

1969

# Molecular weight distribution in emulsion polymerisation

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MOLECULAR WEIGHT DISTRIBUTION  
IN EMULSION POLYMERISATION

by

ASHOK K. TAORI

A THESIS

Presented to the Graduate Faculty  
of Lehigh University  
in Candidacy for the Degree of  
Master of Science  
in  
Chemical Engineering.

Lehigh University

1969

CERTIFICATE OF APPROVAL

This research report is accepted and approved in partial fulfillment of the requirements for the Degree of Master of Science in Chemical Engineering.

23 MAY 1969  
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### NOTATION

- A - Transfer Area of the latex Particle
- $E_n^*, E_{n+1}^*$  - Active free radical polymer chain of length 'n' and 'n+1' respectively
- $E_n$  - Deactivated (or Dead) free radical polymer chain of length 'n'
- $f_d$  - Fraction of free radicals which are effective in initiation of polymerisation
- $f_r(n)$  - Distribution of chain lengths in a particle of radius between 'r' and  $r+dr$
- $f_p(r)$  - Steady state particle size distribution
- $f(\cdot), h(\cdot)$  - Probability density function
- $F_{q,n}(t)$  - Fraction of inactive polymer chains of length 'n' monomer molecules at time 't' in a particle containing 'q' active free radical molecules
- $F_{q,n}^*(t)$  - Fraction of active polymer chains of length 'n' monomer molecules at time 't' in a particle containing 'q' active free radicals
- $I_{-m}, I_{1-m}, I_{m-2}$  - Bessel functions
- $I_0, I_1$
- $(I_2)$  - Concentration of Initiator
- $(I\cdot)$  - Concentration of free radicals

$k_d$	-	Decomposition rate constant
$k_i$	-	Initiation rate constant
$k_p$	-	Propagation rate constant
$k_{tc}$	-	Termination rate constant for combination reaction
$k_{td}$	-	Termination rate constant for disproportionation
$k_{trs}$	-	Termination rate constant for chain transfer
$k_{out}$	-	Rate constant for transfer out of a particle
(M)	-	Monomer concentration
(M $\cdot$ )	-	Free radical concentration
$M_r\cdot, M_s\cdot, M_{r+1}\cdot$	-	Long chain free radicals containing r, s, r+1, monomer units respectively
$\bar{M}_n$	-	Number average molecular weight
$\bar{M}_w$	-	Weight average molecular weight
$M_0$	-	Molecular weight of monomer
$M_n$	-	Molecular weight of polymer of chain length 'n'
$n, n', x, y$	-	Polymer chains of length n, n', x, and y monomer units respectively
$N_0^n$	-	Number of micelles/cm <sup>3</sup>
N	-	Number of particles per unit volume of emulsion

$N_q, N_{q-1}, N_{q+1}$	-	Number of particles with $q, q-1, q+1$
$N_{q+2}$		and $q+2$ free radicals respectively
$N_a$	-	Avagadro's Number
$P_q(t), P_{q-1}(t)$	-	Probability of finding $q, q-1, q+2$
$P_{q+2}(t)$		free radicals respectively
$p$	-	Probability of propagation
$q$	-	Number of free radicals present in a
		polymer particle
$\bar{q}$	-	Average number of free radicals in a
		polymer particle
$Q_{q,n}(t)$	-	Total fraction of $n$ -mer chains
		irrespective of activity at time ' $t$ '
		in a particle containing ' $q$ ' free
		radicals
$\bar{Q}_n$	-	Distribution of polymer chains of
		length ' $n$ ' in the whole emulsion
$Q_n(r)$	-	Distribution of polymer chains of
		length ' $n$ ' in a particle of radius ' $r$ '
$r$	-	Radius of a latex particle
$\bar{r}$	-	Average radius of the particles at
		steady state particle size distribution
$r_m$	-	Radius of micelle
$R_p$	-	Rate of propagation $\text{gmol}/\text{cm}^3 \cdot \text{sec}$ .
$R_{tr}$	-	Rate of termination by chain transfer
$R_t$	-	Rate of termination by coupling and
		disproportionation

- $R_1$  - Rate of generation of free radicals per unit volume of total emulsion per unit time
- $S_p(n)$  - Distribution of chain lengths in a latex particle that grows from ' $r_m$ ' to ' $r$ '
- $\bar{S}_p(n)$  - Distribution of chain lengths in an emulsion system
- $t$  - Time
- $v$  - Volume of a latex particle
- $\beta, k_{pt}^*$  - Rate of propagation - number of monomer units added/polymer chain. sec.
- $\Delta t_1, \tau_1$  - Interarrival time between two free radical entries in a particle
- $\mu$  - Average rate of arrival of free radicals
- $\tau_\mu$  - Average time between free radical entries into the particle
- $\theta$  - Residence time
- $\theta_q(r)$  - Rate of termination of free radicals in a particle of radius ' $r$ ' and containing ' $q$ ' free radicals
- $\bar{\Delta}$  - Average life span of the second free radical - average time/period
- $\gamma_t$  - Rate of termination/free radical/sec.

