a, p)\,. \tag{10}$$

Without reference to the coefficients or to the first and last symbols in the parentheses we see that the $n(l, a, k)$ are merely the number of particles of each size group in the system. The mechanism here described places all the particles initially in $n(1, a, 1)$, thus initially (10) could be replaced by $n(1, a, 1)$. As time goes on, other $n(l, a, k)$'s will arise but the most unlikely distribution, one perfectly flat, would lead to a multiplicative factor equal to the number of particle sizes. For any other distribution the factor for any p would be in general a function of p but less than p. The factor $\beta(p)$ would behave in the same manner, although the numerical value would be different from that of $\alpha(p)$. We can relieve ourselves from too much specificity by putting

$$\alpha(p) = p^a,\ a < 1;\ \beta(p) = p^b,\ b \leqq 1\,.$$

On closer inspection, (10) is seen to be equivalent to replacing the size-distribution curve by a rectangle of height $n(r, a, p)$ and width $\alpha(p)$. In (9) we replace the three dimensional distribution by a solid of cross-sectional area $\beta(p)$ and height $n(r, a, p)$. It is of interest to observe that p will be a function of time, for the distribution curve of particle size will move towards the maximum size with increasing time. Instead of the variation of $n(r, a, p)$ with time we think it best to keep p, which we shall call the degree of aggregation, as the independent variable.

If $N_s > N_c$ then practically all the N_c will be used as $n(1, a, 1)$ before the formation of any higher associated particles. This permits the division of the problem into two sections, the initial aggregation to form $n(1, a, 1)$ and the subsequent reactions to form higher aggregates. This first is essentially J. M. Reiner's problem. Both are contained in our analysis as we see upon introducing the approximations and the relations

$$n(l, a, p) \sim \frac{n(1, a, 1)}{p} = \frac{N_c}{p} \text{ and } N_c = \varepsilon N_s,\qquad \varepsilon < 1;$$

whence

$$D = D_s\left[1 - p^a \frac{\partial n(l,a,p)}{\partial N_s}\right] + \frac{D(1,a,1)}{p(2/3-b)} \frac{\partial n(l,a,p)}{\partial N_s}$$
$$= D_s\left[1 - \frac{\varepsilon}{p(1-a)}\right] + \frac{\varepsilon D(1,a,1)}{p(5/3-b)}. \qquad (11)$$

In terms of time, (11) holds from t_1 to t_m where $(t_1 - t_o)$ would be the time required for all N_c to become $n(1, a, 1)$ and $t_m - t_1$ would be the time for the formation of maximum size. For $t_o \leqq t \leqq t_1$ Reiner's (3) holds

$$D = D_s\left[1 - \frac{\partial n(1,a,1)}{\partial N_s}\right] + D(1,a,1) \frac{\partial n(1,a,1)}{\partial N_s},$$

FIGURE 1

which is observed to be the same as our (11) with $p = 1$. Represented graphically these equations join exactly at $p = 1$ as is shown in Figure 1.

The removal of the assumption that $N_s > N_c$ and the precise sequential reactions do not influence the shape of the curve. This would not contradict (3) so long as the binding energy of colloid for colloid is not considerably greater than that of colloid for solute. It may cause a smoother transition at the minimum and a raising of the minimum so that D does not reach $D(1, a, 1)$. Furthermore we need not limit the number of adsorbed particles to one for the surface area of a simple colloid particle. If we would consider the number of adsorbed particles per cm^2, then the resulting curve for the variation of the diffusion coefficient would probably have the same shape. We may also weaken the requirement that the agglomeration gives spherical particles by introducing a shape factor γ, so that

$$S_k = \gamma\, k^{2/3} S_1, \qquad k^{1/3} > \gamma \geqq 1.$$

The shape factor will be a function of k, the number of particles in

the complex. With our assumptions the inclusion of this factor would raise the maximum for 1 with a given k to $\gamma\ k^{2/3} - 1 < l \leqq \gamma\ k^{2/3}$ but would cause no change in the other equations.

E. L. MacBain's data on the diffusion coefficient of long chain sulfonic acids, C_{10} to C_{14}, exhibit a minimum at dilute solution followed by a rise at higher concentrations. The curve is similar to Figure 1 but the data do not seem susceptible to interpretation by our mechanism These experiments are instructive, however, in calling our attention to the fact that the D-p curve in Figure 1 could be transferred into a D-concentration curve. Since the aggregation is directly proportional to the concentrations by measuring the diffusion coefficient of various concentrations of N_s and N_c a test of the mechanism outlined here could be carried through so long as the degree of aggregation does not vary appreciably during an experimental determination.

If the reaction takes place within a cell we may take $N_s = q_s t$ and $N_c = q_c t$ where the q's are the average rates of production of the solute and the adsorbing particle within the cell. In (11) ε would be $q_{/c}/q_{/s}$. For sufficiently rapid aggregation the action of this mechanism within a cell may give a purely physical interpretation of certain trigger mechanisms and other aspects of cellular behavior.

The rather simple extension that the presence of n_s primes the release of n_c in spurts gives a sinusoidal curve for the variation of the diffusion coefficient.

Finally the view that the diffusion solute lowers the permeability of the cell membrane to another diffusing substance admits a variation of the membrane permeability, h, inverse to that of D in Figure 1.

The author wishes to express his thanks to the Julius Rosenwald Fund for a grant which supported this investigation. He wishes also to acknowledge the helpful suggestions of Prof. N. Rashevsky out of which came this problem and the discussions with the University of Chicago group of mathematical biophysicists. The author is especially indebted to Dr. Alvin Weinberg who read the paper and made some valuable suggestions.

LITERATURE

MacBain, E. L. 1939. "Diffusion of Long-Chain Sulfonic Acids." *Proc. Royal Soc. A*, **170**, 415-423. See also the discussion of these data by G. S. Hartley. 1939. *Faraday Soc. Trans.*, **35**, 1109-1113.

Rashevsky, N. 1939. *Mathematical Biophysics*. Chicago: The University of Chicago Press.

Reiner, John M. 1939. "Diffusion in Colloidal Media." *Bull. Math. Biophysics*, **1**, 143-149.

Delayed Adsorption and Diffusion in Colloidal Media

Herman Branson
Howard University, Washington, D.C.

The behavior of the diffusion coefficient of a solute which can be adsorbed by a colloid only after the colloid has aggregated to a certain size is deduced on the basis of a few assumptions. Some relations of such a mechanism to cell reactions are indicated.

completed
Feb. 26, 1942

A type of reaction plausible in cell behavior is one in which two or more substances may be released under a stimulus. This paper considers such a release with two substances one of which can aggregate into larger miscelles and upon reaching an optimum size adsorbs the second substance, which we call the solute. After this initial adsorption we may consider either no further aggregation and adsorption or further aggregation with adsorption as being the possibilities of greatest interest. For our purposes the significant point is what effect these alternative possibilities have upon the diffusion coefficient of the solute. In addition, we indicate how this mechanism may be used to interpret certain reactions in a cell, e.g. reactions which begin at a certain rate, proceed at that rate for some time, and then fall to a minimum.

The aggregation of the colloid particles is assumed to take place in the following chain:

$$\begin{aligned} n_1 + n_1 &\rightarrow n_2 \\ n_2 + n_1 &\rightarrow n_3 \\ &\cdots\cdots \\ n_{m-1} + n_1 &\rightarrow n_m \end{aligned} \qquad (1)$$

where n_m is the size at which adsorption of the solute occurs. This chain expresses the assumption that a higher aggregate is formed from the next lower by the adjoining of a simple micelle, in short there is no aggregation of higher aggregates with each other. We shall consider first the mechanism which allows no aggregation after adsorption. The differential equations for this chain are

$$\begin{aligned} \frac{dn_1}{dt} &= -k_1 n_1^2 - k_2 n_1 n_2 - \cdots - k_{m-1} n_{m-1} n_1 \\ \frac{dn_2}{dt} &= \frac{k_1}{2} n_1^2 - k_2 n_1 n_2 \\ &\vdots \\ \frac{dn_\ell}{dt} &= k_{\ell-1} n_1 n_{\ell-1} - k_\ell n_1 n_\ell \\ &\vdots \\ \frac{dn_m}{dt} &= k_{m-1} n_1 n_{m-1} \end{aligned} \qquad (2)$$

On making the substitution $n_1 dt = dx$ these equations are transformed into the linear forms

$$\begin{aligned} \frac{dn_1}{dx} &= -\sum_{i=1}^{m-1} \kappa_i n_i \\ \frac{dn_2}{dx} &= \frac{\kappa_1 n_1}{2} - \kappa_2 n_2 \\ &\vdots \\ \frac{dn_m}{dx} &= \kappa_{m-1} n_{m-1} \end{aligned} \tag{3}$$

The characteristic equation of this set is

$$\begin{vmatrix} \lambda+\kappa_1 & \kappa_2 & \kappa_3 & \cdots & \kappa_{m-1} & 0 \\ -\frac{\kappa_1}{2} & \lambda+\kappa_2 & 0 & & 0 & 0 \\ 0 & -\kappa_2 & \lambda+\kappa_3 & & & \\ & & & & & \\ 0 & & \cdots & & -\kappa_{m-1} & \lambda \end{vmatrix} = 0 \tag{4}$$

A simple relationship is found between the determinants of each order. Consider for $m=3$, we have

$$D_2(\lambda) = \begin{vmatrix} \lambda+\kappa_1 & \kappa_2 \\ -\frac{\kappa_1}{2} & \lambda+\kappa_2 \end{vmatrix}$$

observe that

$$D_3(\lambda) = (\lambda+\kappa_3) D_2(\lambda) + \frac{\kappa_1 \kappa_2 \kappa_3}{2}$$

and in general

$$D_\ell(\lambda) = (\lambda+\kappa_\ell) D_{\ell-1}(\lambda) + \frac{\kappa_1 \kappa_2 \cdots \kappa_\ell}{2} \tag{5}$$

The necessary and sufficient conditions that the roots of (5) have negative real parts has been given by A. Hurwitz (1895). The conditions are awkward to apply to the mth order equation. Inasmuch as we shall not treat the general case, except to observe that the physical conclusions will probably not be much different for large values of m, we can state that in order to be physically meaningful the λ_i should have negative real parts and the solutions of (3)

$$n_k = \sum_{j=1}^{m} c_{kj} e^{\lambda_j x} \tag{6}$$

satisfy the boundary conditions at all values of time

$$\sum_{k=1}^{m} \kappa n_k = n_0$$

All the information needed for our purpose can be had from a detailed treatment of the set for m = 3. That is there will be an aggregate of three colloid particles built up before adsorption of the solute occurs. The problem immediately suggested is the relative behavior of n_1 and n_2. This behavior can be obtained from the integral curves. Using the notation of L. R. Ford (1933),

$$\frac{dn_2}{dn_1} = \frac{-\frac{k_1}{2}n_1 + k_2 n_2}{k_1 n_1 + k_2 n_2} \tag{7}$$

$$\Delta = (k_1 + k_2)^2 - 6k_1k_2$$

Since $k_1 + k_2 \neq 0$, the integral curves are not conics.

For M_1 : $n_2 = \mu_1 n_1$ M_2 : $n_2 = \mu_2 n_1$

where

$$\mu_{1,2} = \frac{-(k_1 - k_2) \pm \sqrt{\Delta}}{2k_2} \tag{8}$$

the integral curves are shown in fig. 1.

These solutions are physically well-behaved in that all show that either n_1 disappears before n_2 or they disappear together. But the presence of n_2 after the disappearance of n_1, makes it impossible for all of n_2 to be transformed into n_3. Thus for the simple case of n_1, n_2, n_3, we can expect as a resultant state only n_3 or a mixture of n_2 and n_3. The first will result if $k_2 > k_1$, $\Delta > 0$ and $n_2 = 0$. The k's will be determined by the reaction, hence in a specific experiment we can examine the products present after sufficient time which will decide whether n_2 and n_3 or only n_3 remains.

The solutions of the set satisfying the boundary conditions

$$n_1 + 2n_2 + 3n_3 = n_0$$

and at $x = 0$, $n_1 = n_0$ where n_0 is the initial number of simple colloid particles, are

$$n_1 = \frac{n_0}{\lambda_1 - \lambda_2}\left[(\lambda_1 + k_1)e^{\lambda_2 x} - (\lambda_2 + k_1)e^{\lambda_1 x}\right]$$

$$n_2 = \frac{n_0(\lambda_1 + k_1)(\lambda_2 + k_1)}{k_2(\lambda_1 - \lambda_2)}\left[e^{\lambda_1 x} - e^{\lambda_2 x}\right] \tag{9}$$

$$n_3 = \frac{n_0}{3}\left[1 + \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_1(\lambda_1 - \lambda_2)}e^{\lambda_1 x} - \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_2(\lambda_1 - \lambda_2)}e^{\lambda_2 x}\right]$$

where $\lambda_{1,2} = \frac{-(k_1+k_2) \pm \sqrt{\Delta}}{2}$

The relation between x and $t^{\frac{1}{2}}$ is $n_1 dt = dx$

$$t = \int_0^{\bar{x}} \frac{dx}{n_1}$$

where x = 0 when t = 0. Before the integration can be performed the upper limit must be fixed. Calling this upper limit $\bar{x}$ and recalling that we are concerned about the value of the time from the beginning of the reaction until the appearance of the first particle capable of adsorbing a solute particle, we have on introducing $n_3 = 1$ into (9) and calling the coefficients of exponentials α and β respectively

$$\frac{3}{n_0} = 1 + \alpha e^{\lambda_1 \bar{x}} - \beta e^{\lambda_2 \bar{x}} \qquad (10)$$

This equation cannot be solved explicitly for $\bar{x}$. Making the substitutions

$$y_1 = \alpha e^{\lambda_1 \bar{x}} + 1 - 3/n_0$$

$$y_2 = \beta e^{\lambda_2 \bar{x}}$$

we can solve graphically if we have numerical values for α, β, and n_0. Taking $n_0 = 10^3$, $k_2 = 9k_1 = k$ then $\Delta = k^2$; $\lambda_1 = -9k$, $\lambda_2 = -6k$, and we find $\alpha = -5.55$, $\beta = 3.75$. Substituting these values we have $\bar{x} = 0.48/k$

$$\tau = 2 \times 10^{-3} \int_0^{0.48/k} \frac{e^{9kx}}{5 - 3e^{-2kx}} dx$$

where τ is the time required for the first n_3 to appear in the system. Integrating numerically by using Simpson's rule, whence

$$\tau = \frac{48.1\text{f}}{k} \times 10^{-3} \text{ secs.} \qquad (11)$$

Our analysis culminating in (12) can be summarized: when the aggregation takes place according to (3) with m = 3, at the end of $\frac{48.1\text{f}}{k} \times 10^{-3}$ secs. the particles capable of adsorbing solute particles appear in the system. Before their appearance, the other colloid particles would have negligible effect upon the diffusion coefficient of the solute. After their appearance, however, they would act to reduce the value of D according to J. Reiner's curve (1939). The effect is shown in fig. 2. If the aggregation continues with the number of adsorbed solute particles a function of the surface area as in an earlier paper (H. Branson, 1942), we would have the variation represented in fig. 3.

In order for the mechanism to be applicable to cellular reactions, τ has

to be in general small, except for some reactions where it may be of the order of a second. From physical considerations we see that K is a function of the diffusion coefficient and the radius of the aggregating particles; M. V. Smoluchowski (1918) found for a colloid solution $K = 4\pi r D$. Introducing values given in that paper from Zsigmondy's experiments we have $K \sim 10^{-12}$ and $\tau \sim 10^{10}$ secs. Thus unless the diffusion coefficient within the cell is considerably larger than in solution, this reaction gives an inordinately long time for the beginning of the decrease in the diffusion coefficient. More plausible values of τ can be obtained by considering n_o to be much larger in (11). Raising n_o to 10^7 causes practically no change in $\bar{x}$, and taking $\tau \sim 10^{-6}$, then for D of the order of 10^3, τ will be of the order of a hundreth of a second. This is not an unreasonable value of D for aggregations where the binding energy is large.

The author wishes to express his thanks to the Julius Rosenwald Fund for a grant which supported the initial steps in this problem. His thanks are again extended to Prof. N. Rashevsky and the University of Chicago group of mathematical biophysicists, especially Dr. Alston S. Householder, for discussions and suggestions.

LITERATURE

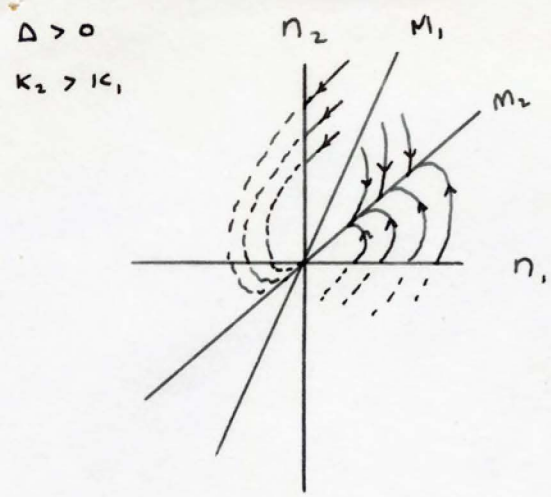
Branson, Herman. 1942. "Diffusion as a Function of Aggregation in Colloidal Media." Bull. Math. Biophysics, in press.

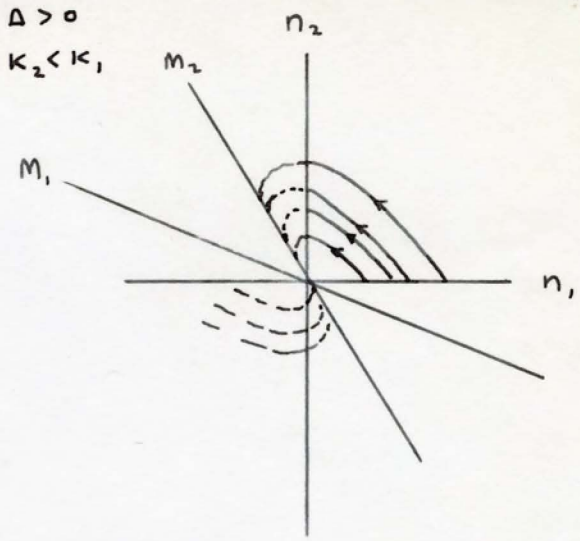
Ford, Lester R. 1933. Differential Equations. New York: McGraw-Hill Book Co.

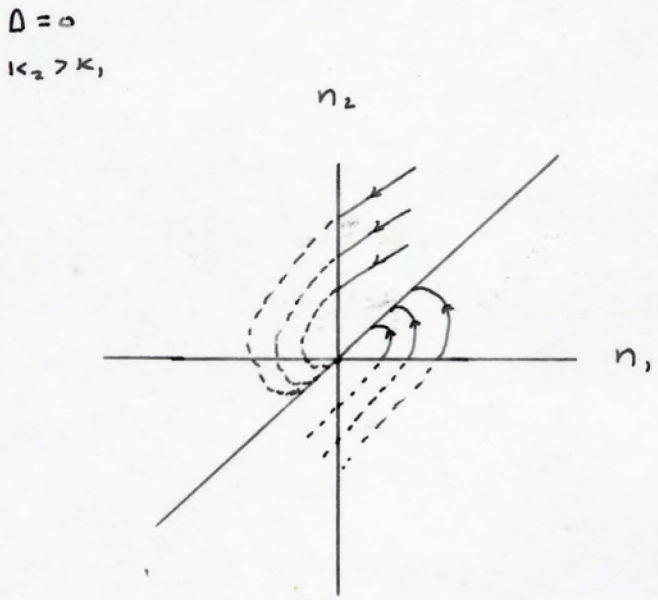
Hurwitz, A. 1895. "Über die Bedingungen, unter welchen eine Gleichung nur Wurzeln mit negativen reellen Theilen besitzt." Mathematische Annalen, 46, 273-284.

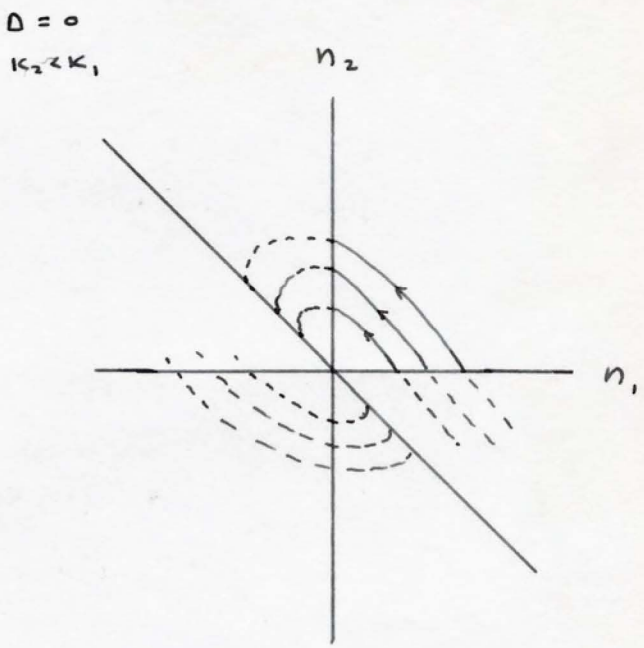
Reiner, John M. 1939. "Diffusion in Colloidal Media." Bull. Math. Biophysics, 1, 143-149.

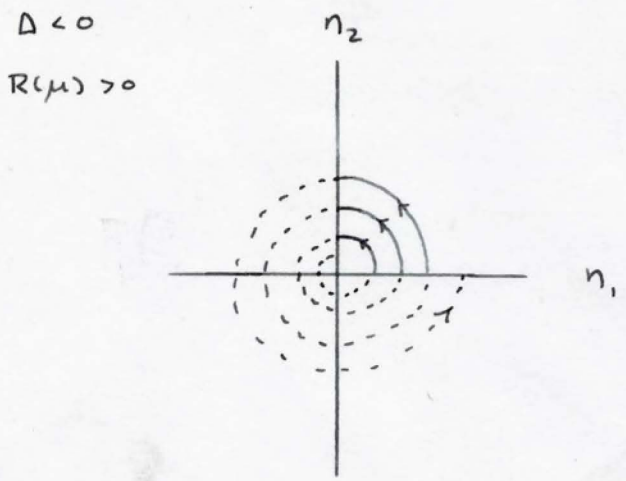
Smoluchowski, M.v. 1918. "Versuch siner mathematischen Theorie der Koagulationskinetik Kolloider Losungen." Zeitschrift für physikalische Chemie, 152, 129-168.











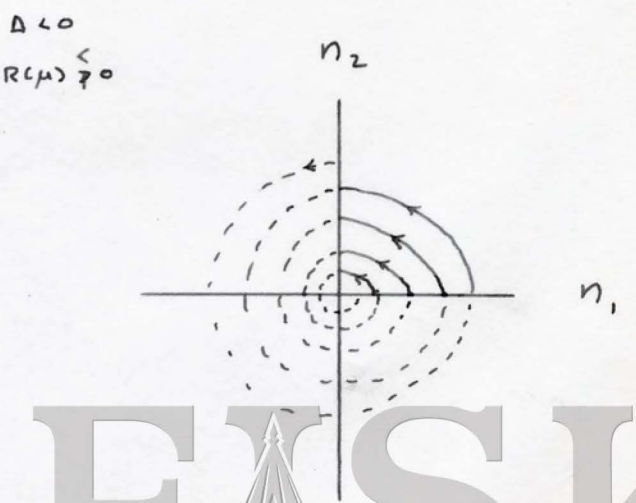


Fig. 1.

if $K_2 = K_1$, $\Delta < 0$, $R(\mu) = 0$ and the integral curves are

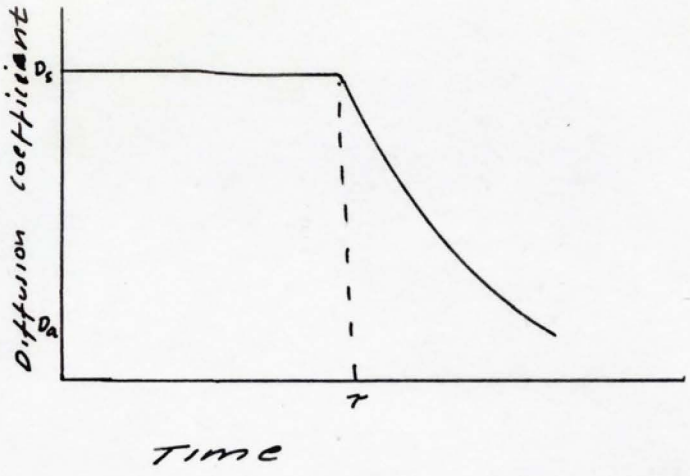


Fig. 2. D_s is the diffusion coefficient of the solute, D_a that of the ~~aggregate~~ adsorption complex of solute + colloid particle.

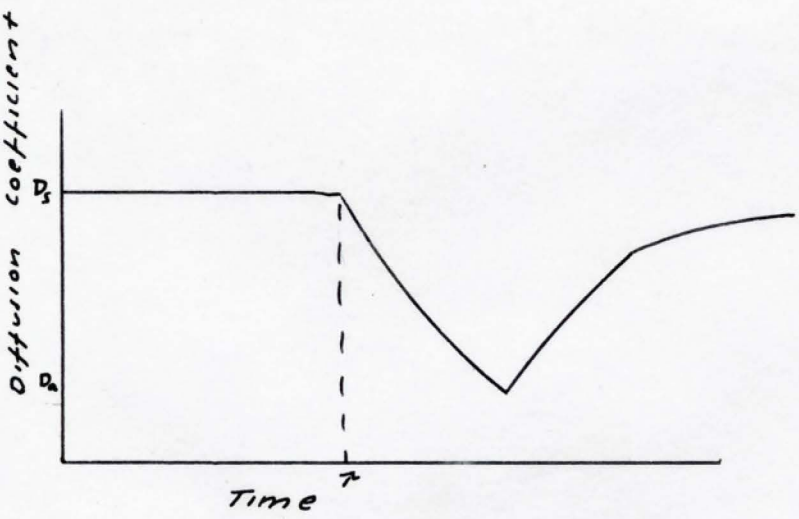


Fig. 3. Designations as in fig. 2.

FELLOWSHIPS

April 24, 1942

Dear Mr. Branson: The Committee on Fellowships of the Julius Rosenwald Fund has had its final meeting and has decided on this year's awards. I regret to have to write you that your application for another summer of work at the University of Chicago was not favorably acted upon. This, as I am sure you will understand, was not because of lack of interest or confidence either in you or your research, but because your application did not fit into the Committee's reaffirmed policy of not accepting applications for less than six months of work.

The members of the Committee have asked me to write you to request that, if at all possible, you apply next year on the basis of a project involving continuous work for a period of six months or longer.

Sincerely yours,

WILLIAM C. HAYGOOD

WCH:MLU

Mr. Herman Branson
Howard University
Washington, D. C.

HOWARD UNIVERSITY
WASHINGTON, D. C.

DEPARTMENT OF PHYSICS

October 31, 1942

	WCH	2	WCH	3

Brawson, Herman

Mr. William Haygood
4901 Ellis Avenue
Chicago, Illinois

My dear Mr. Haygood:

I am sending with this letter five reprints of the paper which represents work begun at the University of Chicago last summer and completed at Howard during the last school year. I believe that this work bears out my contention that such summer projects carried through the year are excellent opportunities for in-service growth.

I would like to apply for a grant from the Foundation for next year and I ask your advice as to what type of request I should make.

Since coming to Howard University I find that the opportunities for work are much greater than they have been before. I think that in the next few years we shall have good research laboratories in various phases of physics. I would like, therefore, to begin working on those laboratories with great intensity next summer. Specifically, I would like to spend three months at the Massachusetts Institute of Technology and return to Howard where I would continue the work begun there. I am not certain whether I should make a request for a grant in aid or apply for one of your yearly grants. I cannot give up next years teaching since physicists are in such demand in the war effort and we believe that we are doing a good job in training young people at this time. I think, however, the fact that during the last year I published six papers shows that it is possible to do work while carrying on a regular program. I wonder, therefore, if I may not ask a grant say for six months or longer, with the understanding that one-third of the grant will be spent for maintenance for three months at the Massachusetts Institute of Technology and the other will be spent at Howard University for the purchase of some materials for research. I believe that some sort of arrangement like this is common for workers in social studies. I would appreciate having your reaction to such a proposal. I do not intend to make an applica-

tion if you think the board would react unfavorably. Nevertheless, I hope that it is possible for us to work out some sort of program for I believe that research in our schools needs additional encouragement other than that given for work specifically relating to the Negro and his problems.

Very sincerely yours,

Herman Branson

Herman Branson,
Assistant Professor of Physics

HB:B

Enclosure

uopwa #27

BULLETIN OF
MATHEMATICAL BIOPHYSICS
VOLUME 4, 1942

DELAYED ADSORPTION AND DIFFUSION IN COLLOIDAL MEDIA

HERMAN BRANSON
HOWARD UNIVERSITY, WASHINGTON, D. C.

The behavior of the diffusion coefficient of a solute which can be adsorbed by a colloid only after the colloid has aggregated to a certain size is deduced on the basis of a few assumptions. Some relations of such a mechanism to cell reactions are indicated.

A type of reaction plausible in cell behavior is one in which two or more substances may be released under a stimulus. This paper considers such a release with two substances one of which can aggregate into larger micelles and upon reaching an optimum size adsorbs the second substance, which we call the solute. After this initial adsorption we may consider either no further aggregation and adsorption or further aggregation with adsorption as being the possibilities of greatest interest. For our purposes the significant point is what effect these alternative possibilities have upon the diffusion coefficient of the solute. In addition, we indicate how this mechanism may be used to interpret certain reactions in a cell, e.g. reactions which begin at a certain rate, proceed at that rate for some time, and then fall to a minimum.

The aggregation of the colloid particles is assumed to take place in the following chain:

$$\begin{aligned} n_1 + n_1 &\rightarrow n_2 , \\ n_2 + n_1 &\rightarrow n_3 , \\ &\cdot \\ &\cdot \\ &\cdot \\ n_{m-1} + n_1 &\rightarrow n_m , \end{aligned} \tag{1}$$

where n_m is the size at which adsorption of the solute occurs. This chain expresses the assumption that a higher aggregate is formed from the next lower by the adjoining of a simple micelle, in short there is no aggregation of higher aggregates with each other. We

shall consider first the mechanism which allows no aggregation after adsorption. The differential equations for this chain are

$$\begin{aligned}
\frac{dn_1}{dt} &= -k_1 n_1^2 - k_2 n_1 n_2 - \cdots - k_{m-1} n_1 n_{m-1}, \\
\frac{dn_2}{dt} &= \frac{k_1 n_1^2}{2} - k_2 n_1 n_2, \\
&\cdot \\
&\cdot \\
\frac{dn_e}{dt} &= k_{e-1} n_1 n_{e-1} - k_e n_1 n_e, \\
&\cdot \\
&\cdot \\
&\cdot \\
\frac{dn_m}{dt} &= k_{m-1} n_1 n_{m-1}.
\end{aligned} \tag{2}$$

On making the substitution $n_1 \, d\, t = d\, x$ these equations are transformed into the linear forms

$$\begin{aligned}
\frac{dn_1}{dx} &= -\sum_{i=1}^{m-1} k_i n_i, \\
\frac{dn_2}{dx} &= \frac{k_1}{2} n_1 - k_2 n_2, \\
&\cdot \\
&\cdot \\
\frac{dn_r}{dx} &= k_{m-1} n_{m-1}.
\end{aligned} \tag{3}$$

The characteristic equation of this set is

$$\begin{vmatrix}
\lambda + k_1 & k_2 & k_3 & \cdots & k_{m-1} & 0 \\
-\frac{k_1}{2} & \lambda + k_2 & 0 & \cdots & & 0 \\
0 & -k_2 & \lambda + k_3 & \cdots & & \\
\cdots & \cdots & \cdots & \cdots & -k_{m-1} & \lambda
\end{vmatrix} = 0. \tag{4}$$

A simple relationship is found between the determinants of each or-

der. Consider for $m = 3$ we have

$$D_2(\lambda) = \begin{vmatrix} \lambda + k_1 & k_2 \\ -\frac{k_1}{2} & \lambda + k_2 \end{vmatrix},$$

observe that

$$D_3(\lambda) = (\lambda + k_3) D_2(\lambda) + \frac{k_1 k_2 k_3}{2},$$

and in general

$$D_e(\lambda) = (\lambda + k_e) D_{e-1}(\lambda) + \frac{k_1 k_2 \cdots k_e}{2}. \tag{5}$$

Inasmuch as we shall not treat the general case, except to observe that the physical conclusions will probably not be much different for large values of m, we can state that in order to be physically meaningful the solutions of equation (3)

$$n_k = \sum_{j=1}^{m} c_{kj} \, e^{\lambda_j x} \tag{6}$$

satisfy the boundary conditions at all values of time

$$\sum_{1}^{m} k \, n_k = n_0.$$

Since x and not time occurs in equation (6), we see that it is not necessary that the real part of the λ be negative. From the defining equation for x, we have $x \to x_0$, x_0 finite, $n_1 \to 0$, then $t(x) \to \infty$; thus an infinite time is required for all the n_1 to disappear even though the x_0 is finite.

All the information needed for our purpose can be had from a detailed treatment of the set for $m = 3$. That is there will be an aggregate of three colloid particles built up before adsorption of the solute occurs. The problem immediately suggested is the relative behavior of n_1 and n_2. This behavior can be obtained from the integral curves. Using the notation of L. R. Ford (1933),

$$\frac{dn_2}{dn_1} = \frac{-\frac{k_1}{2} n_1 + k_2 n_2}{k_1 n_1 + k_2 n_2}, \tag{7}$$

$$\Delta = (k_1 + k_2)^2 - 6 k_1 k_2.$$

Since $k_1 + k_2 \neq 0$, the integral curves are not conics.

For

$$M_1: \quad n_2 = \mu_1 n_1 \qquad M_2: \quad n_2 = \mu^2 n_1$$

where

$$\mu_{1,2} = \frac{-(k_1 - k_2) \pm \sqrt{\Delta}}{2 k_2}, \tag{8}$$

the integral curves are shown in Figure 1.

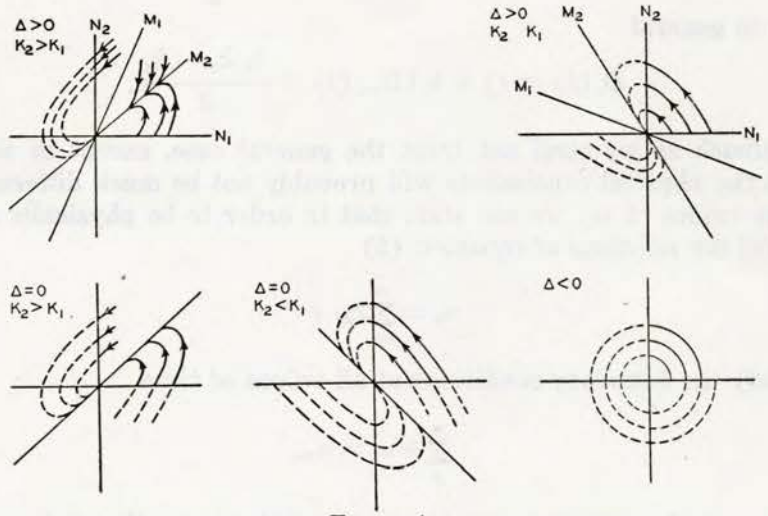


FIGURE 1

These solutions are physically well-behaved in that all show that either n_1 disappears before n_2 or they disappear together. But the presence of n_2 after the disappearance of n_1, makes it impossible for all of n_2 to be transformed into n_3. Thus for the simple case of n_1, n_2, n_3, we can expect as a resultant state only n_3 or a mixture of n_2 and n_3. The first will result if $k_2 > k_1$ and $\Delta \geqq 0$. The k's will be determined by the reaction, hence in a specific experiment we can examine the products present after sufficient time which will decide whether n_2 and n_3 or only n_3 remains.

An alternative treatment of the integral curves which is immediately applicable to the general case has been suggested in a letter by Dr. A. S. Householder. From the conditions, the integral curves in the n_2, n_1 plane are confined to the region bounded by the coordinate axes and the line $n_1 + 2n_2 = n_0$. Since $dn_1/dx < 0$ for any n_1 and n_2 not both zero, the integral curve can cross the n_2 axis ($n_1 = 0$). While for $n_2 = 0$, unless $n_1 = 0$ simultaneously, the integral curve is directed into the region. The scalar product of the vector with the

normal is $-3k_2n_2$ which is always negative for $n_2 > 0$. Initially $n_2 = 0$ and $n_1 = n_0$, thus the curve begins at the intersection of the line $n_1 + 2n_2 = n_0$ and the n_1 axis; the integral curve is tangent to the line and directed upward from the n_1 axis. As n_2 builds up the integral curve turns inward away from the line $n_1 + 2n_2 = n_0$.

The general set is treated in the same manner. Here the integral curves are confined to the region bounded by the $m-1$ coordinate hyper-planes and the hyper-plane $\sum_1^{m-1} k\, n_k = n_0$. The integral curve can cross the hyper-plane $n_1 = 0$ for always $dn_1/dx < 0$. But when $n_k = 0$, $k \neq 1$, $dn_k/dx = k_{k-1}\, n_{k-1} > 0$ unless n_{k-1} is also 0; but if n_{k-1} is 0, $dn_{k-1}/dx, > 0$, etc., until we meet an $n_r \neq 0$. Hence if any n_k, $k \neq 1$, approaches zero the integral curve turns toward a region where the n_k is increasing. Finally the scalar product of the tangent and the outward normal is $-(m-1)k_{m-1}\, n_{m-1}$ which completes the proof that for a finite x, but an infinite t, n_1 vanishes in the general case; and although some of the other n's may vanish simultaneously with n_1, they cannot vanish ahead of n_1.

The solutions of the set satisfying the boundary conditions

$$n_1 + 2n_2 + 3n_3 = n_0,$$

and at $x = 0$, $n_1 = n_0$ where n_0 is the initial number of simple colloid particles, are

$$\begin{aligned}
n_1 &= \frac{n_0}{\lambda_1 - \lambda_2}\left[(\lambda_1 + k_1)\, e^{\lambda_2 x} - (\lambda_2 + k_1)\, e^{\lambda_1 x}\right], \\
n_2 &= \frac{n_0(\lambda_1 + k_1)(\lambda_2 + k_1)}{k_2(\lambda_1 - \lambda_2)}\left[e^{\lambda_1 x} - e^{\lambda_2 x}\right], \\
n_3 &= \frac{n_0}{3}\left[1 + \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_1(\lambda_1 - \lambda_2)}\, e^{\lambda_1 x}\right. \\
&\qquad \left. - \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_2(\lambda_1 - \lambda_2)}\, e^{\lambda_2 x}\right],
\end{aligned} \tag{9}$$

where

$$\lambda_{1,2} = \frac{-(k_1 + k_2) \pm \sqrt{\Delta}}{2}.$$

The relation between x and t is $n_1\, d\, t = d\, x$

$$t = \int_0^x \frac{dx}{n_1}$$

where $x = 0$ when $t = 0$. Before the integration can be performed the upper limit must be fixed. Calling this upper limit x and recalling that we are concerned about the value of the time from the beginning of the reaction until the appearance of the first particle capable of adsorbing a solute particle, we have on introducing $n_3 = 1$ into (9) and calling the coefficients of exponentials α and β respectively

$$3/n_0 = 1 + \alpha\, e^{\lambda_1 x} - \beta\, e^{\lambda_2 x}. \tag{10}$$

This equation cannot be solved explicitly for x. Making the substitutions

$$y_1 = \alpha\, e^{\lambda_1 x} + 1 - 3/n_0,$$

$$y_2 = \beta\, e^{\lambda_2 x},$$

we can solve graphically if we have numerical values for α, β, and n_0. Taking $n_0 = 1000$, $k_2 = 4\ k_1 = 4\ k$ then $\Delta = k^2$, $\lambda_1 = -4\ k$, $\lambda_2 = -6\ k$ and we find $\alpha = -5.55$, $\beta = 3.75$. Substituting these values we have $x = 0.48/k$

$$\tau = \frac{2}{1000} \int_0^x \frac{e^{4kx}}{5 - 3\, e^{-2kx}}\, dx,$$

where τ is the time required for the first n_3 to appear in the system. Integrating numerically by using Simpson's rule, we find

$$\tau = 48.18/1000\ k \quad \text{secs.} \tag{11}$$

Our analysis culminating in (11) can be summarized: when the aggregation takes place according to (3) with $m = 3$, at the end of $48.18/1000\ k$ secs. the particles capable of adsorbing solute particles appear in the system. Before their appearance, the other colloid particles would have negligible effect upon the diffusion coefficient of the solute. After their appearance, however, they would act to reduce the value of D according to J. Reiner's curve (1939). The effect is shown in Figure 2a. If the aggregation continues with the number of adsorbed solute particles a function of the surface area as in an

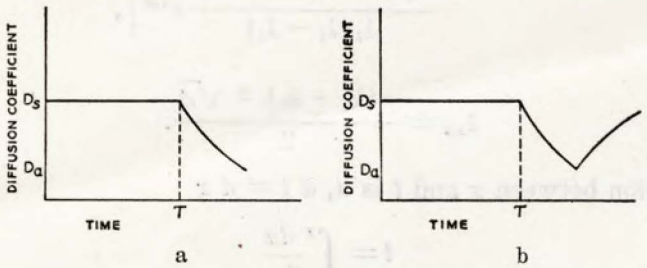


FIGURE 2

earlier paper (H. Branson, 1942), we would have the variation represented in Figure 2b.

In order for the mechanism to be applicable to cellular reactions, τ has to be in general small, except for some reactions where it may be of the order of a second. From physical considerations we see that k is a function of the diffusion coefficient and the radius of the aggregating particles; *M. V.* Smoluchowski (1918) found for a colloid solution $k = 4\pi\tau D$. Introducing values given in that paper from Zsigmondy's experiments we have $k \sim 10^{-12}$ and $\tau \sim 10^{10}$ secs. Thus unless the diffusion coefficient within the cell is considerably larger than in solution, this reaction gives an inordinately long time for the beginning of the decrease in the diffusion coefficient. More plausible values of τ can be obtained by considering n_o to be much larger in (10). Raising n_o to 10^7 causes practically no change in x, and taking $r \sim 10^{-6}$ cm then for D of the order of 10^3, τ will be of the order of a hundredth of a second. This is not an unreasonable value of D for aggregations where the binding energy is large.