0.12 times less than the value obtained

### ABSTRACT

There is no theoretical information available for molecular weight distribution in emulsion polymerisation. The only experimental data available (23) is physically unrealisable.

An attempt is made in this paper to formulate mathematical models to predict the distribution for some simplified ideal and semi-ideal systems. The theory for emulsion polymerisation is considered as a stochastic process and a probabilistic approach is made towards the problem.

The distribution predicted for ideal emulsion systems both batch and continuous is exponential. A reasonable comparison of number and weight average molecular weights with De Graff's (22) experimental work (unpublished) in continuous emulsion polymerisation is not possible since the data obtained by Gel Permeation Chromatograph technique needs to be corrected by the calibration constant of the chromatograph for the solvent used. Yet, it is felt that the theoretically predicted values are twice as high as the experimental values.

The semi-ideal theory for batch process is compared with Schulz et. al's (23) experimental data. The theoretical number average molecular weight is twice the experimental though the theoretical weight average molecular weight is 0.72 times less than the value obtained experimentally.

The principles of Birth and Death Stochastic process have been applied to continuous emulsion polymerisation systems and the probability of the population of free radicals in a latex particle as a function of time have been predicted. Further, the above principles are expanded to predict the molecular weight distribution.

---

## INTRODUCTION

Emulsion polymerisation is one of the four major industrial processes for free radical polymerisation and co-polymerisation. The four basic ingredients are, monomer; water, which is the continuous medium; initiator and emulsifier to form loci of reaction and also stabilise the emulsion.

Emulsion polymerisation offers the advantages of high reaction rates, easy heat dissipation, high molecular weight products, low viscosity and directly processable final products. The colloidal behaviour, however makes the process rather complex.

Molecular weight is a fundamental property in the classification of polymers and is related to its mechanical, structural and chemical properties. This makes the control and study of molecular weight distribution important.

The purpose of this work was to develop mathematical models to predict the molecular weight distribution of polymer manufactured in both batch and continuous emulsion polymerisation systems.

---

## THEORY

Harkins (7) and his collaborators were the first to suggest a qualitative mechanism for emulsion polymerisation. Their work during World War II is now generally accepted.

Emulsifier when added to water above the 'critical micelle concentration' forms clusters of soap molecules called 'Micelles'. Generally the amount of emulsifier dissolved in water is about 0.015 gms/ml. Thus the greatest portion of the emulsifier exists as micelles. The shape of these micelles is still uncertain, but for simplicity they are considered spherical of radius about  $25 \text{ \AA}$ .

The hydrocarbon end ( hydrophobic ) of the emulsifier molecules constitutes the interior of the micelle and the surface is formed of the ionic groups (hydrophilic).

The hydrophobic interior of the micelle accounts for the apparent increase in the solubility when a water insoluble or partially soluble monomer is added to the emulsifier-water mixture. Styrene has a solubility of 0.00368 gmoles/litre in water at  $50^{\circ}\text{C}$ , but in a 0.093 M potassium palmitate solution the apparent solubility rises to 0.139 gmoles/litre. The micelle solubilizes the monomer due to osmotic forces. The unabsorbed monomer is dispersed in the continuous phase in small droplets of about  $10^{-4}$  cm. diameter.

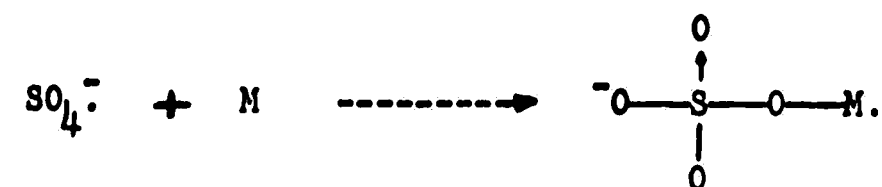
An initiator like potassium persulphate decomposes



into radical ions  $SO_4^{\cdot -}$ ,



The sulphate radical ion possesses an unpaired electron and therefore exhibits extreme reactivity characteristic of free radicals. It reacts with the monomer forming organic sulphate radical molecules.