The author wishes to express his thanks to the Julius Rosenwald Fund for a grant which supported the initial steps in this problem. His thanks are again extended to Prof. N. Rashevsky and the University of Chicago group of mathematical biophysicists, especially Dr. A. S. Householder, for discussions and suggestions.

LITERATURE

Branson, Herman. 1942. "Diffusion as a Function of Aggregation in Colloidal Media." *Bull. Math. Biophysics*, 4, 1-6.

Ford, Lester R. 1933. *Differential Equations*. New York: McGraw-Hill Book Co.

Reiner, John M. 1939. "Diffusion in Colloidal Media." *Bull. Math. Biophysics*, 1, 143-149.

Smoluchowski, M.v. 1918. "Versuch siner mathematischen Theorie der Koagulationskinetik Kolloider Losungen." *Zeitschrift für physikalische Chemie*, 152, 129-168.

FELLOWSHIPS

November 3, 1942

Dear Mr. Branson: I have read your letter of October 31 with interest, and thank you for the reprint of your article.

As to the type of application you should make to us, the best advice I can give is that you apply for a regular fellowship on the basis of a specified project encompassing at least six months or more of full-time work. I realize that this is not exactly what you have in mind, but at the last meeting of our Committee on Fellowships, it was definitely decided that no grants-in-aid for summer work will be considered in the future. In addition, I am certain that the Committee would not accept a request for materials.

I am sending you herewith a set of application blanks, and will be glad to receive your application, but I cannot help feeling that one of the other foundations which have programs for direct aid to research might be a better source of funds.

WCH:MLU
Enc.

Sincerely yours,

WILLIAM C. HAYGOOD

Mr. Herman Branson
Department of Physics
Howard University
Washington, D. C.

HOWARD UNIVERSITY
WASHINGTON 1, D. C.

FELLOWSHIPS

please answer in ERE absence

DEPARTMENT OF PHYSICS

18 February 1946.

	ERE	20	ERE	3/4
	WCH		WCH	2/20

Dr. Edwin R. Embree, President,
Julius Rosenwald Fund,
4901 Ellis Avenue,
Chicago 15, Illinois.

My dear Dr. Embree:

In November of last year, Professor N. Rashevsky of the University of Chicago approached me concerning my availability to accept a research associateship with the understanding that I would remain permanently at the university if conditions were favorable. (See letters exhibits 1 & 2) I replied that I was not desirous of leaving Howard University. I would prefer a research program here; and inasmuch as I have received excellent support for my work, I believe that the future is quite promising. We agreed, however, that a year at Chicago now would be desirable, for it would give me an opportunity to ascertain whether I would like to remain there and it would nurture my talent for research which has suffered during the war period. Professor Rashevsky and I agreed that it would be more appropriate, since I do not now intend to remain permanently at Chicago, for me to come on a fellowship. (See exhibit 3). Professor Rashevsky has written the Rockefeller Foundation. We had not worked out a procedure until the final date for receipt of applications for your regular fellowships had passed. It is my hope that this case merits consideration outside of your regular fellowship program.

My estimate is that for the 12 month period beginning October, 1946, I shall need at least $3500. My family plans to remain in Washington. Our budget appropriates $2000. for the expenses of our home (which we are purchasing) and of my wife and two children. My expenses in Chicago are set at $1500. The $3500 is well below my present salary as Professor of Physics which without Summer School is over $4500. and with Summer School is over $5500.

There are in your files some data concerning my training and experience. I am sending with this letter a revised list of my publications as of September, 1945 and a few reprints you may not have. I would appreciate knowing your reaction to the proposal that you grant the $3500 to finance the year of research at the University of Chicago. We have not yet received a reply from the Rockefeller Foundation because of the illness of Dr. Warren Weaver. I shall, of course, keep you informed of their reaction. I would appreciate your returning the letters. The other enclosures may be placed in your files.

done so

Very sincerely yours,

Herman Branson

Herman Branson, Professor
Dept of Physics.

8 Encl.

Publications
of
Dr. Herman Branson, ~~Assoc.~~ Prof.
Howard University
Washington, D. C.

1. "The Differential Action of X-Rays on the Anterior and Posterior Regions of Tubifex Tubifex"
   Radiology, 34, 200-204, February, 1940.
2. "On the Quantization of Mass"
   The Physical Review, 57, 495-500, March 15, 1940
3. "A Reader for Microfilm"
   School Science and Mathematics, pp. 411-412, May, 1940.
4. "Microfilm Equipment for the Individual Worker"
   School Science and Mathematics, pp. 140-143, February, 1941.
5. "A Microfilm Camera"
   Science, 93, p. 312, March 28, 1941
6. "Microfilm in the Negro College"
   Journal of Negro Education, 11, pp. 14-17, January, 1942.
7. "Diffusion as a Function of Aggregation in Collodial Media"
   Bulletin of Mathematical Biophysics, 4, 1-6, March, 1942.
8. "Delayed Adsorption and Diffusion in Collodial Media"
   Bulletin of Mathematical Biophysics, 4, pp. 131-137, September, 1942.
9. "The Role of the Negro College in the Preparation of Technical Personnel for the War Effort".
   Journal of Negro Education, 11, pp. 297-303, July, 1942.
10. "Physics Training for the Negro Student"
    American Journal of Physics, 10, p. 201, August, 1942.
11. "Effect of Soft X-Rays Upon Chaetopods"
    Nature, 141, March 26, 1938.
12. "The Natural Sciences and the Development of Attitudes"
    Proceedings or the National Association of Collegiate Deans and Registrars, 1941.
13. "On the Difference Equation of a General Quantum Mechanical Problem"
    Bulletin of American Mathematical Society, 48, 1942.
14. "On the Kinetics of Copolymerization", with R. Simha,
    Journal of Chemical Physics, 11, 297, 1943.
15. "The Training of Negroes for War Industries in World War II"
    Journal of Negro Education, 12, 376, 1943.
16. "Theory of Chain Copolymerization Reactions", with R. Simha
    Journal of Chemical Physics, 12, 253-267, June, 1944.
17. "Flow in an Elastic Tube", in Press,
    Bulletin of Mathematical Biophysics, 1945.
18. Analytical review of The Mathematical Biophysics of the Central Nervous System by Householder and Landahl,
    In Press, Bulletin of Mathematical Biophysics, 1945.
19. Many abstracts for Biological Abstracts since 1938 covering biophysics.

BULLETIN OF
MATHEMATICAL BIOPHYSICS
VOLUME 7, 1945

BOOK REVIEW

ALSTON S. HOUSEHOLDER AND HERBERT D. LANDAHL. *Mathematical Biophysics of the Central Nervous System* (Mathematical Biophysics Monograph Series, No. 1). 1945. ix + 124 pp. Bloomington, Indiana: The Principia Press. $2.00.

The readers of this journal will welcome this monograph which systematizes and elaborates most of the work done since 1938 by A. S. Householder, H. D. Landahl, N. Rashevsky, W. Pitts, and others on the mathematical biophysics of psychological processes. The authors have undertaken the difficult task of writing about a rapidly growing research field. They realize their position but conclude that the value of a comprehensive treatment at this time to theorists and experimenters interested in contributing to the development of this subject far outweighs the risk of their treatment becoming rapidly dated.

Following a brief preface, the authors in the introduction set forth the threefold development of the work: first, an idealized neural model; second, an investigation of the properties of certain neural complexes; third, comparison of predictions with experiment:

In Part I, p. 1 to p. 36, with Chapters

I. Trans-synaptic Dynamics
II. Chains of Neurons in Steady-State Activity
III. Parallel, Interconnected Neurons
IV. The Dynamics of Simple Circuits
V. The General Neural Net

the theoretical structure is elaborated from the two-factor dynamical model of Rashevsky. From plausible assumptions, they deduce testable conclusions which check the appositeness of the simple model as an approximation to certain actual neural mechanisms.

In Part II, p. 37 to p. 102, with Chapters

VI. Single Synapse: Two Neurons
VII. Single Synapse: Several Neurons
VIII. Fluctuations of the Threshold
IX. Psychological Discrimination
X. Multidimensional Psychophysical Analysis
XI. Conditioning
XII. A Theory of Color-Vision
XIII. Some Aspects of Stereopsis

the authors follow two paths in testing their conclusions: they examine specific neural structures seeking to determine for each the response as a function of the stimulus, while in the final chapters they start with a function and construct a mechanism. The comparisons with experiment are uniformly good. Although this section is primarily concerned with applications, a great deal of the material of Chapter XI and most of Chapters X, XII, and XIII is theoretical.

The reviewer believes that a careful reading of this part especially would go far in convincing the most skeptical psychologist of the efficacy of this technique in his field. And from that viewpoint, the monograph as a whole is more impressive evidence "that mathematics, even *in a relatively fundamental sense*, will from time to time be of use to biology" (Harris, Reginald G. 1935. "Mathematics in Biology." *The Scientific Monthly*, 40, 504-510). (Italics mine.)

In Part III, p. 103 to p. 113, with Chapters

XIV. The Boolean Algebra of Neural Nets
XV. A Statistical Interpretation

the authors shift from a macroscopic time scale to the microscopic in the use of a time unit of the order of a millisecond. The treatment follows the work of W. S. McCulloch and W. Pitts who employed some of the concepts of Boolean Algebra to give a formalized picture of neural activity. Their technique is used to construct a net capable of giving the sensation of heat produced by transient cooling. In Chapter XIV, they present the work of H. D. Landahl, W. S. McCulloch, and W. Pitts which enables one to translate from the microscopic theory to the macroscopic.

The concluding chapter has one of the clearest statements of a basic tenet of such theoretical developments that this reviewer has seen:

> "The advantage of having a theory lies not only in the fact that the theory, if it should prove accurate in its predictions, provides just that much of an increase to our fund of knowledge, or increases by just that much our command over nature. A well-formulated theory, in addition, gives direction and meaning to experimental work even when the experiments fail to confirm the theory, since the failure must occur in a certain direction, by a certain amount, and must therefore provide the necessary, hitherto lacking, background for the construction of a better theory."

The monograph requires little mathematical knowledge beyond the elements of differential equations, and, for Part III, some knowledge of symbolic logic. The reviewer believes that a short appendix on Boolean Algebra would have been of value to psychologists and others who know the calculus but who may be repelled by this strange sounding mathematics! The reviewer observed only one unimportant typographical error. There is a bibliography and an excellent index. The format and typography are excellent even when judged by pre-war standards.

This monograph is a worthy and important addition to the growing literature of mathematical biophysics. It should be of inestimable aid to psychologists and neurologists seeking a fresh, stimulating vantage point from which to view their subjects. The reviewer believes that a more auspicious inauguration of a research series would be difficult to find.

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BULLETIN OF
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THE FLOW OF A VISCOUS FLUID IN AN ELASTIC TUBE: A MODEL OF THE FEMORAL ARTERY

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The solutions of the classical differential equations for flow of a viscous fluid in an elastic tube are shown to yield a description of some aspects of the flow of blood in the femoral artery. The parameters influencing the speed of the pulse wave, the pressure, and the velocity for non-pulsating and pulsating flow are exhibited. The relation between pressure and velocity are considered in some detail. It is shown that for pulsating flow the slope of the pressure versus fluid velocity curve is equal to the pulse wave speed multiplied by the density of the blood.

The mathematical treatment of blood circulation has the usual intractable features of general hydrodynamics as mentioned by N. Rashevsky (1945a, b) further complicated by such factors as the variation of the viscosity and of the compressibility of the blood mainly due to the corpuscular structure, as well as by the nervous and the chemical control of the size of the blood vessels. In spite of the present impossibility of even a good approximate general treatment, the classical equations do yield results which have significance for the physiologist and biophysicist.

This paper discusses the equation of flow of a viscous fluid in an elastic tube and uses data on flow in the femoral artery to test the solutions.

The Differential Equations of Flow:

The equations for this problem may be derived by the usual methods as exemplified by O. Frank (1926) or A. Foch (1932). The equations are

$$\rho \frac{\partial u}{\partial t} + \frac{\partial p}{\partial x} = \mu \nabla^2 u, \tag{1}$$

$$\rho \frac{\partial u}{\partial x} + \frac{1}{v^2} \frac{\partial p}{\partial t} = 0, \tag{2}$$

where

$u =$ velocity along the axis of the tube (In x-direction)

$p =$ pressure
$\rho =$ density of fluid
$\mu =$ viscosity of fluid
$E =$ the modulus of elasticity of the tube wall
$\nabla^2 u =$ the Laplacian of u
$K =$ the compressibility of the blood
$e =$ thickness of the tube wall
$r_0 =$ radius of the unstretched tube.

In our treatment, ρ is constant and, therefore, $K = 0$.
Differentiating equation (1) with respect to t and equation (2) with respect to x, and eliminating the p-term, we find

$$\rho \frac{\partial^2 u}{\partial t^2} = \rho v^2 \frac{\partial^2 u}{\partial x^2} + \mu \frac{\partial}{\partial t} (\nabla^2 u).$$

On expressing the Laplacian in cylindrical coordinates and substituting $u = C \exp(-\alpha t - \beta x) R(r)$, we are led to Bessel's equation for $R(r)$ (Von Kárman and Biot, 1940),

$$\frac{d^2 R}{d r^2} + \frac{1}{r} \frac{d R}{d r} + \lambda^2 R = 0 ,$$

where

$$\mu \alpha \lambda^2 = \rho \alpha^2 + (\mu \alpha - \rho v^2) \beta^2. \tag{3}$$

The final solution is then

$$u = \exp(-\alpha t - \beta x) [C_1 J_0(\lambda r) + C_2 Y_0(\lambda r)] . \tag{4}$$

Inasmuch as u must be finite at the axis and since

$$Y_0(\lambda r) \to -\infty \quad \text{as} \quad r \to 0 , \quad C_2 = 0 .$$

the complete solution is therefore

$$u = \sum_{n=1}^{\infty} C_n J_0(\lambda_n r) \exp(-\alpha_n t - \beta_n x) . \tag{5}$$

In our flow problem, we are primarily interested in the pulse wave speed, the pressure, and the fluid velocity.

The speed of the pulse wave:

If we are treating flow of a non-viscous fluid, the μ-term on the right of equation (1) would be absent. Elimination of the u-term between equations (1) and (2) would lead to the wave equation for p where the speed of propagation of the pressure wave, v, would be given by

$$v = \sqrt{\frac{e E}{2 \rho r_0}}. \tag{6}$$

This is the well-known Moens' equation (Moens, 1878). Although derived for a non-viscous liquid, it has been found to apply quite satisfactorily to viscous flow.

In the v-equation we seem to have a valuable equation for finding a relation among some physically significant parameters (e, E, ρ, r_0). These parameters are, however, most difficult to measure and even to define satisfactorily. J. C. Bramwell and A. V. Hill (1922) found that Moen's equation held for flow in an artery but they transformed it by replacing the original parameters by the compressibility of the artery which is more easily measured:

$$v = 0.357 \sqrt{V \frac{dp}{dV}},$$

where p is measured in mm of mercury (Hg), V is the volume per unit length of the artery, and v is in meters/sec.

Non-pulsating flow:

The elastic tube is connected to a reservoir where the pressure may be maintained constant for any desired length of time (i.e., at $x = 0$, $p = p_1$, for all t's). The tube will stretch to some maximum radius, b. At the tube wall ($r = b$) we assume the usual Poiseuille condition, $u = 0$, hence

$$J_0(\lambda b) = 0. \tag{7}$$

Using equation (3) and equations (2), we get for the pressure

$$p = f(x) - \frac{v^2 \rho \beta}{\alpha} u. \tag{8}$$

At the wall $r = b$, $u = 0$ and

$$f(x) = p_b.$$

But also at wall, the pressure is distributed in overcoming the tension of the walls and the outside pressure, so

$$p_b = p_0 + e E \left(\frac{1}{r_0} - \frac{1}{b} \right), \tag{9}$$

where p_0 is the pressure in the medium surrounding the tube. If b varies along the tube, as it probably will, p_b is not constant. For variable b there would have to be a different value of λ for each point. A more tractable procedure would be to treat the tube as composed of sections of constant radii, but the radii decreasing as we go from section to section. For each section then there would be a series of solutions corresponding to equation (7) for the radius of that sec-

tion. There is, however, no need for our doing that for this discussion.

The data of S. R. F. Whittaker and F. R. Winton (1933) may be used to test equations (3) and (8). Whittaker and Winton (1933) perfused the hind leg of a dog with whole blood through the femoral artery and recorded the relation between pressure and velocity of flow. The flow took place through the entire complex of artery, connecting arterioles, capillaries, and finally into the veins which were cut to allow the liquid to run into a collector. The equations used in our derivation are for a single vessel; hence, in all correctness, we may consider our theory as yielding the *single vessel equivalent* of their complex system.

Their data may be expressed approximately as

$$\bar{p} = 20 + \tfrac{1}{2}\,\bar{u}\,, \tag{10}$$

where $\bar{p}$, the average pressure in the cross-section of the artery, is in mm of H_g and $\bar{u}$ is in cc/sec while our p is in dynes/cm^2 and u is in cm/sec. Using equation (4), we have for the flow in cc/sec,

$$u = 2\pi \int_0^b \text{rudr} = \sum_{n=1}^{\infty} 2\,\pi\, C_n \exp(-\alpha_n\, t - \beta_n\, x) \int_0^b r\, J_0(\lambda_n\, r)\, dr\,,$$

since

$$\frac{d}{d\,x}\,[x^m\, J_m(x)\,] = x^m\, J_{m-1}(x)\,.$$

We have corresponding to equation (5)

$$\bar{u} = 2\,\pi\, b \sum_{n=1}^{\infty} C_n\, \lambda_n^{-1}\, J_1(\lambda_n\, b)\, \exp(-\alpha_n\, t - \beta_n\, x)\,, \tag{11}$$

where the $J_m(x)$ is the Bessel function of the first kind of order m (Von Kárman and Biot, 1940).

Equation (11) should be able to satisfy the conditions here imposed and the pressure equation derived from it should satisfy at least approximately the condition $\bar{p} = p_1$ at $x = 0$ for all t.

The relation between $\bar{p}$ and $\bar{u}$ is of the same type as that between p and u, that is, equation (8). We see then that α and β may both be real, that β is negative and that

$$-\frac{v^2\,\rho\,\beta}{\alpha} = \frac{1}{2}\left(\frac{1333}{\pi\, b^2}\right).$$

The preceding equation relates α and β. From the roots of equation (7): $\lambda_1 = 2.40/b$; $\lambda_2 = 5.52/b\,, \cdots, \cdots$ we have the various λ's to be substituted into equation (3) so that we may determine both α and

β in terms of ρ, v, μ, and b. The algebraic expressions are easily obtained and show that there is a choice of sign so that $\alpha > 0$ and that α varies inversely as μ.

Although the preceding analysis seems quite adequate for a description of the flow in the hind leg of a dog, so far as the relation between pressure and velocity for non-pulsating flow, the data of T. E. Machella (1933) reveal that p and u are also *linearly* related for the femoral artery proper. His data were for pulsating flow, which we shall consider in the next section.

Pulsating Flow:

In pulsating flow, the pressure and velocity are some periodic functions of time and possibly also of position. We assume that velocity, u, and pressure, p, may be represented as a Fourier series of time. In order that our solution may be amenable to such expression, we may take

$$\alpha = a + i\,\omega \quad \text{and} \quad \beta = l + i\,m\,.$$

Equation (3) becomes on equating real and imaginary parts

$$\begin{aligned} \mu\,\lambda^2\,a &= \rho\,(a^2 - \omega^2) + (\mu\,a - \rho\,v^2)\,(l^2 - m^2) - 2\,\mu\,l\,m\,k\,, \\ \mu\,\lambda^2\,\omega &= 2\,\rho\,a\,\omega + 2\,l\,m\,(\mu\,a - \rho\,v^2) + \mu\,\omega\,(l^2 - m^2)\,. \end{aligned} \tag{12}$$

The velocity must be zero at the wall as before; thus λ will again satisfy equation (7). We still have four parameters (a, ω, l, m) and two equations (12) besides the boundary conditions.

T. E. Machella (1936) gave curves showing the relation between the velocity and pressure curves at the same point in the femoral artery (see his Figure 7). The curves have the same shape, but the numerical values of maxima and minima differ. We shall show that solution for u fits his data. We may write

$$u = \sum_{n=1}^{\infty} F(x_1\,r)\,\exp(-a_n\,t)\,[C_n \cos\omega_n\,t + C_n'\sin\omega_n\,t]\,.$$

Since x is fixed and r may be considered as constant, we must ascertain whether a u of the form

$$u = \sum_{n=1}^{\infty} \exp(-a_n\,t)\,[C_n \cos\omega_n\,t + C_n'\sin\omega_n\,t]$$

can fit Machella's results for both u and p. We have a choice. Either we may fit our u for a single cycle of systole and diastole or fit a complete curve of many similar cycles. If we choose to find u for the general curve with many cycles, $a_n = 0$, and our problem becomes one

of finding the C_n and C_n' to fit the experimental data by harmonic analysis. The author reproduced Machella's curve for u and p found the coefficients by a numerical method (Von Kármán and Biot, 1940). By taking a sufficiently large number of terms the series may be made to fit as closely as desired.