The product is a surface active radical ion which soon diffuses into a micelle, because of the dynamic equilibrium between micellar and molecularly dissolved emulsifier. The micelle thus stung by a free radical is called a 'Latex Particle', and it is stabilised with emulsifier.

Polymerisation proceeds very rapidly in these locii and termination occurs when another free radical enters the latex particle. The monomer required for the rapid growth comes into the latex particle by diffusion from the monomer drops. This rate of diffusion is much faster than its consumption during polymerisation. With the growth of the particle, its surface area increases and more emulsifier is absorbed. The micelles provide the needed emulsifier.

Smith and Ewart (10,11) divided the whole single charge isothermal emulsion polymerisation process into three intervals. This division was further expanded by Gardon (2)

and is:

Interval I :

1. All latex particles are formed in 1.

Interval II :

1. Number of particles is constant and they are saturated with monomer.
2. Monomer droplets are also present in the continuous phase of the emulsion.
3. There are no micelles.

Interval III :

1. Number of particles is constant and they are no longer saturated with monomer.
2. No monomer droplets exist.

Harkins assumed that as long as monomer droplets were present a constant monomer concentration existed in the latex particle. Morton, et. al. (9) and recently a review by Gardon (6) confirmed the constant monomer concentration and attributed its existence to the equilibrium swelling of the polymer particles. They, as did Flory (21), also established that the rate of diffusion of monomer molecules from the droplets to the particles is sufficiently fast and does not interfere with the rate of polymerisation in the particle.

The three intervals outlined above do not exist in continuous emulsion polymerisation. Once the process reaches

steady - state the total number of particles is constant and they are saturated with monomer. Thus the system always exists in the so called interval II. The above fact can be used advantageously by nucleating all the particles in the first C.S.T.R. with a low residence time and low conversion, further conversion taking place in the remaining C.S.T.R.'s, in a reactor train with a high residence time.

QUANTITATIVE DESCRIPTION  
OF EMULSION POLYMERISATION KINETICS

The steady state free radical kinetics of emulsion polymerisation involve the following three basic mechanisms :

INITIATION :

Decomposition of initiator into free radicals :

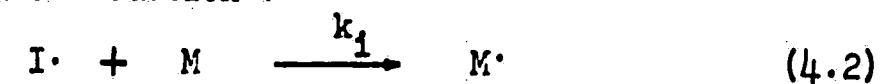


$(I_2)$  = Concentration of Initiator

$(I\cdot)$  = Concentration of Free Radical

$k_d$  = Decomposition rate constant

Initiation of reaction :



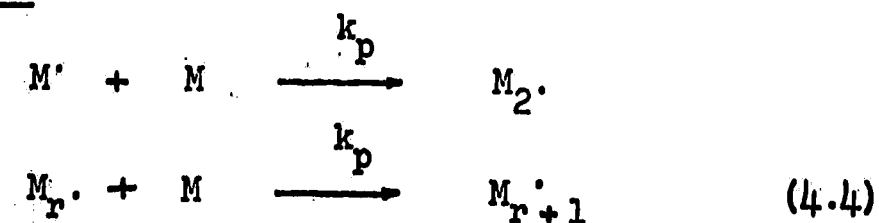
$(M)$  = Monomer concentration

$k_i$  = Initiation rate constant

$$\text{Rate of Initiation} = R_i = 2k_i f_d (I_2) \quad (4.3)$$

$f_d$  = Fraction of free radicals which are effective in initiation of polymerisation.

PROPAGATION :



- (M·) = Total free radical concentration
- (M) = Monomer concentration
- $M_r·$  = Long chain free radicals containing 'r' monomer units.
- $k_p$  = Propagation rate constant

$$\text{Rate of Propagation} = R_p = k_p (M) (M·) \quad (4.5)$$

The rate of propagation in a latex particle of volume 'v' and containing 'q' free radicals is,

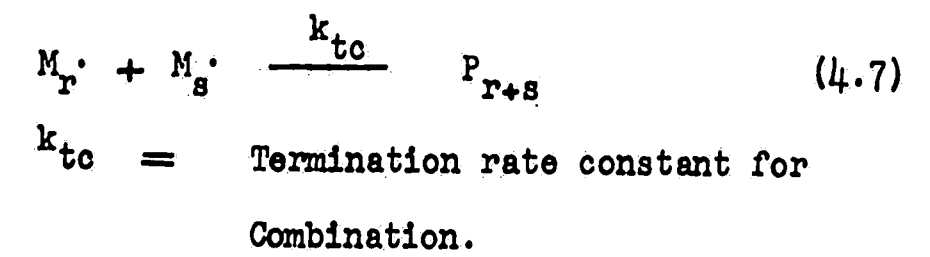
$$R_p = k_p (M) (q/N_a v) \quad (4.6)$$

$N_a$  = Avogadro's number

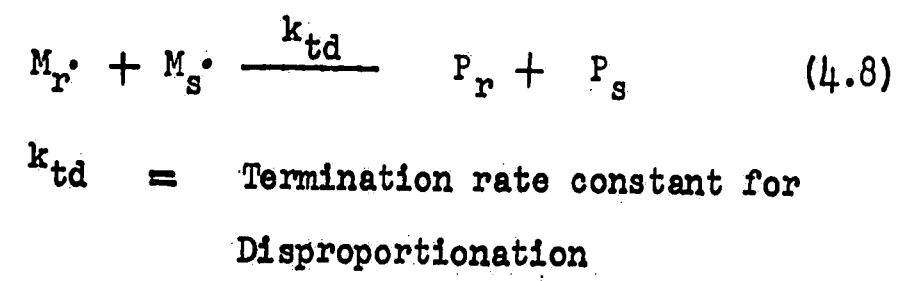
TERMINATION :

Various mechanisms can cause termination of a growing chain.

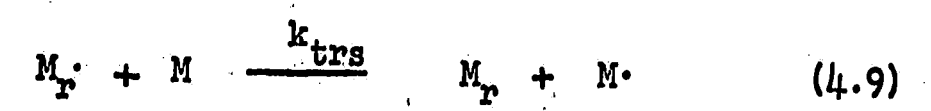
A. Combination :



B. Disproportionation :



C. Chain Transfer :



$M_r$  = Terminated polymer molecule of chain length 'r'.

$k_{tr}$  = Termination rate constant for chain transfer.

The rate of termination by chain transfer is,

$$R_{tr} = k_{tr} (M_r \cdot) (M) \quad (4.10)$$

$$R_t = \sum_{r=1}^{\infty} R_{tr} \quad (4.11)$$

The transfer reaction results in a terminated chain and a molecule capable of continuing polymerisation. Transfer can also take place with solvent, transfer agents, etc.

The rate of termination for the case of combination and disproportionation mechanism is,

$$\begin{aligned} R_t &= 2k_{tc} (M \cdot)^2 \\ &= 2k_{tc} (q/N_a v) ((q-1)/N_a v) \end{aligned} \quad (4.12)$$

The factor (q-1) is necessary since the terminating free radical cannot react with itself. Also 'q' is small and thus 'q' and 'q-1' can be considerably different.

Smith and Ewart (11) derived a relation for the average number of free radicals in a particle when free radicals are generated outside the particle. They assumed pseudo steady state, where the number of particles containing 'q' free radicals is constant and obeys the following recursion relationship :

$$N_q (k_{to} q(q-1)/v + k_{out} Aq/v + R_1/N) = (4.13)$$

$$(R_1/N)N_{q-1} + k_{out} A(q-1/v)N_{q+1} \quad (k_{to} (q+2)(q+1)/v)N_{q+2}$$

$N_q, N_{q-1}, N_{q+1}, N_{q+2}$  = Number of particle with  $q, q-1, q+1, q+2$  free radicals respectively.

$k_{out}$  = Rate constant for transfer out of a particle.

$A$  = Transfer area of the particle

$R_1$  = Rate of generation of free radicals per unit volume of total emulsion per unit time.

$N$  = Number of particles per unit volume of emulsion.

The three terms on the left hand side of equation (4.13) express the rate of loss of particles containing 'q' free radicals by termination, transfer out and arrival of a free radical respectively. Terms on the right give the rate of formation of particles containing 'q' free radicals, by arrival, transfer out and termination respectively.