The expression for p is from equation (8)

$$p = \frac{v^2 m \rho}{\omega} u + p_b. \tag{13}$$

Thus if the velocity, u, can be expressed as a Fourier series with real coefficients, the pressure, p, must be expressed by the same series with each coefficient multiplied by a constant factor. Machella's p ranges from 88 to 156 mm of Hg and his u from 5 to 93 cm/sec. These two points are sufficient, of course, to determine the slope and intercept in equation (13). However, equations (1) and (2) are not applicable for the assumption that $a_n = 0$ involves a non-viscous fluid, for in order to satisfy equation (3) and the experimental conditions, it is necessary that $\mu = l \doteq 0$ which is the non-viscous flow problem. The relation between p and u is still given by equation (13). But the differential equation now requires that

$$\omega = v\, m\,,$$

so that equation (10) becomes

$$p = (v\, \rho)\, u + p_b\,. \tag{14}$$

Machella's (1936) curve 7 gives

$$\bar{p} = 0.773\, u + 84.13\,,$$

where $\bar{p}$ is in mm of Hg. In order to compare with equation (14) we must multiply by (1,013,000/760) to convert p to dynes/cm^2. We have then

$$p = 1020u + 110{,}000\,.$$

Therefore, the Fourier Series calculated for u gives p through this linear equation. Probably the most interesting aspect is that the *slope of the* p—u *curve gives the speed of the pulse wave,* for since $\rho \sim 1$, the slope is very nearly v. In Machella's (1936) experiment we have that $v = 10$ meters/sec which is a reasonable value. Alternately knowing v, we can calculate the compressibility or the other parameters from Moens' equation.

The preceding analysis is not quite as attractive as it seems, for the pulse velocity has been found to vary with the pressure. J. C. Bramwell and A. V. Hill's (1922) values for pulse velocity as a func-

tion of effective pressure, $(p - p_0)$, of an excised section of artery reveals that as $(p - p_0)$ varies from 0 to 70 mm of Hg, the pulse velocity goes from 1.5 to 4.9 meters/sec. This experiment was for non-pulsating flow and is relevant to our equation (9). We cannot explain the variation, however, by a mere increase in radius, since the velocity for the unstretched tube, is too small ($v_0 = 1.5$ meters/sec). The logical explanation is that the elasticity, E, varies with pressure. Equation (9) is still valid physically; and it can be used to determine the variation of E with effective pressure by measuring the radius. Equation (14) is still valuable in that it yields an approximate value of the pulse velocity.

If we are interested in finding u for one cycle only, we may take $a_n \neq 0$, and we have a slightly more difficult problem in harmonic analysis. From Machella's (1936) data, we may determine the coefficients of u. In place of equation (13) we have

$$p = \frac{v^2 \rho (a\, l + m\, \omega)}{a^2 + \omega^2} u + p_b.$$

In order that p may be real the imaginary part of p must vanish:

$$l\, \omega = a\, m. \tag{15}$$

The coefficient of u here must equal 1020 gm/sec cm^2 as before. The equation resulting from equating the coefficient to 1020 gm/sec cm^2 with the equations (5), (7) and (15) determine the relations among the parameters, a, l, m, λ (since ω is determined by the period of the cycle), and ρ, v, and μ.

Although the solution for a single cycle may initially seem rather artificial, the fact that it involves the complete equation recommends it to the author. We look upon the flow as being initiated at each systole, continuing the diastole and the values of u and p being altered by the characteristics of the elastic tube (the femoral artery).

It is interesting to note that Machella's pressure—velocity curves for the carotid artery do not show similarity of shape. This lack of similarity may be explained by the nearness of the carotid to the heart, thus the surge is so great that the approximations inherent in our differential equations are much too crude.

The author wishes to thank Professor N. Rashevsky for the opportunity of examining his recent papers on flow (1945a, b) in manuscript. He is indebted to certain members of the Howard University Medical School for data.

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LITERATURE

Bramwell, J. C. and A. V. Hill. 1922. "The Velocity of the Pulse Wave in Man." *Proc. Roy. Soc. London,* (B), 93, 298.

Foch, Adrien. 1932. *Introduction a la Mecanique des Fluides.* Paris: Armand Colin.

Frank, Otto. 1926. "Die Theorie der Pulsewellen." *ZS. f. Biol.,* 85, 91-130.

Machella, T. E. 1936. "Velocity of Blood Flow in Arteries." *Amer. Jour. Physiol.,* 115, 632-644.

Moens, A. I. 1878. *Die Pulskurve.* Leiden: E. J. Brill.

Rashevsky, N. 1945a. "A Problem in the Mathematical Biophysics of Blood Circulation: I." *Bull. Math. Biophysics,* 7, 25-33.

Rashevsky, N. 1945b. "A Problem in the Mathematical Biophysics of Blood Circulation: II. Relation between Pressure and Flow in an Elastic Distensible Tube." *Bull. Math. Biophysics,* 7, 35-39.

Von Kárman, T. and M. Biot. 1940. *Mathematical Methods in Engineering.* New York: McGraw-Hill Book Co.

Whittaker, S. R. F. and F. R. Winton. 1933. "The Apparent Viscosity of Blood Flowing in the Isolated Hind Limb of the Dog and its Variation with Corpuscular Concentration." *Jour. Physiol.,* 78, 339-369.

On the Kinetics of Copolymerization

HERMAN BRANSON AND ROBERT SIMHA

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On the Kinetics of Copolymerization

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TWO general developments of the kinetics of polymerization reactions have been recently given. One[1] involves the assumption of a steady state in regard to the concentration of active nuclei; the other[2] is more general.

Copolymerization reactions have been treated in a few instances[3] by introduction of certain *ad hoc* assumptions. In view of present interests it seems desirable to undertake a more complete analysis of these reactions. Because of the difficulty of a general development, the analysis rests on the steady state method which is valid as long as the rate of initiation is negligibly small in comparison with that of growth and that of termination. Mainly termination involving a radical chain and a stable monomer is considered at present. A few of the results are outlined in the following.

We postulate the mechanism:

$$\begin{aligned}
&\text{Initiation:} && N_1 \xrightarrow{k_{11}} n_{10}; && N_2 \xrightarrow{k_{12}} n_{01},\\
&\text{Propagation:} && n_{rs} \xrightarrow{k_{21}(r,s)} n_{r+1s}; && n_{rs} \xrightarrow{k_{22}(r,s)} n_{rs+1}, \qquad (1)\\
&\text{Termination:} && n_{rs} \xrightarrow{k_{31}(r,s)} N_{r+1s}; && n_{rs} \xrightarrow{k_{32}(r,s)} N_{rs+1}.
\end{aligned}$$

N_1 and N_2 are mole fractions of monomer 1 and 2, respectively; n_{rs} are mole fractions of polymer radical of specified composition. N_{rs} are stable polymers. Since

$$dn_{rs}/dt = 0,$$

we have from (1)

$$\begin{aligned}
&\alpha_{rs} n_{rs} = \beta_{r-1s} n_{r-1s} + \gamma_{rs-1} n_{rs-1} \quad r, s \geqq 1,\\
&\alpha_{10} n_{10} = k_{11} N_1,\\
&\alpha_{01} n_{01} = k_{12} N_2,
\end{aligned} \qquad (1a)$$

with the definitions

$$\begin{aligned}
\alpha_{rs} &= [k_{21}(r,s) + k_{31}(r,s)] N_1 \\
&\quad + [k_{22}(r,s) + k_{32}(r,s)] N_2,\\
\beta_{rs} &= k_{21}(r,s) N_1,\\
\gamma_{rs} &= k_{22}(r,s) N_2.
\end{aligned}$$

The solution of the difference equations (1a) can be found exactly as a complex function of the

[1] E. F. G. Herrington and Alan Robertson, Trans. Faraday Soc. **38**, 490 (1942).
[2] R. Ginell and R. Simha, J. Am. Chem. Soc. **65**, 706, 715 (1943).
[3] R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. **A171**, 147 (1939); F. T. Wall, J. Am. Chem. Soc. **63**, 1846 (1941).

two probabilities for growth of nuclei:

$$\omega_{ik}=\beta_{ik}/\alpha_{ik}, \quad \omega'_{ik}=\gamma_{ik}/\alpha_{ik}.$$

This solution expresses the total number of ways a chain of composition (r, s) can be built. The probabilities may be expected to be functions of the composition of the unstable polymer. In view of the scarcity of experimental data, it seems hardly warranted to carry through an exact treatment. As a first approximation we may, therefore, replace the probabilities by average values obtained on substituting a mean composition for the individual chain composition. The error will be greatest in respect to the pure polymers, n_{r0} and n_{0s}. However, since their number is small, the error will not be large. With these assumptions the solution of (1a) reduces to

$$n_{rs}=\omega^r(\omega')^s\left[\frac{k_{11}}{k_{21}}\binom{r+s-1}{s}+\frac{k_{12}}{k_{22}}\binom{r+s-1}{r}\right], \quad (2)$$

where k_{21} and k_{22} are the average rates of propagation:

$$k_{21}\sum_{i,k} n_{ik}=\sum_{i,k} k_{21}(i,k)n_{ik} \quad (3)$$

with a similar definition for k_{22}. In this equation k_{21} and k_{22} are independent of the composition of monomer in accordance with our assumption. The first term in (2) enumerates all ways of obtaining the polymer n_{rs} from a nucleus n_{10}; the second term, from a nucleus n_{01}.

Going to the kinetics, we have

$$\frac{dN_1}{dt}=-k_{11}N_1-N_1\sum_{i,k}[k_{21}(i,k)+k_{31}(i,k)]n_{ik}$$

and a similar equation for N_2. Introducing average rates of termination k_{31} and k_{32} defined in analogy to (3), we find from (1a):

$$\sum_{i,k} n_{ik}=\frac{k_{11}N_1+k_{12}N_2}{k_{31}N_1+k_{32}N_2}.$$

Substituting into the rate equations for N_1 and N_2 we obtain for the over-all rate

$$dz/dt=(k_{22}-k_{21})z[(k_{11}z+k_{12})/(k_{31}z+k_{32})], \quad (4)$$

where $z=N_1/N_2$ and all rates of propagation are much larger than the rates of termination. This equation or its integral allows a determination of certain combinations of rate constants. It may be noted that the over-all course of the reaction does not follow a simple first-order law as is found in simple polymerization.[1,2] If the second species is used up more rapidly than the first, $z\to\infty$ for $t\to\infty$; otherwise, $z\to 0$. If $z\to\infty$, the limiting rate is

$$\frac{1}{N_1}\frac{dN_1}{dt}=-\frac{k_{11}k_{21}}{k_{31}}; \quad \frac{1}{N_2}\frac{dN_2}{dt}=-\frac{k_{11}k_{22}}{k_{31}},$$

which is a first-order law; similarly a limiting second-order over-all rate results for a second-order initiation. For the final number average molecular weight, we find with the above approximations simply

$$\bar{M}_n=\frac{M_1N_1(0)+M_2N_2(0)}{(k_{31}/k_{21})N_1(0)+(k_{32}/k_{22})N_2(0)}.$$

M_1 and M_2 are the respective molecular weights of monomer; $N_1(0)$ and $N_2(0)$ represent initial mole fractions.

In the case of radical-radical termination with a rate k_3, the over-all rate can be shown to be:

$$\frac{dz}{dt}=z\left[(k_{12}-k_{11})+\frac{(k_{22}-k_{21})}{(k_3)^{\frac{1}{2}}}N_2^{\frac{1}{2}}(k_{11}z+k_{12})^{\frac{1}{2}}\right].$$

For the change of size distribution with composition we find with (1), (2), and (4):

$$\frac{dN_{rs}}{dz}=\frac{N_2(0)}{z_0(k_{22}-k_{21})}\left(\frac{z_0}{z}\right)^{[k_{22}/(k_{22}-k_{21})]+1}\times\frac{k_{31}z+k_{32}}{k_{11}z+k_{12}}f(r,s)\omega^r(\omega')^{s-1},$$

in which

$$f(r,s)=\left[\frac{k_{11}k_{22}k_{31}}{(k_{21})^2}\binom{r+s-2}{s}+\frac{k_{12}k_{32}}{k_{22}}\binom{r+s-2}{s-2}+\left(\frac{k_{12}k_{31}}{k_{21}}+\frac{k_{11}k_{32}}{k_{21}}\right)\binom{r+s-2}{s-1}\right].$$

From the definition of the ω's we see that they can be written as functions of z. The equation may then be integrated to give the final size distribution. Formulae for the weight average molecular weight may also be derived in this manner.

These preliminary results are presented as a contribution to a treatment of copolymerization which will allow a quantitative evaluation of kinetic data and of the structure of copolymers. A detailed paper dealing with this problem and extensions is being prepared.

Theory of Chain Copolymerization Reactions

ROBERT SIMHA AND HERMAN BRANSON

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Theory of Chain Copolymerization Reactions*

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The kinetics of chain copolymerizations is developed for reactions consisting of three steps: first, an activation of stable monomer; second, a growth of activated polymer radical by means of monomer addition; third, a stabilization of the growing chains by (a) monomer addition, (b) by means of growing polymer [Eq. (1)]. The existence of a steady state in respect to the concentration of growing chains beyond the induction period is assumed. The rate constants of growth and termination will in general depend upon the individual composition and upon the nature of the activated chain end. Equations for the rate of change of mole ratio z of the two monomer species are developed in terms of mean rates of growth and termination obtained by averaging the actual rates over the distribution of growing polymer [(4), (4a), (4′)]. The equilibrium conditions lead to a set of difference equations for this distribution [(5), (5′)]. It is investigated whether the solution and results derived therefrom are of a form which permits a determination of the dependence of the rate constants for growth and termination upon the composition of the polymer molecule (6). In addition, the influence of the type of active chain end involved on over-all rate and size distribution is considered by introducing four constants for propagation and termination, respectively, according to the four possibilities $A-A$, $A-B$, $B-A$, $B-B$ [(6a), (7), (4b), (4b′)], but independent of chain composition. Various special cases according to the relative magnitude of the rates for the two reactants are presented. Experimentally it is difficult to distinguish on the basis of kinetic data between the foregoing mechanism and one in which the rates of growth (and termination) for each of the two kinds of monomer depend solely upon the nature of the monomer molecule added and are independent of the nature of the active chain end [(4c), (4c′), (4c″)]. Relations are derived for the molecular size distribution, the inhomogeneity of the copolymer mixture in regard to composition, the average molecular weight, and the average composition of copolymer as function of the composition of the monomer residue [(8a), (8a′), (9a), (10)]. The importance of these results for soluble and insoluble copolymers and for the theory of gel formation in vinyl-divinyl type polymers is pointed out.

THE kinetics of chain polymerization reactions has been extensively treated.[1] Starting with the main elementary processes of chain initiation, propagation, and termination, it is possible to derive expressions for the over-all consumption of monomer, for the average chain length of the polymer formed during the various stages of the process and for the distribution of molecular weights. This in turn permits an analysis of the elementary rate constants, and therefore of energies of activation and frequency factors.

If two monomer species copolymerize, additional questions arise, e.g., the composition distribution of polymer, the molecular arrangement of the two types within a chain, particularly if one of the two species acts as cross-linking agent, as in the vinyl-divinyl copolymerization.

The kinetics of copolymer formation has received much less attention than that of one-component systems. Norrish and Brookman[2] have considered the over-all rate of the chain process. Jenckel[3] was the first to specify the special types of copolymers obtainable, depending upon the relative values of the rate constants for the two species. However, since he did not introduce the initiation and termination, as pointed out by himself, his method is limited and the results obtained represent rather special cases, as will become evident in the following. Wall[4] has considered this question, however, without treating the process as a chain reaction governed by the above elementary processes. Instead, he starts with the assumption of a first-order over-all rate of disappearance for each of the two kinds of monomer. His equations, therefore, also refer to special cases and are in part identical with those of Jenckel. Recently the present authors approached this problem from the point

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[1] Compare the symposium on "High Polymers" held by the New York Academy of Sciences, Ann. N. Y. Acad. Sci. **44**, 263 (1943).

[2] R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. **A171**, 147 (1939).

[3] E. Jenckel, Zeits. f. physik. Chemie **A190**, 24 (1941).

[4] F. T. Wall, J. Am. Chem. Soc. **63**, 1862 (1941).

position and chain end determines the radical distribution and therefore the variation of the average rates with z.

II. DETERMINATION OF RADICAL DISTRIBUTION

Because of the existence of a steady state

$$\frac{dn_{rs}(A)}{dt}=\frac{dn_{rs}(B)}{dt}=0.$$

Scheme (1) then leads to the following set of difference equations for the concentration of growing polymer of indicated type:

$$\begin{aligned}\alpha_{rs}(A)n_{rs}(A)&=\beta_{r-1s}(A)n_{r-1s}(A)\\&\quad+\beta_{r-1s}(B)n_{r-1s}(B),\\\alpha_{rs}(B)n_{rs}(B)&=\gamma_{rs-1}(A)n_{rs-1}(A)\\&\quad+\gamma_{rs-1}(B)n_{rs-1}(B),\\\alpha_{10}(A)n_{10}&=I_1N_1;\quad \alpha_{01}(B)n_{01}=I_2N_2.\end{aligned}\tag{5}$$

For monomer termination:

$$\begin{aligned}\alpha_{rs}(L)&=[k_{21}(r,s,L)+k_{31}(r,s,L)]N_1\\&\quad+[k_{22}(r,s,L)+k_{32}(r,s,L)]N_2,\\\beta_{rs}(L)&=k_{21}(r,s,L)N_1;\quad \gamma_{rs}(L)=k_{22}(r,s,L)N_2,\end{aligned}$$

with $L=A$ or B. For radical termination:

$$\begin{aligned}\alpha_{rs}(L)&=k_{21}(r,s,L)N_1+k_{22}(r,s,L)N_2\\&\quad+\sum_{i,j}[k_3(r,s,i,j,L,A)n_{ij}(A)\\&\quad+k_3(r,s,i,j,L,B)n_{ij}(B)]\\&=k_{21}(r,s,L)N_1+k_{22}(r,s,L)N_2\\&\quad+\bar{k}_3(r,s,L,A)\sum_{i,j}n_{ij}(A)\\&\quad+\bar{k}_3(r,s,L,B)\sum_{i,j}n_{ij}(B).\end{aligned}\tag{5'}$$

$\bar{k}_3(r,s,L,A)$ and $\bar{k}_3(r,s,L,B)$ with $\bar{k}_3(A,B)=\bar{k}_3(B,A)$ are suitably defined average rates.

The general solution of system (5) leads to complex expressions, depending upon the specific nature of the rates as function of the individual chain composition r, s. Herington and Robertson[7] have developed equations for simple polymerization processes permitting in principle to deduce the dependence of the growth to termination ratio upon individual molecular size from determinations of the instantaneous distribution curve. One may think of a similar procedure here. To investigate this, the complexity of (5) is reduced first by disregarding the dependence of growth and cessation upon the type of active end involved. This will be nearly correct, if no further steric conditions remain to be satisfied once an active end has been formed. The only important contribution of the growing chain to the rate constant then depends upon its size and composition only. In this case one has:

$$n_{rs}(A)+n_{rs}(B)=2n_{rs}(A)=n_{rs}$$

and (5) reduces to:

$$\alpha_{rs}n_{rs}=\beta_{r-1s}n_{r-1s}+\gamma_{rs-1}n_{rs-1};\quad r,s\geqq 1.\tag{5a}$$

This set may be solved by induction, as shown in Appendix I. The solution is:

$$n_{rs}=\frac{\alpha_{0s}}{\beta_{rs}}\prod_{l=0}^{r}\left(\frac{\beta_{ls}}{\alpha_{ls}}\right)n_{0s}+\sum_{j=1}^{r}n_{js-1}\frac{\gamma_{js-1}}{\beta_{rs}}\prod_{l=j}^{r}\frac{\beta_{ls}}{\alpha_{ls}}.$$

For the pure polymers, n_{r0} and n_{0s}, we have:

$$\beta_{r-10}n_{r-10}=\alpha_{r0}n_{r0};\quad \gamma_{0s-1}n_{0s-1}=\alpha_{0s}n_{0s}.$$

Therefore:

$$I_1N_1=\beta_{r0}n_{r0}\prod_{l=1}^{r}\frac{\alpha_{l0}}{\beta_{l0}};\quad I_2N_2=\gamma_{0s}n_{0s}\prod_{l=1}^{s}\frac{\alpha_{0l}}{\gamma_{0l}}.$$

Whereupon:

$$n_{rs}=\frac{I_2N_2}{\alpha_{rs}}\prod_{l=0}^{r-1}\frac{\beta_{ls}}{\alpha_{ls}}\prod_{l=1}^{s-1}\frac{\gamma_{0l}}{\alpha_{0l}}+\frac{1}{\alpha_{rs}}\sum_{j=1}^{r}\gamma_{js-1}n_{js-1}\prod_{l=j}^{r-1}\frac{\beta_{ls}}{\alpha_{ls}}.$$

Defining:

$$\frac{\beta_{ij}}{\alpha_{ij}}=\omega_{ij}\quad\text{and}\quad\frac{\gamma_{ij}}{\alpha_{ij}}=\omega'_{ij},$$

the probabilities for growth by means of monomer 1 and 2, respectively, n_{rs} becomes finally:

$$\begin{aligned}n_{rs}&=\frac{I_1N_1}{\alpha_{rs}}\sum_{i_1=1}^{r}\sum_{i_2=1}^{i_1}\cdots\sum_{i_s=1}^{i_{s-1}}\prod_{l=1}^{i_s-1}\omega_{l0}\omega'_{i_s0}\prod_{l=i_s}^{i_{s-1}-1}\omega_{l1}\omega'_{i_{s-1}1}\\&\times\prod_{l=i_{s-1}}^{i_{s-2}-1}\omega_{l2}\cdots+\frac{I_2N_2}{\alpha_{rs}}\sum_{i=0}^{s-1}\sum_{j_1=1}^{r}\cdots\sum_{j_i=1}^{j_{i-1}}\prod_{l=1}^{s-i-1}\omega'_{0l}\\&\times\prod_{l=0}^{j_i-1}\omega_{ls-i}\omega'_{j_is-i}\prod_{l=j_i}^{j_{i-1}-1}\omega_{ls-i+1}\cdots\omega'_{j_1s-1}\prod_{l=j_1}^{r-1}\omega_{ls}.\end{aligned}\tag{6}$$

The term on the right multiplied by I_1N_1 gives the n_{rs} initiated by monomer species 1. The first product gives the probability that the chain

[7] E. F. G. Herington and A. Robertson, Trans. Faraday Soc. **38**, 490 (1942).

so initiated adds (j_s-1) monomers of species 1 before a species 2 is added, as represented by the factor $\omega'_{j_s 0}$. The second product describes the further growth of the polymer by addition of more 1's until there are $(j_{s-1}-1)$ of the first species. At this stage a monomer of the second type is added. The remaining factors express the further growth. Finally, the summations over the j's give the total number of possible intramolecular arrangements consistent with the composition r, s and initiated by the first species. The second term is interpreted similarly.

In the case of radical termination, the same solution is obtained with the α's defined as in (5′) after suitable specialization.

We may investigate the specific effect of different growing ends upon the reaction by neglecting the dependence upon chain composition. Equation (5) becomes upon division by $\alpha(A)$ and $\alpha(B)$, respectively:

$$\begin{aligned} n_{rs}(A) &= \omega(A) n_{r-1s}(A) + \omega(B) n_{r-1s}(B), \\ n_{rs}(B) &= \omega'(A) n_{rs-1}(A) + \omega'(B) n_{rs-1}(B), \end{aligned} \tag{5b}$$

where the ω's are defined as:

$$\omega(A) = \frac{\beta(A)}{\alpha(A)}; \quad \omega(B) = \frac{\beta(B)}{\alpha(A)};$$

$$\omega'(A) = \frac{\gamma(A)}{\alpha(B)}; \quad \omega'(B) = \frac{\gamma(B)}{\alpha(B)}.$$

They represent probabilities for $-A-A, -B-A, -A-B, -B-B$ addition, respectively. The solutions of (5b) are, as shown in Appendix II:

$$\begin{aligned} n_{rs}(A) &= [\omega(A)]^{r-1}[\omega'(B)]^{s} \\ &\quad \times \left\{ \frac{I_1 N_1}{\alpha(A)} [F(1-r, -s, 1, x) \right. \\ &\quad - F(1-r, 1-s, 1, x)] \\ &\quad \left. + \frac{I_2 N_2}{\alpha(B)} \frac{\omega(A)}{\omega'(A)} F(1-r, 1-s, 1, x) \right\}; \\ n_{rs}(B) &= [\omega(A)]^{r}[\omega'(B)]^{s-1} \\ &\quad \times \left\{ \frac{I_1 N_1}{\alpha(A)} \frac{\omega'(A)}{\omega(A)} F(1-r, 1-s, 1, x) \right. \\ &\quad + \frac{I_2 N_2}{\alpha(B)} [F(-r, 1-s, 1, x) \\ &\quad \left. - F(1-r, 1-s, 1, x)] \right\}, \end{aligned} \tag{6a}$$

where the F's are hypergeometric functions with

$$x = \frac{\omega'(A)\omega(B)}{\omega(A)\omega'(B)} = \frac{\gamma(A)}{\beta(A)} \frac{\beta(B)}{\gamma(B)},$$

corresponding to $\dfrac{-A-B}{-A-A} \dfrac{-B-A}{-B-B}$ addition.

The interpretation of (6a) is analogous to that of (6). The first term always gives the total number of active chains of stated composition initiated by the first species. In the case of radical termination (6a) remains valid with the α's defined as in (5′), but independent of r and s. For the developments in the next section we need the total number of radicals of specified ends (see Appendix II):

$$\begin{aligned} \sum_{r,s \geqq 1} n_{rs}(A) &= \frac{\omega(A)\omega(B)x}{[(1-\omega(A))(1-\omega(B)) - x\omega(A)\omega'(B)]} \left[\frac{I_1 N_1}{\alpha(A)(1-\omega(A))} + \frac{I_2 N_2}{\alpha(B)\omega'(A)} \right], \\ \sum_{r} n_{r0}(A) &= \frac{I_1 N_1}{\alpha(A)} \frac{1}{1-\omega(A)}, \\ \sum_{r,s \geqq 1} n_{rs}(B) &= \frac{\omega(A)\omega'(B)x}{[(1-\omega(A))(1-\omega'(B)) - x\omega(A)\omega'(B)]} \left[\frac{I_1 N_1}{\alpha(A)\omega(B)} + \frac{I_2 N_2}{\alpha(B)(1-\omega'(B))} \right], \\ \sum_{s} n_{0s}(B) &= \frac{I_2 N_2}{\alpha(B)} \frac{1}{1-\omega'(B)}. \end{aligned} \tag{7}$$

III. SPECIAL RATE EQUATIONS

From the results obtained for the radical distribution, it is possible to determine the average rates $\bar{k}_{21}, \bar{k}_{22}, \bar{k}_{31}, \bar{k}_{32}$ and introduce them into the general equations (2) and (4′). The mean rates, obtained

by averaging over the rates for A and B ends, respectively, according to the general equation previously given, are:

$$\bar{k}\sum_{r,s}[n_{rs}(A)+n_{rs}(B)]=\sum_{r,s}[k(A)n_{rs}(A)+k(B)n_{rs}(B)],$$

where, as before, the $\bar{k}$'s are independent of r, s. Substituting for the sums, one has:

$$k=\frac{k(A)[I_1N_1(\alpha(B)-\gamma(B))+I_2N_2\beta(B)]+k(B)[I_1N_1\gamma(A)+I_2N_2(\alpha(A)-\beta(A)]}{I_1N_1[\alpha(B)+\gamma(A)-\gamma(B)]+I_2N_2[\alpha(A)+\beta(B)-\beta(A)]}.$$

Therefrom:

$$-\frac{1}{N_l}\frac{dN_l}{dt}=I_l+(\bar{k}_{2l}+\bar{k}_{3l})[\sum_{r,s}n_{rs}(A)+\sum_{r,s}n_{rs}(B)]$$

with $l=1, 2$. Equation (4a) then yields:

$$\frac{d}{dt}\ln z=(I_1z+I_2)\frac{c_1z^2+c_2z+c_3}{c_4z^3+c_5z^2+c_6z+c_7}, \tag{4b}$$

where

$$c_1=I_1[k_{22}(A)-k_{21}(A)][k_{21}(B)+k_{31}(B)]\doteq I_1k_{21}(B)[k_{22}(A)-k_{21}(A)],$$
$$c_2\doteq I_2k_{21}(B)[k_{22}(A)-k_{21}(A)]+I_1k_{22}(A)[k_{22}(B)-k_{21}(B)],$$
$$c_3\doteq I_2k_{22}(A)[k_{22}(B)-k_{21}(B)],$$
$$c_4\doteq I_1k_{21}(B)k_{31}(A),$$
$$c_5\doteq I_2k_{21}(B)k_{31}(A)+I_1[k_{22}(A)k_{31}(B)+k_{21}(B)k_{32}(A)],$$
$$c_6\doteq I_2[k_{22}(A)k_{31}(B)+k_{21}(B)k_{32}(A)]+I_1k_{22}(A)k_{32}(B),$$
$$c_7\doteq I_2k_{22}(A)k_{32}(B),$$

in which we neglected k_3's with respect to k_2's. It should be noted that for a first-order initiation process I_1 and I_2 are independent of N_1 and N_2, the c's are constants, and the right-hand side of (4b) depends solely upon z. For higher order initiation, $d\ln z/dt$ depends explicitly upon z, the mole ratio, and upon N_2, the number of moles of the second species present.

During the last stages of the reaction, $z\to\infty$, the slope of the $\ln z$ curve becomes $I_1/k_{31}(A)[k_{22}(A)-k_{21}(A)]$ which is constant for first-order initiation. The rate of monomer consumption is then given by

$$\lim_{t\to\infty}\frac{1}{N_l}\frac{dN_l}{dt}=-\frac{k_{2l}(A)I_1}{k_{31}(A)},\quad l=1, 2.$$

The limiting over-all rate follows the same order as the rate of initiation of the slower species. This result is exactly analogous to the one obtained in simple polymerization reactions where it holds throughout the reaction.[6,7] The rate factor depends only upon the constants characteristic for active ends formed by the slower reacting species. This is not unexpected since this type end is the only one formed during the final stages. Equation (4b) can now be specialized to give copolymer systems equivalent to those defined by Jenckel.[3] Case 1: Each species polymerizes independently; expressed by $k_{22}(A)=k_{21}(B)=0$, $k_{32}(A)=k_{31}(B)=0$. The over-all rate is:

$$\frac{d\ln z}{dt}=\frac{I_2k_{22}(B)}{k_{32}(B)}-\frac{I_1k_{21}(A)}{k_{31}(A)}.$$

This shows, as one expected, that the result of the copolymerization is the same as that obtained by separate polymerization and subsequent mixing. The first term on the right equals $-(1/N_2)(dN_2/dt)$ and the second $(1/N_1)(dN_1/dt)$. The same type of result was obtained by Wall.[4] Case 2: In the other extreme, each species adds on to active ends formed by the other type; $k_{21}(A)=k_{22}(B)=0$, $k_{31}(A)$

$=k_{32}(B)=0$. The result is a checker board polymer. One obtains:

$$\frac{d\ln z}{dt}=\frac{(I_1z+I_2)(z-1)}{k_{32}(A)[k_{22}(A)]^{-1}+k_{31}(B)[k_{21}(B)]^{-1}}\frac{1}{z}.$$

Case 3: $-A-A$, $-B-B$, $-B-A$, and $-A-B$ additions occur with equal probability; $k_{21}=k_{22}$, $k_{31}=k_{32}$ for A and B. Equation (4) with constant values for the R_i yields:

$$d\ln z/dt=I_2-I_1.$$

This is a result of the same type as that holding for case 1; furthermore, if the velocities of initiation are also equal, no change of monomer composition results during the whole process and it remains equal to the composition of polymer formed.

Equation (6a) holds also for radical termination. However, the solution (6a) contains the quantities $\sum n_{rs}(A)$ and $\sum n_{rs}(B)$ explicitly, as can be seen from the definition (5) of the α's. In order to determine the sums, we revert to (7), which represents in this case implicit equations for the desired quantities in terms of rate constants and monomer concentrations. On substituting for the ω's in (7) a set of simultaneous cubic equations for $\sum n_{rs}(A)$ and $\sum n_{rs}(B)$ results. The linear term is negligible in comparison with the constant and quadratic terms because of the magnitudes of the different rates. The cubic term is also negligible until N_1 becomes vanishingly small. The solution obtained with these approximations is:

$$\sum n_{rs}(A)=\beta(B)/\gamma(A)\sum n_{rs}(B)$$
$$=\beta(B)\left\{\frac{I_1N_1+I_2N_2}{\beta(B)[k_3(A,A)\beta(B)+k_3(A,B)\gamma(A)]+\gamma(A)[k_3(A,B)\beta(B)+k_3(B,B)\gamma(A)]}\right\}^{\frac{1}{2}}. \quad (7')$$

This expression may be used to determine the average values of the rates. Introduction of the values into (4') and use of the definitions of the β's and γ's yields for the over-all rate for radical termination:

$$\frac{d\ln z}{dt}=I_2-I_1+\frac{N_2^{\frac{1}{2}}(I_1z+I_2)^{\frac{1}{2}}\{k_{21}(B)[k_{22}(A)-k_{21}(A)]z+k_{22}(A)[k_{22}(B)-k_{21}(B)]}{\{k_3(A,A)k_{21}^2(B)z^2+2k_3(A,B)k_{21}(B)k_{22}(A)z+k_3(B,B)k_{22}^2(A)\}^{\frac{1}{2}}}. \quad (4b')$$

If the initiation is first order, (4b') and (4b) show that the distinction between radical and monomer termination lies in the explicit dependence of the over-all rate upon the concentration N_2 in the former case.

If the kinetic distinction between the two types of growing ends is dropped as was done in the derivation of (6) for the distribution of active radical, (4b) and (4b') become

$$\frac{d\ln z}{dt}=(I_1z+I_2)\frac{k_{22}-k_{21}}{k_{31}z+k_{32}} \quad (4c)$$

and

$$\frac{d\ln z}{dt}=(I_2-I_1)+\left(\frac{I_1z+I_2}{k_3}\right)^{\frac{1}{2}}N_2^{\frac{1}{2}}(k_{22}-k_{21}), \quad (4c')$$

where all the k's represent true rates, not average rates as in (4a) and (4') which have the same form.

Unless experimental data are very accurate, it will be difficult to distinguish between the type of behavior described by (4b) and that of (4c); for the ratio of a quadratic to a cubic function of z in (4b) is replaced by the ratio of a constant to a linear term in (4c). Analogous reasoning applies to a comparison of (4b') and (4c'). As far as the dependence of growth and termination upon individual chain composition is concerned, the form of (6) seems to preclude our deriving information from

measurements of over-all rate and from size distribution data. We shall, therefore, make (4c) and (4c') the basis for our further considerations.

Equation (4c) or the full equation (4) with constant coefficients R_i can immediately be integrated. Equation (4c) and the first equation in (4) yield for a first-order initiation process (I_1, I_2 constant):

$$k_{32}I_1 \ln \frac{z}{z_0}+(k_{31}I_2-k_{32}I_1)\ln\frac{I_1z+I_2}{I_1z_0+I_2}=I_1I_2(k_{22}-k_{21})t, \tag{4d}$$

$$\ln\frac{N_2}{N_2(0)}=\frac{R_4}{R_2-R_4}\ln z/z_0+\left(\frac{R_4}{R_4-R_2}-\frac{R_3}{R_3-R_1}\right)\ln\frac{(R_1-R_3)z+(R_2-R_4)}{(R_1-R_3)z_0+(R_2-R_4)}\doteq-\frac{k_{22}}{k_{22}-k_{21}}\ln z/z_0,$$

where $N_2(0)$ and z_0 are the initial mole fraction for the second species and mole ratio, respectively. The approximate equation is valid since rates of growth are large with respect to rates of initiation and termination, and since k_{22}/k_{21} is of the same order of magnitude as k_{32}/k_{31}. This procedure is not acceptable if the rates are very nearly equal, but this has already been considered as case 3 in this section.

The rate constants are best determined from the graph of $d \ln z/dt$ *versus* z. That is, one would find experimentally the $\ln z-t$ curve, calculate the slope and plot it *versus* the corresponding values of z. Figure 1[8] is such a curve for selected values of the rate constants and for different ratios of the two termination rates. Equal velocities of initiation are assumed. Inequality of initiations would not change the general shape of the curves, except for a possible change of sign of the slope. Differences in the growth rates merely shift the curves vertically. Jenckel's[3] and Wall's[4] equations yield the horizontal line.

The experimental data of Marvel and co-workers[9] seem to deviate from the horizontal line. It is difficult to judge from these data whether the deviations follow this theory. For very large values of z the slope is zero since both species are reacting independently. The ratio of the two growth rates can easily be found from (4d).

Equations (2') for radical termination yield as intermediate integral a relation between N_1, N_2, and t, which can be written as follows, if the initiations are first order:

$$\ln\frac{N_2}{N_2(0)}=-\frac{k_{22}}{k_{22}-k_{21}}\ln\frac{z}{z_0}+\frac{k_{22}k_{21}}{k_{22}-k_{21}}\left(\frac{I_2}{k_{22}}-\frac{I_1}{k_{21}}\right)t. \tag{4d'}$$

Equation (4c') then gives for the over-all rate:

$$\frac{d\ln z}{dt}=(I_2-I_1)+[N_2(0)]^{\frac{1}{2}}\frac{(k_{22}-k_{21})}{k_3^{\frac{1}{2}}}\left(\frac{z_0}{z}\right)^{k_{22}/2(k_{22}-k_{21})}(I_1z+I_2)^{\frac{1}{2}}\exp\left\{\frac{k_{22}k_{21}}{2(k_{22}-k_{21})}\left(\frac{I_2}{k_{22}}-\frac{I_1}{k_{21}}\right)t\right\}. \tag{4c''}$$

Unless the two rates of propagation are very nearly equal, the coefficient of t in (4d') and (4c'') will be sufficiently small to make the t factor negligible over a wide interval of the reaction. Under these conditions, (4d') becomes identical with the approximate form of (4d). The slope of the $\ln z-t$ curve depends also upon the initial monomer concentrations, while monomer termination gives a dependence upon the instantaneous ratio z only (4c). Extrapolation of the slope of the $\ln z-t$ curve to zero time yields a straight line according to (4c''), if plotted *versus* the square root of the initial mole fraction $N_2(0)$. Its intercept equals I_2-I_1.

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[8] We are indebted to Mr. Charles P. Powell for his aid in carrying out the numerical computations.

[9] C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz, J. Am. Chem. Soc. **64**, 2356 (1942).

IV. COPOLYMER COMPOSITION AND SIZE DISTRIBUTION

The mole fraction of stable polymer N_{rs} is given by the following equations according to scheme (1), for the stable copolymer formed in a time element dt (hereafter called instantaneous copolymer distribution):

$$\frac{dN_{rs}}{dt}=k_{31}N_1n_{r-1s}+k_{32}N_2n_{rs-1};$$

Monomer termination. (8)

$$\frac{dN_{rs}}{dt}=\frac{k_3}{2}\sum_{i,\,j=0}^{r,\,s}n_{r-is-j}n_{ij};\qquad \frac{dN_{rs}}{dt}=k_3n_{rs}\sum_{i,\,j}n_{ij};$$

Radical termination. (8′)

n_{rs} is derived from (6) for rates independent of r and s:

$$n_{rs}=\omega^r(\omega')^s\left[I_1/k_{21}\binom{r+s-1}{s}+\frac{I_2}{k_{22}}\binom{r+s-1}{r}\right], \quad (6a)$$

$$\sum_{i,\,j}n_{ij}=(I_1N_1+I_2N_2)(\alpha-\beta-\gamma)^{-1},$$

where

$\omega=\omega_{ij}$ and $\omega'=\omega'_{ij}$ are independent of i, j.

Equation (6a) is valid for radical termination if the α's in ω and ω' are defined:

$$\alpha=k_{21}N_1+k_{22}N_2+k_3N_2^{\frac{1}{2}}\left(\frac{I_1z+I_2}{k_3}\right)^{\frac{1}{2}}.$$

Elimination of t in (8) leads by means of relations (4c), (4d), and (6a) to the following expressions valid for first-order initiation and monomer termination:

$$\frac{dN_{rs}}{dz}=\frac{N_2(0)}{z_0(k_{22}-k_{21})}\left(\frac{z_0}{z}\right)^{1+k_{22}/k_{22}-k_{21}}\times\frac{k_{31}z+k_{32}}{I_1z+I_2}f(r,\,s)\omega^r(\omega')^{s-1},$$

with

$$f(r,\,s)=\frac{I_1k_{22}k_{31}}{k_{21}^2}\binom{r+s-2}{s}+\frac{I_2k_{32}}{k_{22}}\binom{r+s-2}{s-2}+\left(\frac{I_2k_{31}}{k_{21}}+\frac{I_1k_{32}}{k_{21}}\right)\binom{r+s-2}{s-1}. \quad (8a)$$

Unfortunately it is not possible to integrate this expression in closed form and find in this manner the distribution of stable polymer corresponding to a monomer composition z. Numerical integration is required after the rate constants have been determined from kinetic data. The distribution of stable polymer first formed may be obtained as:

$$N_{rs}(z\rightarrow z_0)=\left[\frac{dN_{rs}}{dz}\right]_{z=z_0}(z-z_0).$$

If the monomer ratio z_0 is maintained, this gives the distribution at any instant. The total number of molecules of a certain total chain length p can be determined by means of the equation derived from (8):

$$\frac{d}{dz}\sum_{r+s=p}N_{rs}=N_2\frac{dt}{dz}(\omega+\omega')^{p-2}\left[I_1\frac{k_{22}k_{31}}{k_{21}^2}\frac{\omega^2}{\omega'}+\frac{(I_2k_{31}+I_1k_{32})}{k_{21}}\omega+\frac{I_2k_{32}}{k_{22}}\omega'\right].$$

For the total number of polymer molecules we obtain

$$\frac{d}{dz}\sum_{r+s=2}^{\infty}N_{rs}=N_2(I_1z+I_2)\frac{dt}{dz},$$

a result which can be written down directly in view of the steady state condition. Integration of the last expression using (4c) and (4d) gives:

$$\sum_{r+s=2}^{\infty}N_{rs}=\frac{k_{31}}{k_{21}}N_1(0)\left[1-\left(\frac{z_0}{z}\right)^{k_{21}/k_{22}-k_{21}}\right]+\frac{k_{32}}{k_{22}}N_2(0)\left[1-\left(\frac{z_0}{z}\right)^{k_{21}/k_{22}-k_{21}}\right].$$

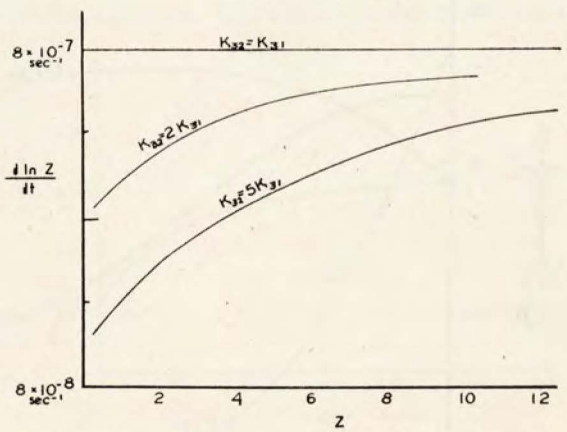

FIG. 1. Slope of $\ln z-t$ curve as a function of z, (4c), for various ratios k_{31}/k_{32}. $I_1=I_2=10^{-9}$ sec.$^{-1}$; $k_{21}=2.10^{-3}$ mole^{-1} liter sec.$^{-1}$; $k_{22}=5k_{21}$; $k_{31}=10^{-5}$ mole^{-1} liter sec.$^{-1}$.

The number average molecular weight of the polymerized material is given by

$$\bar{M}_n(z)=\frac{M_1[N_1(0)-N_1(z)-n_{10}]+M_2[N_2(0)-N_2(z)-n_{01}]}{\sum_{r+s=2}^{\infty} N_{rs}+\sum_{r,s} n_{rs}-n_{10}-n_{01}}. \tag{9}$$

M_1 and M_2 denote the molecular weights of the two monomer species. All mole fractions can be expressed as functions of z by means of relations (3), (4d), and (6a). For the final number average molecular weight we find in this manner, if the small amount of monomer radical is neglected:

$$\bar{M}_n(\infty)=\frac{M_1 z_0+M_2}{\frac{k_{31}}{k_{21}}z_0+\frac{k_{32}}{k_{22}}}. \tag{9a}$$

For a one-component polymerization one has in place of (9a) the familiar result:

$$\bar{M}_n(\infty)=M_1 k_{21}/k_{31}.$$

As is to be expected, the result (9a) depends upon the initial monomer composition which appears here as a weight factor in the average formed over the contribution of the two species to the total. One may guess that the weight average molecular weights of copolymer and pure polymer will be similarly related. The quotient of the two terms in (9) equals the weight ratio w of the two species in the polymerized material:

$$w(z)=\frac{M_1}{M_2}z_0\frac{1-(z_0/z)^{k_{21}/(k_{22}-k_{21})}}{1-(z_0/z)^{k_{22}/k_{22}-k_{21}}}. \tag{10}$$

For $z\to\infty$, the polymer composition naturally becomes equal to the initial monomer composition $(M_1/M_2)z_0$. The result (10) can be valid only beyond the induction period, when the concentration of activated chains n_{rs} is stationary and when n_{10} and n_{01}, whose initial values cannot be determined by the method used here, are negligible in comparison with the terms retained in the numerator and denominator of (10). On extrapolating, however, the composition curve to zero time, $z=z_0$, (10) reduces to:

$$w(z_0)=\frac{M_1}{M_2}z_0\frac{k_{21}}{k_{22}}.$$

Hence the intercept of the polymer composition curve gives the ratio of the rates of growth for the two components. Equation (10) may easily be expressed in terms of weight percentage composition of monomer which gives a more accurate graph for large values of z. Because of the identity of (4d′) and (4d) previously discussed, (10) holds approximately also in the case of radical termination. The instantaneous distribution by weight, $(d/dz)[(M_1r+M_2s)N_{rs}]$ according to (8a), is plotted in Figs. 2 and 3 *versus* the total chain length for constant chain composition $\delta=s/r$ and

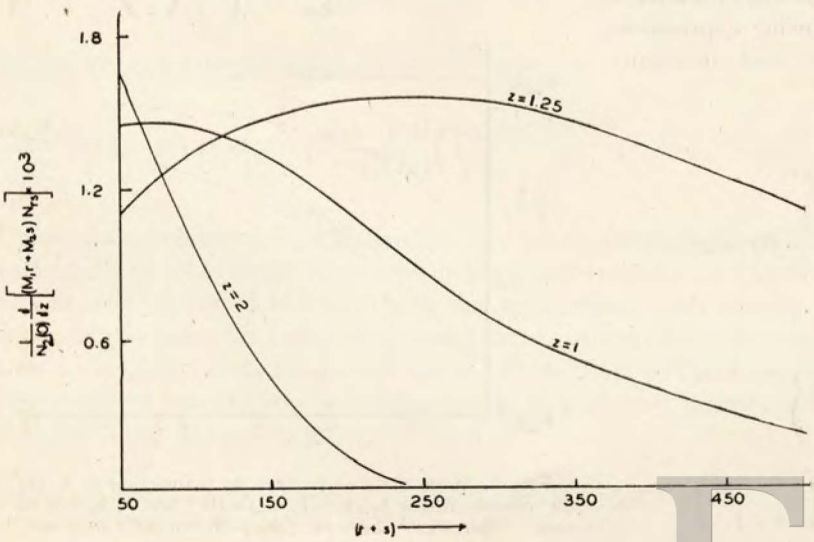

FIG. 2. Instantaneous weight distribution (9) at constant chain composition $\delta=s/r=4$ as a function of chain length $r+s$, at various stages of the reaction. Rates identical with those in Fig. 1 with $k_{32}=2k_{31}$, $z_0=0.4$. Vertical scale should be divided by ten for $z=2$.

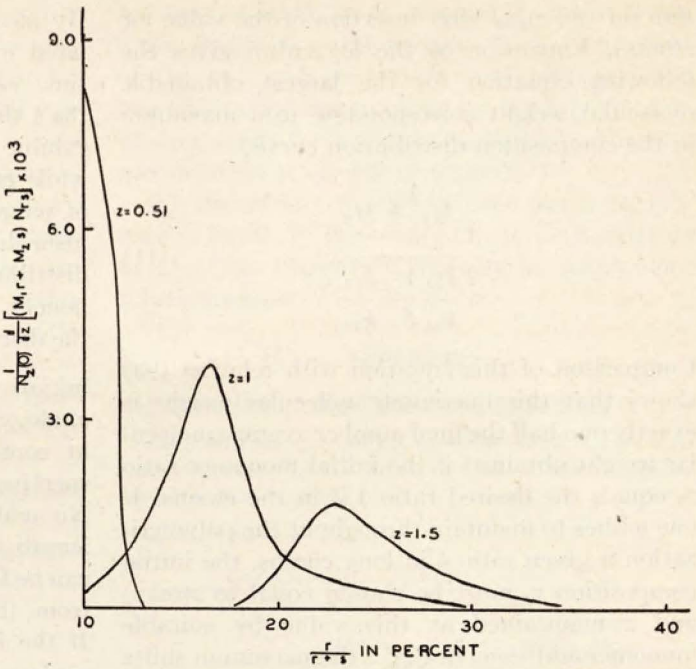

FIG. 3. Instantaneous weight distribution (9) at constant chain length $r+s=200$ as a function of chain composition $r/r+s$ at various stages of the reaction. Numerical values of constants identical with those in Fig. 2. Ordinate scale for curve $z=0.51$ should be multiplied by two.

versus the composition $r/r+s$ for constant chain length, respectively, at various stages z of the reaction. Some of the values chosen were suggested by Reinhardt's[10] data on the vinyl chloride (species 1) vinylidene chloride (species 2) system. Stirling's formula can be used to replace the factorials for most of the values of r and s shown in the graphs. In the plots at constant δ, (8a) leads to:

$$(M_1r+M_2s)\frac{dN_{rs}}{dz}=A(z)r^{\delta}\left\{\frac{(\delta+1)^{\delta+1}}{\delta^{\delta}}\times\frac{k_{22}^{\delta}k_{21}z}{[(k_{21}+k_{31})z+(k_{22}+k_{32})]^{\delta+1}}\right\}^{r}. \quad (9)$$

The maximum of the distribution is at

$$(r+s)_{\max}=r_{\max}(1+\delta)=\left(\frac{1+\delta}{2}\right)\times\left[\ln\left(\frac{\delta^{\delta}}{(\delta+1)^{\delta+1}}\frac{[(k_{21}+k_{31})z+k_{22}+k_{32}]^{\delta+1}}{k^{\delta}_{22}k_{21}z}\right)\right]^{-1}.$$

It may be seen that both for very large and very small values of z, the maximum shifts to very small values of r. If the composition of the monomer residue is such that (depending essentially upon the growth rates) the mean composition of polymer just formed deviates pronouncedly from the desired one (δ), then the latter will, because of statistical reasons, occur only in very small chains. Accordingly one may expect the maximum in Fig. 2 to be farthest to the right, when the monomer composition z(max) obeys the relation

$$\delta=\frac{k_{22}+k_{32}}{k_{21}+k_{31}}\frac{1}{z\ (\max)}. \quad (10)$$

Setting $d(r+s)_{\max}/dz$ equal to zero actually leads to this result. The corresponding value of the molecular weight is found from the above equa-

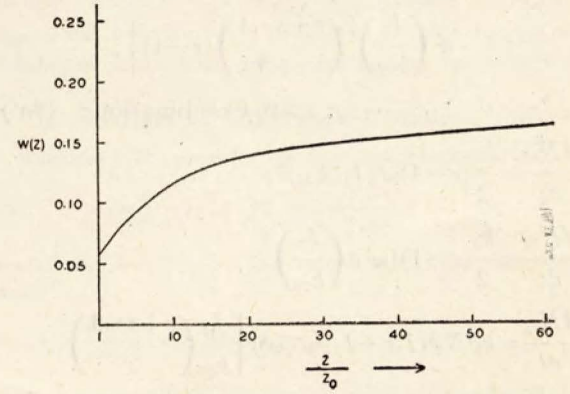

FIG. 4. Weight ratio $w(z)$ of reactants in copolymer as a function of mole ratio z of monomer (10). Numerical values of constants are the same as those in Fig. 2.

[10] R. C. Reinhardt, Ind. Eng. Chem. **35**, 422 (1943).

tion for $(r+s)_{\max}$ after insertion of the value for $z(\max)$. Expansion of the logarithm gives the following equation for the largest obtainable molecular weight corresponding to a maximum in the composition distribution curve:

$$\frac{1}{2}\frac{M_1\frac{1}{\delta}+M_2}{\frac{k_{31}}{k_{21}}\frac{1}{\delta}+\frac{k_{32}}{k_{22}}}. \tag{11}$$

Comparison of this equation with relation (9a) shows that this maximum molecular weight is exactly one-half the final number average molecular weight obtained if the initial monomer ratio z_0 equals the desired ratio $1/\delta$ in the chains. If one wishes to maintain throughout the polymerization a given ratio δ in long chains, the initial composition z_0 must be chosen equal to $z(\max)$ and z maintained at this value by suitable monomer addition. In Fig. 3 the maximum shifts to larger contents of type one monomer with progressing copolymerization, as is to be expected. The instantaneous distributions of polymer formed by the interaction of two activated chains are given by the following equations, derived from (8′) and (6a) in the Appendix III:

$$\frac{dN_{rs}}{dt}=\frac{k_3}{2}\omega^r(\omega')^s\left\{\left(\frac{I_1}{k_{21}}\right)^2\binom{r+s-1}{s+1}(s-1)+\frac{I_1I_2}{k_{21}k_{22}}\left[\binom{r+s-1}{s}(s-1)+\binom{r+s-1}{r}(r-1)\right]+\left(\frac{I_2}{k_{22}}\right)^2\binom{r+s-1}{r+1}(r-1)\right\};$$

$r, s>0$, Combination; (8a′)

$$\frac{dN_{r0}}{dt}=\frac{k_3}{2}(r-1)\omega^r(I_1/k_{21})^2;$$

$$\frac{dN_{0s}}{dt}=\frac{k_3}{2}(s-1)(\omega')^s\left(\frac{I_2}{k_{22}}\right)^2;$$

$$\frac{dN_{rs}}{dt}=k_3^{\frac{1}{2}}N_2^{\frac{1}{2}}(I_1z+I_2)^{\frac{1}{2}}\omega^r(\omega')^s\left[\frac{I_1}{k_{21}}\binom{r+s-1}{s}+\frac{I_2}{k_{22}}\binom{r+s-1}{r}\right].$$ Disproportionation.

By means of (4c″), (8a′) may again be formulated in terms of z through elimination of the time variable. It may be noted from (8a) and (8a′) that the distribution by number, N_{rs}, will exhibit a maximum in the case of combination, while curves for polymer terminated by means of monomer or by a disproportionation mechanism shows a maximum only if plotted as weight distribution, similarly as in the case of one-component systems.[7] Equation (8a[1]) gives at once the distribution $\lim_{z\to z_0} N_{rs}$ of stable polymer formed initially, if t is eliminated by means of z in analogy to the case previously discussed. Plots at constant composition and chain length, respectively, lead to the same conclusions as before. No analytical expression for the maximum chain length obtainable with a desired composition δ can be found because of the complications arising from the definition of ω and ω' in this case. If the factor containing k_3 in ω and ω' can be neglected, Eq. (10) with omission of k_{31} and k_{32} is again obtained.

Relations for the size and composition distribution developed here or found by similar methods for other polymerization mechanisms should permit at least an estimation of the homogeneity of a copolymer with respect to size and composition at various stages of the reaction, once the kinetics of the process is established and the velocity constants for the elementary steps are known. In the case of insoluble or nearly insoluble cross-linked polymers of the vinyl-divinyl type the only thermodynamic method available at present for an analysis of the product formed is a study of the swelling isotherms.[11] This allows a determination of the average chain length between two cross links. Kinetic investigations enable one to supplement this information with distribution data. Jenckel[3] has carried out fractionations on four soluble copolymer systems, namely, styrene and methacrylic acid ester, methyl methacrylate and vinyl acetate, respectively, and vinyl pyrrolidine-vinyl carbazole. He furthermore attempted to draw conclusions as to the kinetics of the process on this basis. However, in his analysis the inhomogeneity in respect to size was neglected. In general, chain

[11] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. **11**, 521 (1943).

composition as well as chain length[12] determine the thermodynamic equilibrium at a given temperature.[13] It is evident for instance, that the shorter chains precipitated from a solution contain more of that component which, as a pure polymer, is less soluble in the same solvent.

Finally, considerations of this type will play a role in the application of Flory's[14] and Stockmayer's[15] theory of gel formation to cross-linked polymers, by determining the relative probabilities with which mono- and divinyl enter the chains, and therefore the average number of cross bonds per chain. The intramolecular distribution of cross bonds can then be calculated in terms of the extent of reaction. The number P_i of groups of monovinyl units containing i members in N_{rs} cross-linked chains of length $(r+s)$ which have been formed in an interval dz, is given by:[16]

$$P_i = N_{rs}(r+s)(1-\omega)^2\omega^i;$$

for $i \ll r+s$, with

$$\omega = \frac{k_{21}z}{k_{21}z+k_{22}}.$$

k_{22} designates the rate of cross-bond formation, k_{21} that of addition of monovinyl units. If the chain length is not sufficiently large, the effect of the two ends and their mode of formation must be taken into account by the introduction of parameters for initiation and termination and modification of the above formula.[16]

We should like to acknowledge our indebtedness to Dr. R. F. Boyer and Dr. R. C. Reinhardt of The Dow Chemical Company for many helpful discussions.

APPENDIX

I. Solution of the Difference Equations (5a)

The result for n_{r0} and n_{0s} is easily found. Direct substitution in (5a) for low values of r and s leads to the following typical equations:

$$\alpha_{12}n_{12} = \beta_{02}n_{02} + \gamma_{11}n_{11};$$

$$\alpha_{32}n_{32} = \frac{\beta_{02}\beta_{12}\beta_{22}n_{02} + \gamma_{11}\beta_{12}\beta_{22}n_{11}}{\alpha_{12}\alpha_{22}} + \frac{\gamma_{21}\beta_{22}}{\alpha_{22}}n_{21} + \gamma_{31}n_{21};$$

or

$$\alpha_{r2}n_{r2} = \alpha_{02}\prod_{l=0}^{r-1}\left(\frac{\beta_{l2}}{\alpha_{l2}}\right)n_{02} + \sum_{j=1}^{r} n_{j1}\gamma_{j1}\prod_{l=j}^{r-1}\frac{\beta_{l2}}{\alpha_{l2}}.$$

The first term on the right expresses that an n_{r2} may be built from an n_{02} by adding on r units of the first kind; the second term that n_{r2} may be built from n_{11}, $n_{21}\cdots n_{r1}$ by joining a unit of the second kind and then completing the structure by adding a sufficient number of the first species. This may be generalized to

$$\alpha_{rs}n_{rs} = \alpha_{0s}\prod_{l=0}^{r-1}\left(\frac{\beta_{ls}}{\alpha_{ls}}\right)n_{0s} + \sum_{j=1}^{r} n_{j\,s-1}\gamma_{j\,s-1}\prod_{l=j}^{r-1}\left(\frac{\beta_{ls}}{\alpha_{ls}}\right)$$

which can be explained as before. It is equivalent to the intermediate result presented in the text. On substituting n_{0s} and ω's from the text this becomes:

$$\alpha_{rs}n_{rs} = I_2N_2\prod_{l=0}^{r-1}\omega_{ls}\prod_{l=1}^{s-1}\omega_{0l} + \sum_{j_1=1}^{r}\gamma_{j_1\,s-1}n_{j_1\,s-1}\prod_{l=j_1}^{r-1}\omega_{ls}.$$

This expression can be utilized to establish a recurrence formula between n_{j_1s-1} and n_{j_2s-2} with $1 \leqq j_2 \leqq j_1$. n_{j_2s-2} may be expressed in terms of n_{j_3s-1} with $1 \leqq j_3 \leqq j_2$. Continued substitution and rearrangement leads to (6).

II. Solution of Difference Equations (5b)

Equations (5b) gives for the pure radical species:

$$n_{r0} = \frac{I_1N_1}{\beta(A)}[\omega(A)]^r; \quad n_{0s} = \frac{I_2N_2}{\gamma(B)}[\omega'(B)]^s.$$

Examining a $n_{rs}(A)$ for low values of r, s, for example, $n_{22}(A)$:

$$n_{22}(A) = \frac{I_1N_1}{\alpha(A)}\omega'(A)\omega'(B)\omega(B) + \frac{I_2N_2}{\alpha(B)}[\omega(B)\omega'(A)\omega(B) + \omega'(B)\omega(B)\omega(A)].$$

We see that there will be in all cases two expressions, one

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[12] See, for instance, H. Staudinger and J. Schneiders, Ann. **541**, 151 (1939).

[13] This can be expressed roughly by an extension of the theory of P. J. Flory, J. Chem. Phys. **10**, 51 (1942) and M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942). Let the heat of mixing depend solely upon the polymer composition and be independent of the intramolecular arrangement, which is reasonable. Applying G. Scatchard's [Chem. Rev. **8**, 321 (1931)] expression for the heat of mixing to the ternary system, the parameter K (in Flory's notation), a ratio between cohesional and thermal energy, assumes the following form:

$$K = 2v_1/RT[A_{12}\kappa + A_{13}(1-\kappa) - A_{23}\kappa(1-\kappa)].$$

κ is the chain composition $r/r+s$ in the notation adopted, v_1 the molar volume of the solvent. The indices 2 and 3 refer to the two monomer species. The A coefficients depend upon the nature of the respective components only and monomers 2 and 3 are assumed to be approximately equal in size. The relations for the partial molal entropies will in general depend upon the intramolecular arrangement of the two species which determines the internal flexibility of the polymer molecule, unless they are chemically similar enough. Disregarding this factor, the above authors' results give at once a relation between chain length and composition at the critical point of formation of a two-phase system at a given temperature. Furthermore, the slope of the plot of reduced osmotic pressure *versus* concentration (in weight per volume) for small concentrations is proportional to $(1-K)$ and is therefore a function of the chain composition. Osmotic data on copolymers are very desirable in this connection.

[14] P. J. Flory, J. Am. Chem. Soc. **63**, 3096 (1941).

[15] W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943); W. H. Stockmayer and H. Jacobson, *ibid.* **11**, 393 (1943).

[16] F. T. Wall, J. Am. Chem. Soc. **62**, 803 (1940); **63**, 821 (1941). R. Simha, *ibid.* **63**, 1479 (1941).

corresponding to initiation by the first species, the other by the second. The terms in the ω's again express the manner of growth of the active nuclei. From the meaning of the ω's we can interpret for this example the first product in the I_2 term as growth in the following order: $B-A-B-A-$, and the second: $B-B-A-A$. The I_1 term represents: $A-B-B-A$. The total number of terms in the expression for $n_{rs}(A)$ will evidently be equal to the number of ways of arranging the structural units within the chain with specified ends:

$$\underbrace{\frac{(r+s-2)!}{(r-2)!s!}}_{\text{Initiated by } A}+\underbrace{\frac{(r+s-2)!}{(r-1)(s-1)}}_{\text{Initiated by } B.}=\binom{r+s-1}{s}$$

Likewise for $n_{rs}(B)$:

$$\binom{r+s-1}{r}.$$

Let us now characterize a possible intramolecular configuration by i, the number of $A-A$, j, the number of $B-A$, k, the number of $A-B$, and by l, the number of $B-B$ linkages. Each configuration gives rise to a term $\omega(A)^i\omega(B)^j\omega'(A)^k\omega'(B)^l$ multiplied by a statistical weight factor. To determine this factor we consider first the $n_{rs}(A)$ initiated by B. The conditions to be fulfilled by i, j, k, and l are: $i+j=r$, since an A must follow an A or a B; $j=k+i$, since all the groups formed by B except the first are preceded by an A ($A-B$ linkage) and all are succeeded by an A including the first ($B-A$ bond); $j+l=s$, since a B must be followed by an A or by a B. Let m_t be the number of groups formed by t structural units of type A, whence $\Sigma m_t=j$, $\Sigma t m_t=r$. Let m_t' have the same meaning for type B and $\Sigma m_t'=j$, $\Sigma t m_t'=s$. The weight factor for the specified configuration i, j, k, l is

$$\sum_{m_t'}\frac{(\Sigma m_t')!}{\Pi(m_t')!}\sum_{m_t}\frac{(\Sigma m_t)!}{\Pi(m_t)!}=\sum_{m_t'}\frac{j!}{\Pi(m_t')!}\sum_{m_t}\frac{j!}{\Pi(m_t)!}\quad(A-1),$$

to be summed over all values of m_t and m_t' compatible with the auxiliary conditions. The sum over m_t' gives the independent configurations resulting from a permutation of the B groups, that over m_t of the A groups. The product therefore gives the total number of independent configurations. Using the multinomial theorem to evaluate one of these sums we find:

$$(\Sigma_t x_t{}^t z^t)^j=j!\sum_{m_t}\prod_t\frac{(x_t{}^t z^t)^{m_t}}{m_t!}=j!\sum_m z^{\Sigma t m_t}\prod_t\frac{x_t{}^{tm_t}}{m_t!}\quad(\Sigma m_t=j),$$

whence:

$$\sum_{m_t}\frac{j!}{\prod_t m_t!}=\lim_{x_t\to 1}\{\text{coeff. of } z^r \text{ in } (\Sigma_t x_t{}^t z^t)^j\}$$

$$=\text{coeff. of } z^r \text{ in } \frac{z^j}{(1-z)^j}=\binom{r-1}{j-1}.$$

Replacing r by s gives the sum over m_t'. The final weight factor is:

$$\binom{r-1}{j-1}\binom{s-1}{j-1}.$$

For $m_{rs}(A)$ initiated by A, the conditions for i, j, k, and l are $\Sigma m_t=j+1$, $\Sigma m_t'=j$, $i+j+1=r$, $j=k$, $j+l=s$. Substituting these values for the sums into $(A-1)$ and using the multinomial theorem, we obtain for the weight factor

$$\binom{r-1}{j}\binom{s-1}{j-1}.$$

For $n_{rs}(B)$ initiated by A, the analysis is the same as for $n_{rs}(A)$ initiated by B with $\Sigma m_t'=\Sigma m_t=k$, $i+k=r$, $j=k-1$, $k+l=s$, hence the weight factor:

$$\binom{r-1}{k-1}\binom{s-1}{k-1}.$$

$n_{rs}(B)$ initiated by B carries the conditions $\Sigma m_t'=k+1$, $\Sigma m_t=k=j$, $i+k=r$, $k+l+1=s$. The weight factor is:

$$\binom{r-1}{k-1}\binom{s-1}{k}.$$

Introducing the weight factors as coefficients of the ω's and substituting the values of the exponents in terms of r and s, we find:

$$n_{rs}(A)=\frac{I_1N_1}{\alpha(A)}\sum_{j=1}^{s}\binom{r-1}{j}\binom{s-1}{j-1}\times[\omega'(A)]^j[\omega'(B)]^{s-j}[\omega(B)]^j[\omega(A)]^{r-j-1}$$

$$+\frac{I_2N_2}{\alpha(B)}\sum_{j=1}^{s}\binom{r-1}{j-1}\binom{s-1}{j-1}\times[\omega'(A)]^{j-1}[\omega'(B)]^{s-j}[\omega(B)]^j[\omega(A)]^{r-j};$$

$$n_{rs}(B)=\frac{I_1N_1}{\alpha(A)}\sum_{k=1}^{r}\binom{r-1}{k-1}\binom{s-1}{k-1}\times[\omega'(A)]^k[\omega'(B)]^{s-k}[\omega(B)]^{k-1}[\omega(A)]^{r-k}$$

$$+\frac{I_2N_2}{\alpha(B)}\sum_{k=1}^{r}\binom{r-1}{k-1}\binom{s-1}{k}\times[\omega'(A)]^k[\omega'(B)]^{s-k-1}[\omega(B)]^k[\omega(A)]^{r-k}.$$

The first expression on the right for $n_{rs}(A)$ may be written as:

$$I=\frac{I_1N_1}{\alpha(A)}[\omega(A)]^{r-1}[\omega'(B)]^s\sum_{j=1}^{s}\binom{r-1}{j}\binom{s-1}{j-1}\left[\frac{\omega'(A)\omega(B)}{\omega(A)\omega'(B)}\right]^j.$$

Now

$$\binom{r-1}{j}\binom{s-1}{j-1}=\binom{r-1}{j}\binom{s}{j}-\binom{r-1}{j}\binom{s-1}{j}.$$

$$\sum_{j=1}^{s}\binom{r-1}{j}\binom{s}{j}x^j=(r-1)sx+\frac{(r-1)(r-2)}{1\cdot 2}\frac{s(s-1)}{1\cdot 2}x^2+\cdots$$

$$=F(1-r,\,-s,\,1,\,x)-1,$$

where $F(a, b, c, x)$ is the hypergeometric function[17]

$$F(a,b,c,x)=1+\frac{ab}{c}x+\frac{a(a+1)}{1\cdot 2}\frac{b(b+1)}{c(c+1)}x^2+\cdots.$$

Likewise:

$$\sum_{j=1}^{s}\binom{r-1}{j}\binom{s-1}{j}x^j=-F(1-r,\,1-s,\,1,\,x)+1$$

and

$$I=\frac{I_1N_1}{\alpha(A)}[\omega(A)]^{r-1}[\omega'(B)]^s\times[F(1-r,\,-s,\,1,\,x)-F(1-r,\,1-s,\,1,\,x)].$$

[17] E. T. Whittaker and G. N. Watson, *Modern Analysis* (The Cambridge University Press, 1940).

Application of this procedure to the other summations gives (6a).

In computing the sums over $n_{rs}(A)$ and $n_{rs}(B)$, the sums over the pure polymer species are easily evaluated. In the copolymer $n_{rs}(A)$ we have for the first term, substituting $i=j-1$.

$$\frac{I_1N_1}{\alpha(A)}\frac{1}{\omega(A)}\sum_{j=1}^{s}\sum_{r,s\geqq 1}^{\infty}[\omega(A)]^r[\omega'(B)]^s\binom{r-1}{j}\binom{s-1}{j-1}x^j$$

$$=x\frac{I_1N_1}{\alpha(A)\omega(A)}\sum_{i=0}^{\infty}x^i\sum_{s=i+1}^{\infty}[\omega'(B)]^s\binom{s-1}{i}\times\sum_{r=i+2}^{\infty}[\omega(A)]^r\binom{r-1}{i+1}$$

$$=x\frac{I_1N_1}{\alpha(A)\omega(A)}\sum_{i=0}^{\infty}x^i\left[\frac{\omega'(B)}{1-\omega'(B)}\right]^{i+1}\left[\frac{\omega(A)}{1-\omega(A)}\right]^{i+2}$$

$$=\frac{I_1N_1}{\alpha(A)[1-\omega(A)]}\frac{\omega(A)\omega'(B)x}{[1-\omega(A)][1-\omega'(B)]-x\omega(A)\omega'(B)}.$$

The second term gives

$$\frac{I_2N_2x}{\alpha(B)\omega'(A)}\sum_i x^i\sum_{r,s\geqq 1}[\omega(A)]^r[\omega'(B)]^s\binom{r-1}{i}\binom{s-1}{i}$$

$$=\frac{I_2N_2}{\alpha(B)\omega'(A)}\frac{x\omega(A)\omega'(B)}{[1-\omega(A)][1-\omega'(A)]-x\omega(A)\omega'(B)}.$$

Combination of these terms gives the sums in (7). $\Sigma n_{rs}(B)$ is determined in the same manner.

III. Derivation of (8a′)

Introducing the values for n_{ij} and $n_{r-i\,s-j}$ from (6a) into (8′) one is led to four sums. The first is:

$$\left(\frac{I_1}{k_{21}}\right)^2\frac{k_3}{2}\omega^r(\omega')^s\sum_{i,j}\binom{r-i+s-j-1}{s-j}\binom{i+j-1}{j}$$

$$=\left(\frac{I_1}{k_{21}}\right)^2\frac{k_3}{2}\omega^r(\omega')^s\sum_{\lambda=2}^{r+s-2}S_\lambda=\left(\frac{I_1}{k_{21}}\right)^2\frac{k_3}{2}\omega^r(\omega')^sS_I,$$

where

$$S_\lambda=\sum_{i=1}^{s-1}\binom{r+s-1-\lambda}{s-j}\binom{\lambda-1}{j}$$

$$=\sum_{j=0}^{s}\binom{r+s-1-\lambda}{s-j}\binom{\lambda-1}{j}-\binom{r+s-\lambda-1}{s}-\binom{\lambda-1}{s}.$$

Now

$$\binom{m+n}{p}=\sum_{j=0}^{p}\binom{m}{p-j}\binom{n}{j};\quad\binom{m+1}{p+1}=\sum_{j=0}^{m-p}\binom{m-j}{j}.$$

Consequently:

$$S_\lambda=\binom{r+s-2}{s}-\binom{r+s-\lambda-1}{s}-\binom{\lambda-1}{s}$$

and

$$S_I=\binom{r+s-2}{s}(r+s-3)-\sum_{\lambda=2}^{r+s-2}\binom{r+s-\lambda-1}{s}-\sum_{\lambda=2}^{r+s-2}\binom{\lambda-1}{s}.$$

The first summation on the right gives with $\delta=\lambda-2$:

$$\sum_{\delta=0}^{r+s-4}\binom{r+s-3-\delta}{s}=\sum_{\delta=0}^{r-3}\binom{r+s-3-\delta}{s}=\binom{r+s-2}{s+1},$$

since the binomial coefficient is zero when the bottom term exceeds the top. The second summation in S_I may be written with $\delta=r+s-2-\lambda$:

$$\sum_{\lambda=s+1}^{r+s-2}\binom{\lambda-1}{s}=\sum_{\delta=0}^{r-3}\binom{r+s-3-\delta}{s}=\binom{r+s-2}{s+1}.$$

Finally:

$$S_I=\binom{r+s-2}{s}(r+s-1)-2\binom{r+s-2}{s+1}=\binom{r+s-1}{s+1}(s-1).$$

The second sum is

$$\left(\frac{I_1}{k_{21}}\right)\left(\frac{I_2}{k_{22}}\right)\frac{k_3}{2}\omega^r(\omega')^s\sum_{i,j}\binom{i+j-1}{j}\binom{r+s-i-j-1}{r-i}.$$

Since

$$\binom{r+s-i-j-1}{s-j-1}=\binom{r+s-i-j}{s-j}-\binom{r+s-i-j-1}{s-j},$$

$$S_{II}=\sum_{i,j}\binom{i+j-1}{j}\binom{r+s-i-j}{s-j}-S_I.$$

The first term above on the right may be obtained from S_I by replacing r by $r+1$:

$$S_{II}=(s-1)\binom{r+s-1}{s}.$$

The third and fourth terms are

$$\left(\frac{I_1}{k_{21}}\right)\left(\frac{I_2}{k_{22}}\right)\frac{k_3}{2}\omega^r(\omega')^s\sum_{i,j}\binom{i+j-1}{i}\binom{r+s-i-j-1}{s-j}$$

and

$$\left(\frac{I_2}{k_{22}}\right)^2\frac{k_3}{2}\omega^r(\omega')^s\sum_{i,j}\binom{i+j-1}{i}\binom{r+s-i-j-1}{r-i}.$$

The sums become identical with the second and first upon interchange of r and s, i and j. Substitution of the values found in this manner gives (8a′).

FELLOWSHIPS

February 20, 1946

Dear Mr. Branson: Mr. Embree is in California and will not return until the first of next month, and your letter of 18 February has been routed to me.

As you yourself are aware, it is impossible for your request to be considered in this year's fellowship competition owing to the lateness of the date; and, as you point out, it probably should be considered outside our regular fellowship program since it has somewhat different implications. I am, therefore, going to hold your letter and the enclosures until Mr. Embree returns, at which time they will be shown to him.

Sincerely yours,

WILLIAM C. HAYGOOD

WCH:RFL

Mr. Herman Branson
Department of Physics
Howard University
Washington 1, D. C.

FELLOWSHIPS

March 5, 1946

Dear Mr. Branson: Mr. Haygood has passed on to me your letter of February 18 on my return from a brief absence from the office. I am afraid there is no way by which we can help in your case. As you know, our fellowships are intended to develop two types of persons: (a) Negroes and (b) white Southerners who are working on some problem of special concern to the southern region. We have not attempted to develop professors for general work either at Negro universities or elsewhere and are not willing to enter this very large group.

I am very sorry that we cannot be of assistance to you, but I am sure you will understand and appreciate our position.

Very truly yours,

EDWIN R. EMBREE

ERE:SO
Encs.

Mr. Herman Branson
Department of Physics
Howard University
Washington 1, D. C.

P.S. In line with your request, enclosed herewith are the three letters.

HOWARD UNIVERSITY
WASHINGTON 1, D. C.

DEPARTMENT OF PHYSICS

attached air mail

	ERE	11	ERE	12
	WCH		WCH	o

FELLOWSHIPS

8 March 1946.

Mr. Edwin R. Embree, President,
Julius Rosenwald Fund,
4901 Ellis Avenue,
Chicago 15, Illinois.

Dear Mr. Embree:

I have your letter of 5 March 1946, which implies that my request was denied because I am neither a Negro nor a white Southener interested in some problem incident to the southern region. I am a Negro. I did not say anything about it in my letter since you have data on me in your files. You granted me a fellowship when I was at Dillard University for working with Professor N. Rashevsky at the University of Chicago in 1940.

If this disclosure makes any difference in your handling of my request, I would be pleased to return the letters from Professor Rashevsky and any other information you may wish.

Sincerely yours,

Herman Branson

Herman Branson, Professor

FELLOWSHIPS

March 12, 1946

Dear Dr. Branson: No, I was not questioning your standing as a candidate for a fellowship. I was attempting to stress that we have no machinery for aiding individuals outside of our regular fellowship program. Over and over again, we are asked to make exceptions or give special consideration to individual cases. It has seemed to us that we can accomplish most by adhering strictly to the program of fellowships that we have worked out with great care.

I am sorry not to be of help in this specially interesting case, and I hope that by some means it will be possible for you to continue to do your profitable work at the University of Chicago.

Very truly yours,

EDWIN R. EMBREE

Dr. Herman Branson
Department of Physics
Howard University
Washington 1, D. C.

HOWARD UNIVERSITY
WASHINGTON 1. D. C.

DEPARTMENT OF PHYSICS

April 14, 1948.

HR 4/15 HR 15

Miss Hilde Reitzes,
Julius Rosenwald Fund
4901 Ellis Avenue,
Chicago, Ill.

Dear Miss Reitzes:

I have been informed that the National Research Council will grant me a fellowship for study next year on my sabbatical leave. I would like, therefore to withdraw my name from your list.

Please accept my sincere thanks for your courteous assistance.

Sincerely yours,

Herman Branson

Herman Branson, Professor
Department of Physics

HB/cab

April 15, 1948

Dear Mr. Branson: Many thanks for your letter of April 14 informing us of your National Research Council fellowship. As you requested, I have withdrawn your application from this year's fellowship competition.

Congratulations and very best wishes for your important work!

Sincerely yours,

HR

For the Committee
on Fellowships

Mr. Herman Branson
Department of Physics
Howard University
Washington 1, D. C.

Microfilm in the Negro College

HERMAN BRANSON

A perennial topic in conversations of teachers in small Negro colleges is the lament for the lack of research facilities. In a large measure the difficulties are real: there is little material for laboratory work; there is no well equipped library with many original documents; often there is a too full teaching schedule with committee work. The present financial condition of our schools gives no hope that there will be any sudden influx of large donations which will enable these problems to be written off. The individual teacher may find himself with a genuine desire for research and a willingness to give the extra energy demanded. There still faces him, however, the lack of original sources and of files of research periodicals. If he is in one of the sciences, he may find refuge in the realization that research is most expensive: the electric power for a cyclotron easily costs more than the combined budgets in all the physical sciences in his school. Yet his most promising approach is to delve into his ingenuity for some mitigating technique.

There is of course no logical formula or magical instrument which will remedy our deficiencies overnight, but an emphasis on microfilm and microfilm technique may be a partial solution for our research problems.[1] One recommendation for the use of microfilm in the small school is that it can be used by most schools even with extremely modest budgets. Even the individual worker can organize equipment for the making and reading of microfilm at small cost.

Microfilm technique is a method of reproducing copy exactly and inexpensively on photographic film. Since it is fundamentally the same as making the ordinary snapshot, the essential equipment is camera, film, and final reproduction—in this technique, this last is a reader for magnifying the reduced image. The cameras which have been devised for microfilm work range from the simplest machines having practically no adjustments to the most complicated multitasked assemblies. A typical gamut would be headed by a $10 "candid" camera with a homemade mount and would end with the $5,750 Eastman Recordak. Within the gamut are excellent little machines which can be built by the individual for $30 or others which can fill the needs of the small school for about $150.[2] Such inexpensive installations would load with 35 mm perforated film and would give pictures measuring either ¾ inch by 1 inch or

[1] Robert C. Binkley, *Manual on Methods of Reproducing Research Materials,* Edward Brothers, Ann Arbor, Mich., 1936; J. Perian Danto, "Microphotography in a University Library," *Journal of Documentary Reproduction,* 14:297-315, Fall, 1938; Herman H. Fussler, "Microphotography and the Future of Interlibrary Loans," *Journal of Documentary Reproduction,* 2:3-10, Mr 1939; M. Llewellyn Raney, "Microphotography—A Lay Appraisal," *Journal of Documentary Reproduction,* 1:20-32, Spring 1938; Atherton Seidell, "Reforms in Chemical Publication," *Science,* 80:70-72, Jl 20, 1934; Eugene Adhemar Tilleux, "Microphotography in 1940," *Journal of Documentary Reproduction,* 4:25-41, Mr 1941.

[2] H. L. Fleming, "The New S.R.S. Camera," *Journal of Documentary Reproduction,* 2:225-227, S 1939.

1 inch by 1½ inches. Other sizes of film are obtainable. Some work with newspapers is done on 35 mm unperforated film (i.e., film about 1½ inches wide without holes along the edges) and on 16 mm film (⅝ inch wide). There has been some investigation of the possibility of using sheet film. A suggested size in this format would give 100 ordinary book pages on a single 3 x 5 card. In spite of certain advantages of sheets, the 35 mm roll film camera seems too well entrenched for removal.[3] Practically all of the microfilm services supply copy on this form.

More important than the size of film is the type of film available for microfilming. Recent research has produced inexpensive film more durable than 100 per cent rag paper. Moreover, work is in progress to adapt thin metallic strips for this use. In addition to the film base, the emulsion, in which the image is laid in silver grains, has undergone vast improvement in contrast, color rendering and resolution (the ability of the film to seperate fine lines); and the silver is even being ousted by a less expensive agent.[4] It is possible now to copy seemingly hopelessly faded documents to give crisp contrasty microfilm.

The interested worker may well renounce all attempts at making his own microfilm and still find the technique extremely valuable, for there are many laboratories and agencies supplying microfilm,[5] some in general, others in specific fields; but he will still need a reader. Until quite recently there was no good microfilm reader selling for less than $50. Many workers have devised magnifiers and projectors for their own use. Some of these were made for as little as $1.[6]

The reading machine subvened by the Committee on Scientific Aids to Learning released by the Spencer Lens Company in 1941 has been designed especially for the individual scholar. Selling for $32, it lacks many desirable mechanical features but should meet the needs of the individual and the small school. The Argus reader, selling

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[3] R. D. Bennett, "Sheet Microfilm," *Journal of Documentary Reproduction,* 3:39-41, Mr 1940; R. D. Bennett, "Lilliputian Libraries," *The Technology Review,* 42:114, 1940.

[4] Robert W. Carter, "Metal Film for Permanent Records," *Journal of Documetary Reproduction,* 1:354-361, Fall 1938; W. Raths, "Recent Photo-Material for Documentation," *Journal of Documentary Reproduction,* 3:216-219, S 1940; Pierre Weiss, "Ozaphane," *Journal of Documentary Reproduction,* 1:362-365, Fall 1938.

[5] "Guide to the Material in the National Archives," Superintendent of Documents, Government Printing Office, Washington, D.C.; "Microfilm Abstracts," University Microfilms, Ann Arbor, Michigan; Medicofilm Service, Army Medical Library, 7th and Independence Ave., Washington, D.C.; "Sources of Microfilm for Use with the Argus Microfilm Reader," International Research Corporation, Ann Arbor, Michigan; "Microfilm Service in the Geological Survey," *Science,* 88:517-518, D 2, 1938; Harold P. Brown, "A Survey of Microfilm Sources," *Journal of Documentary Reproduction,* 2: 118-124, Je 1939; E. B. Powers, "University Microfilms," *Journal of Documentary Reproduction,* 2:21-28, Mr 1939.

[6] Herman Branson, "A Reader for Microfilm," *School Science and Mathematics,* 40: 411-412, My 1940; see also the Federal Film Viewer ($6.50), Federal Stamping and Engineering Corporation, 15 Lafayette Street, Brooklyn, N.Y. Note: Fatigue is a factor in using the visual magnifiers. The author has used one costing about 80¢ in some work where he reads only a few lines and then turns to a pad for working out steps. This can be carried on all evening without undue fatigue. See Walter R. Miles, "Subjective Impressions of Efficiency in Reading Microfilm," *Journal of Documentary Reproduction,* 3:61-65, Mr 1940; Irvin Stewart, "Reports on the Reading of Microfilm," *Journal of Documentary Reproduction,* 1:145-150, Spring 1938.

for $87.50, has been mentioned as a good machine.[7]

The small college might find the purchase of a reader not beyond its resources. If no money remains for the purchase of microfilm, the teacher wishing to use the machine might find it possible to supply his own microfilm. Many agencies are now supplying microfilm of a large range of scholarly material which would not be available in the original. It does not seem unreasonable to believe that a scholar would hesitate to purchase a valuable manuscript at 1¢ or 2¢ a page. Nevertheless, there will be circumstances when the individual cannot purchase such microfilm. Some disposition of a departmental budget might be made so that a few dollars can be used by the instructor for this use. There always remains the possibility of interesting a philanthropic foundation in such work. With an initial outlay of less than $100 a library could contribute greatly to the research facilities of its faculty.

It is by no means difficult to envision specific problems in which microfilm could be used.[8] It is equally possible to build up a cogent argument for our possessing our own microfilming equipment. A camera, lights and stand which will give microfilm in no way inferior to that issued by some agencies,[9] can be got together for approximately $40. A student could use an assembly of this type for a few weeks during his vacation to microfilm enough material for analysis all winter. Such a student might be trained in linguistics, or music or drama or history or science.[10] He might spend his vacation in Mexico examining old Spanish papers, at a conservatory in Boston collating old music texts, or collecting notes on the Negro in the settlement of New Orleans. Any of the material which would have to be expensively and tediously hand-copied would be microfilmed for more leisurely and prolonged study. Although other students have reported little difficulty in getting permission to copy such materials, we might en-

[7] "The Argus Reading Machine," *Journal of Documentary Reproduction,* 1:79-80, Winter 1938.

[8] See references under 5 and 10.

[9] This equipment may be built around an inexpensive second-hand 6 x 9 cm camera with a 35 mm adapter back. A stand can be made for a few dollars. See also F. L. English, *American Photography,* 32:825-828, N 1938; Harris F. Fletcher, "Textual Microphotography for the Individual Scholar," *Journal of Documentary Reproduction,* 1: 316-319, Fall 1938; Frank R. Fraprie and Robert H. Morris, *Copying Technique,* American Photographic Publishing Co., Boston, 1940; D. H. Cook and J. H. Axtmayer, "A Projection Reader for Filmstats," *Science,* 87:331-332, Ap 8, 1938; James A. Austin and Harold P. Brown, "Projection and Filing of Microphotographic Reproductions," *Journal of Chemical Education,* 15: 24, Ja 1938; Lee R. Dice, "Simple Method of Filing Miniature Negatives and Microfilm Records in Strips," *Science,* 89:39-40, Ja 13, 1939.

[10] J. H. Chase, Jr. "Latin-American Microfilming Project at Brown University," *Journal of Documentary Reproduction,* 3:200-203, S 1940; Grace G. Griffin, "Foreign American History Manuscript Copies in Library of Congress," *Journal of Documentary Reproduction,* 3:3-9, Mr 1940; Sarah Jones, "Documenting Studies in Anthropology," *Journal of Documentary Reproduction,* 2: 239-248, D 1939; Barnes F. Lathrop, "Microfilming Materials for Southern History," *Journal of Documentary Reproduction,* 2: 91-108, Je 1939; Eugene B. Power, "Sources of Materials for the Study of American Culture," *Journal of Documentary Reproduction,* 3:192-197, S 1940; Eugene B. Power, "Report of Progress of Filming English Books before 1550," *Journal of Documentary Reproduction,* 1:45-49, Winter 1938; C. S. Smith, "Music on Microfilm," *Journal of Documentary Reproduction,* 2:249-253, D 1939; George A. Schwegmann, Jr., "Preliminary Checklist of Newspapers in Microfilm," *Journal of Documentary Reproduction,* 4:122-134, Je 1941.

counter a little reluctance in getting permission to copy some materials pertaining to the Negro. Non-controversial material might be as accessible to us as to others.

An ideal situation for the Negro schools might be the establishment of good microfilm laboratories at the larger schools.[11] A good laboratory can be equipped with essentials for less than $1,000, roughly half a fellowship grant from one of the foundations. A center might sponsor a project to microfilm the records of the Negro in all the county offices of a Southern state or group of states. Such a project would cost several thousands of dollars; it is not unreasonable to think that one of the foundations could be induced to support it. The resulting film could be deposited at one of the key universities and positive copies sent to any other school which might have use for them. Needless to say this would give a welter of material for historical research. Even though under present conditions such an undertaking might have to have white personnel, the important consideration is the releasing of invaluable material to Negro scholars.

We shall not consider here other technical and commendatory aspects of the use of microfilm as space saving in libraries, preserving perishable records and in visual education; however, some of the author's use of microfilm may be of interest. Recently a problem had to be traced through *Zeitschrift für Physik, Journal of Applied Physics, Science,* and *Philosophy of Science.* In all some 15 papers had to be consulted. Of these about 10 were of sufficient importance to demand either extensive notetaking or copying. Either method of copying would have been laborious and liable to error. The problem was easily solved by microfilming the lot. The development of the problem has thus been able to proceed with the papers on hand for consultation whenever necessary. Recently a colleague asked that microfilm be made of approximately 80 pages from an early issue of a journal which probably never could have been successfully copied by any other method because of the large number of detailed plates. These experiences have convinced the author that this technique can make available otherwise inaccessible material and may encourage research among workers in small Negro schools.[12]

[11] "The Gentlemen's Agreement and the Problem of Copyright," *Journal of Documentary Reproduction,* 2:29-36, Mr 1939, (Agreement of the National Association of Book Publishers permitting microfilming of copyrighted publications with extremely mild restrictions); Irvin Stewart, "Microphotography for Scholarly Purposes," *Journal of Documentary Reproduction,* 4:44-52, Mr 1941; J. Perian Danton and Charles Elfont, "Microphotography at Work," *Journal of Documentary Reproduction,* 4:97-108, Je 1941. (This is an excellently suggestive discussion of the work of the microfilm laboratory at Temple University, Philadelphia: the service to the faculty and students, the operating difficulties and the limitations in type of work of the small laboratory.)

[12] Prices given in this article were taken from catalogs current in January, 1941.

BULLETIN OF
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DELAYED ADSORPTION AND DIFFUSION IN COLLOIDAL MEDIA

HERMAN BRANSON
HOWARD UNIVERSITY, WASHINGTON, D. C.

The behavior of the diffusion coefficient of a solute which can be adsorbed by a colloid only after the colloid has aggregated to a certain size is deduced on the basis of a few assumptions. Some relations of such a mechanism to cell reactions are indicated.

A type of reaction plausible in cell behavior is one in which two or more substances may be released under a stimulus. This paper considers such a release with two substances one of which can aggregate into larger micelles and upon reaching an optimum size adsorbs the second substance, which we call the solute. After this initial adsorption we may consider either no further aggregation and adsorption or further aggregation with adsorption as being the possibilities of greatest interest. For our purposes the significant point is what effect these alternative possibilities have upon the diffusion coefficient of the solute. In addition, we indicate how this mechanism may be used to interpret certain reactions in a cell, e.g. reactions which begin at a certain rate, proceed at that rate for some time, and then fall to a minimum.

The aggregation of the colloid particles is assumed to take place in the following chain:

$$\begin{aligned} n_1 + n_1 &\rightarrow n_2 , \\ n_2 + n_1 &\rightarrow n_3 , \\ &\cdot \\ &\cdot \\ &\cdot \\ n_{m-1} + n_1 &\rightarrow n_m , \end{aligned} \tag{1}$$

where n_m is the size at which adsorption of the solute occurs. This chain expresses the assumption that a higher aggregate is formed from the next lower by the adjoining of a simple micelle, in short there is no aggregation of higher aggregates with each other. We

shall consider first the mechanism which allows no aggregation after adsorption. The differential equations for this chain are

$$\begin{aligned}
\frac{dn_1}{dt} &= -k_1 n_1^2 - k_2 n_1 n_2 - \cdots - k_{m-1} n_1 n_{m-1}, \\
\frac{dn_2}{dt} &= \frac{k_1 n_1^2}{2} - k_2 n_1 n_2, \\
&\cdot \\
&\cdot \\
\frac{dn_e}{dt} &= k_{e-1} n_1 n_{e-1} - k_e n_1 n_e, \\
&\cdot \\
&\cdot \\
&\cdot \\
\frac{dn_m}{dt} &= k_{m-1} n_1 n_{m-1}.
\end{aligned} \tag{2}$$

On making the substitution $n_1 \, d\, t = d\, x$ these equations are transformed into the linear forms

$$\begin{aligned}
\frac{dn_1}{dx} &= -\sum_{i=1}^{m-1} k_i n_i, \\
\frac{dn_2}{dx} &= \frac{k_1}{2} n_1 - k_2 n_2, \\
&\cdot \\
&\cdot \\
\frac{dn_r}{dx} &= k_{m-1} n_{m-1}.
\end{aligned} \tag{3}$$

The characteristic equation of this set is

$$\begin{vmatrix}
\lambda + k_1 & k_2 & k_3 & \cdots & k_{m-1} & 0 \\
-\frac{k_1}{2} & \lambda + k_2 & 0 & \cdots & & 0 \\
0 & -k_2 & \lambda + k_3 & \cdots & & \\
\cdots & \cdots & \cdots & \cdots & -k_{m-1} & \lambda
\end{vmatrix} = 0. \tag{4}$$

A simple relationship is found between the determinants of each or-

der. Consider for $m = 3$ we have

$$D_2(\lambda) = \begin{vmatrix} \lambda + k_1 & k_2 \\ -\frac{k_1}{2} & \lambda + k_2 \end{vmatrix},$$

observe that

$$D_3(\lambda) = (\lambda + k_3) D_2(\lambda) + \frac{k_1 k_2 k_3}{2},$$

and in general

$$D_e(\lambda) = (\lambda + k_e) D_{e-1}(\lambda) + \frac{k_1 k_2 \cdots k_e}{2}. \tag{5}$$

Inasmuch as we shall not treat the general case, except to observe that the physical conclusions will probably not be much different for large values of m, we can state that in order to be physically meaningful the solutions of equation (3)

$$n_k = \sum_{j=1}^{m} c_{kj} \, e^{\lambda_j x} \tag{6}$$

satisfy the boundary conditions at all values of time

$$\sum_{1}^{m} k \, n_k = n_0.$$

Since x and not time occurs in equation (6), we see that it is not necessary that the real part of the λ be negative. From the defining equation for x, we have $x \to x_0$, x_0 finite, $n_1 \to 0$, then $t(x) \to \infty$; thus an infinite time is required for all the n_1 to disappear even though the x_0 is finite.

All the information needed for our purpose can be had from a detailed treatment of the set for $m = 3$. That is there will be an aggregate of three colloid particles built up before adsorption of the solute occurs. The problem immediately suggested is the relative behavior of n_1 and n_2. This behavior can be obtained from the integral curves. Using the notation of L. R. Ford (1933),

$$\frac{dn_2}{dn_1} = \frac{-\frac{k_1}{2} n_1 + k_2 n_2}{k_1 n_1 + k_2 n_2}, \tag{7}$$

$$\Delta = (k_1 + k_2)^2 - 6 k_1 k_2.$$

Since $k_1 + k_2 \neq 0$, the integral curves are not conics.

For

$$M_1: \quad n_2 = \mu_1 n_1 \qquad M_2: \quad n_2 = \mu^2 n_1$$

where

$$\mu_{1,2} = \frac{-(k_1 - k_2) \pm \sqrt{\Delta}}{2 k_2}, \tag{8}$$

the integral curves are shown in Figure 1.

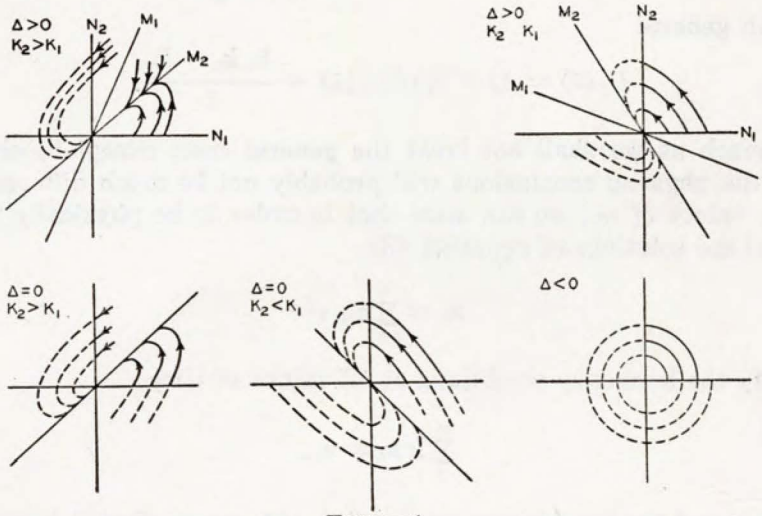


FIGURE 1

These solutions are physically well-behaved in that all show that either n_1 disappears before n_2 or they disappear together. But the presence of n_2 after the disappearance of n_1, makes it impossible for all of n_2 to be transformed into n_3. Thus for the simple case of n_1, n_2, n_3, we can expect as a resultant state only n_3 or a mixture of n_2 and n_3. The first will result if $k_2 > k_1$ and $\Delta \geqq 0$. The k's will be determined by the reaction, hence in a specific experiment we can examine the products present after sufficient time which will decide whether n_2 and n_3 or only n_3 remains.

An alternative treatment of the integral curves which is immediately applicable to the general case has been suggested in a letter by Dr. A. S. Householder. From the conditions, the integral curves in the n_2, n_1 plane are confined to the region bounded by the coordinate axes and the line $n_1 + 2n_2 = n_0$. Since $dn_1/dx < 0$ for any n_1 and n_2 not both zero, the integral curve can cross the n_2 axis ($n_1 = 0$). While for $n_2 = 0$, unless $n_1 = 0$ simultaneously, the integral curve is directed into the region. The scalar product of the vector with the

normal is $-3k_2n_2$ which is always negative for $n_2 > 0$. Initially $n_2 = 0$ and $n_1 = n_0$, thus the curve begins at the intersection of the line $n_1 + 2n_2 = n_0$ and the n_1 axis; the integral curve is tangent to the line and directed upward from the n_1 axis. As n_2 builds up the integral curve turns inward away from the line $n_1 + 2n_2 = n_0$.

The general set is treated in the same manner. Here the integral curves are confined to the region bounded by the $m-1$ coordinate hyper-planes and the hyper-plane $\sum_1^{m-1} k\, n_k = n_0$. The integral curve can cross the hyper-plane $n_1 = 0$ for always $dn_1/dx < 0$. But when $n_k = 0$, $k \neq 1$, $dn_k/dx = k_{k-1}\, n_{k-1} > 0$ unless n_{k-1} is also 0; but if n_{k-1} is 0, $dn_{k-1}/dx, > 0$, etc., until we meet an $n_r \neq 0$. Hence if any n_k, $k \neq 1$, approaches zero the integral curve turns toward a region where the n_k is increasing. Finally the scalar product of the tangent and the outward normal is $-(m-1)k_{m-1}\, n_{m-1}$ which completes the proof that for a finite x, but an infinite t, n_1 vanishes in the general case; and although some of the other n's may vanish simultaneously with n_1, they cannot vanish ahead of n_1.

The solutions of the set satisfying the boundary conditions

$$n_1 + 2n_2 + 3n_3 = n_0,$$

and at $x = 0$, $n_1 = n_0$ where n_0 is the initial number of simple colloid particles, are

$$\begin{aligned}
n_1 &= \frac{n_0}{\lambda_1 - \lambda_2}\left[(\lambda_1 + k_1)\, e^{\lambda_2 x} - (\lambda_2 + k_1)\, e^{\lambda_1 x}\right], \\
n_2 &= \frac{n_0(\lambda_1 + k_1)(\lambda_2 + k_1)}{k_2(\lambda_1 - \lambda_2)}\left[e^{\lambda_1 x} - e^{\lambda_2 x}\right], \\
n_3 &= \frac{n_0}{3}\left[1 + \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_1(\lambda_1 - \lambda_2)}\, e^{\lambda_1 x}\right. \\
&\qquad \left. - \frac{3(\lambda_1 + k_1)(\lambda_2 + k_1)}{\lambda_2(\lambda_1 - \lambda_2)}\, e^{\lambda_2 x}\right],
\end{aligned} \tag{9}$$

where

$$\lambda_{1,2} = \frac{-(k_1 + k_2) \pm \sqrt{\Delta}}{2}.$$

The relation between x and t is $n_1\, d\, t = d\, x$

$$t = \int_0^x \frac{dx}{n_1}$$

where $x = 0$ when $t = 0$. Before the integration can be performed the upper limit must be fixed. Calling this upper limit x and recalling that we are concerned about the value of the time from the beginning of the reaction until the appearance of the first particle capable of adsorbing a solute particle, we have on introducing $n_3 = 1$ into (9) and calling the coefficients of exponentials α and β respectively

$$3/n_0 = 1 + \alpha\, e^{\lambda_1 x} - \beta\, e^{\lambda_2 x}. \tag{10}$$

This equation cannot be solved explicitly for x. Making the substitutions

$$y_1 = \alpha\, e^{\lambda_1 x} + 1 - 3/n_0,$$

$$y_2 = \beta\, e^{\lambda_2 x},$$

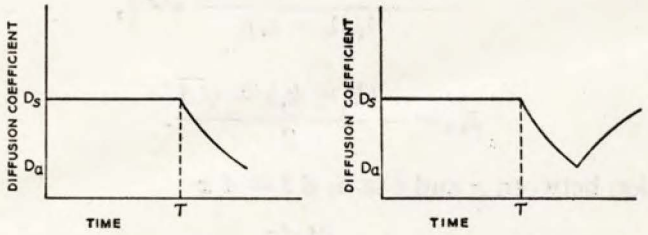
we can solve graphically if we have numerical values for α, β, and n_0. Taking $n_0 = 1000$, $k_2 = 4\ k_1 = 4\ k$ then $\Delta = k^2$, $\lambda_1 = -4\ k$, $\lambda_2 = -6\ k$ and we find $\alpha = -5.55$, $\beta = 3.75$. Substituting these values we have $x = 0.48/k$

$$\tau = \frac{2}{1000} \int_0^x \frac{e^{4kx}}{5 - 3\, e^{-2kx}}\, dx,$$

where τ is the time required for the first n_3 to appear in the system. Integrating numerically by using Simpson's rule, we find

$$\tau = 48.18/1000\ k \quad \text{secs.} \tag{11}$$

Our analysis culminating in (11) can be summarized: when the aggregation takes place according to (3) with $m = 3$, at the end of $48.18/1000\ k$ secs. the particles capable of adsorbing solute particles appear in the system. Before their appearance, the other colloid particles would have negligible effect upon the diffusion coefficient of the solute. After their appearance, however, they would act to reduce the value of D according to J. Reiner's curve (1939). The effect is shown in Figure 2a. If the aggregation continues with the number of adsorbed solute particles a function of the surface area as in an



a b

FIGURE 2

earlier paper (H. Branson, 1942), we would have the variation represented in Figure 2b.

In order for the mechanism to be applicable to cellular reactions, τ has to be in general small, except for some reactions where it may be of the order of a second. From physical considerations we see that k is a function of the diffusion coefficient and the radius of the aggregating particles; *M. V.* Smoluchowski (1918) found for a colloid solution $k = 4\ \pi\ \tau\ D$. Introducing values given in that paper from Zsigmondy's experiments we have $k \sim 10^{-12}$ and $\tau \sim 10^{10}$ secs. Thus unless the diffusion coefficient within the cell is considerably larger than in solution, this reaction gives an inordinately long time for the beginning of the decrease in the diffusion coefficient. More plausible values of τ can be obtained by considering n_o to be much larger in (10). Raising n_o to 10^7 causes practically no change in x, and taking $r \sim 10^{-6}$ cm then for D of the order of 10^3, τ will be of the order of a hundredth of a second. This is not an unreasonable value of D for aggregations where the binding energy is large.

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LITERATURE

Branson, Herman. 1942. "Diffusion as a Function of Aggregation in Colloidal Media." *Bull. Math. Biophysics*, 4, 1-6.

Ford, Lester R. 1933. *Differential Equations*. New York: McGraw-Hill Book Co.

Reiner, John M. 1939. "Diffusion in Colloidal Media." *Bull. Math. Biophysics*, 1, 143-149.

Smoluchowski, M.v. 1918. "Versuch siner mathematischen Theorie der Koagulationskinetik Kolloider Losungen." *Zeitschrift für physikalische Chemie*, 152, 129-168.