Expression (4.13) was solved by Stockmayer (12) to give,

$$\bar{q} = C/4 \cdot (I_{-m}(C) / I_{1-m}(C)) \quad m \leq 1 \quad (4.14)$$

$$= (1-m)/2 + C/4 \cdot (I_{m-2}(C) / I_{m-1}(C))$$

for  $m > 1$  (4.15)

$$C^2 = 8v/(k_{to}\tau_{\mu})$$

$$m = k_{out}/k_{to}$$

$\bar{q}$  = Average number of free radicals in the particle.

$I_{-m}, I_{1-m}, I_{m-1}$  = Bessel Functions.

$\tau_{\mu} = N/R_1$  = Average time between free radical entries.

When  $m=0$ , ie. no free radical desorption out of the particle,

$$\bar{q} = C/4. ( I_0(C)/I_1(C) ) \quad (4.16)$$

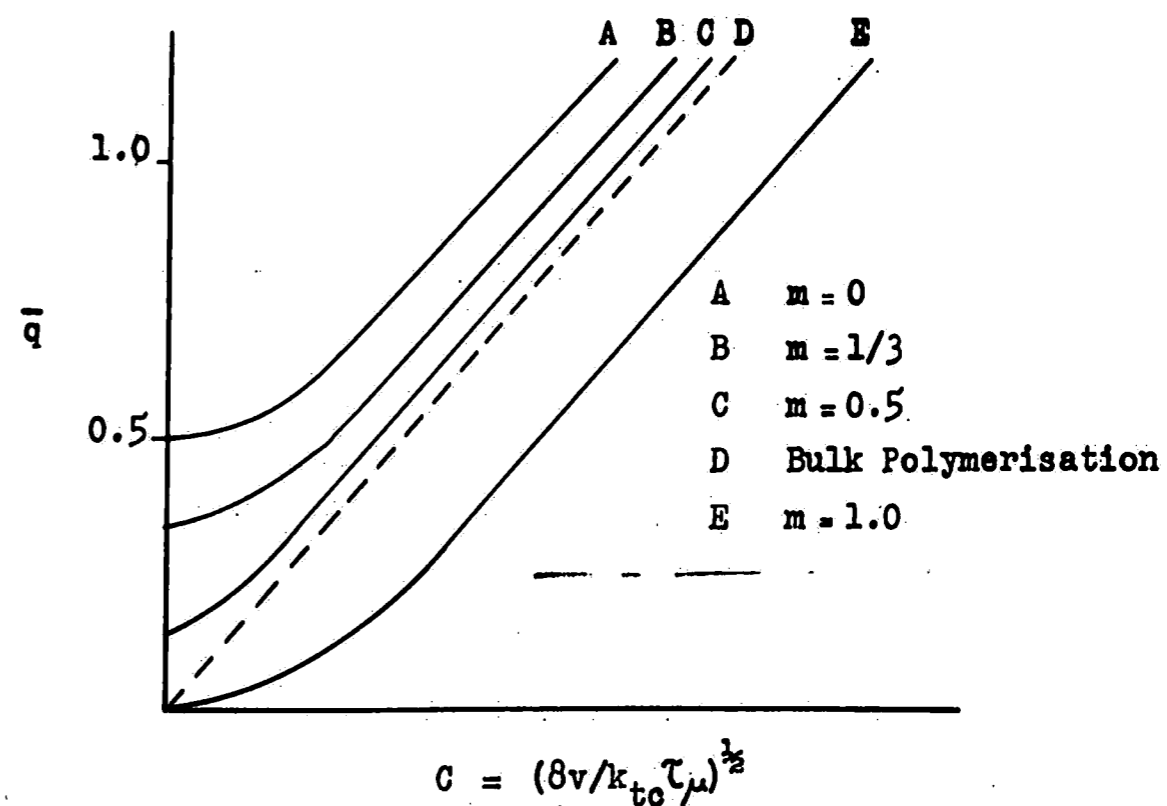


Fig. 1. Average Number of Free Radicals as a function of 'C'



The rate of polymerisation becomes,

$$R_p = k_p(M)(C/4) \cdot (I_0(C)/I_1(C)) \quad (4.17)$$

The factor  $I_0(C)/I_1(C)$  is called the "Sub-Division Factor - Z". Fig. 2 shows the plot of Z-factor for various values of 'C' and shows the regions of emulsion, suspension and bulk polymerisation.

On expanding the Bessel function and letting  $C \rightarrow 0$  we get,

$$\lim_{C \rightarrow 0} \bar{q} = 0.5$$

This region is called "Ideal Emulsion Polymerisation". Real systems under certain physical conditions come close to ideal emulsion polymerisation.

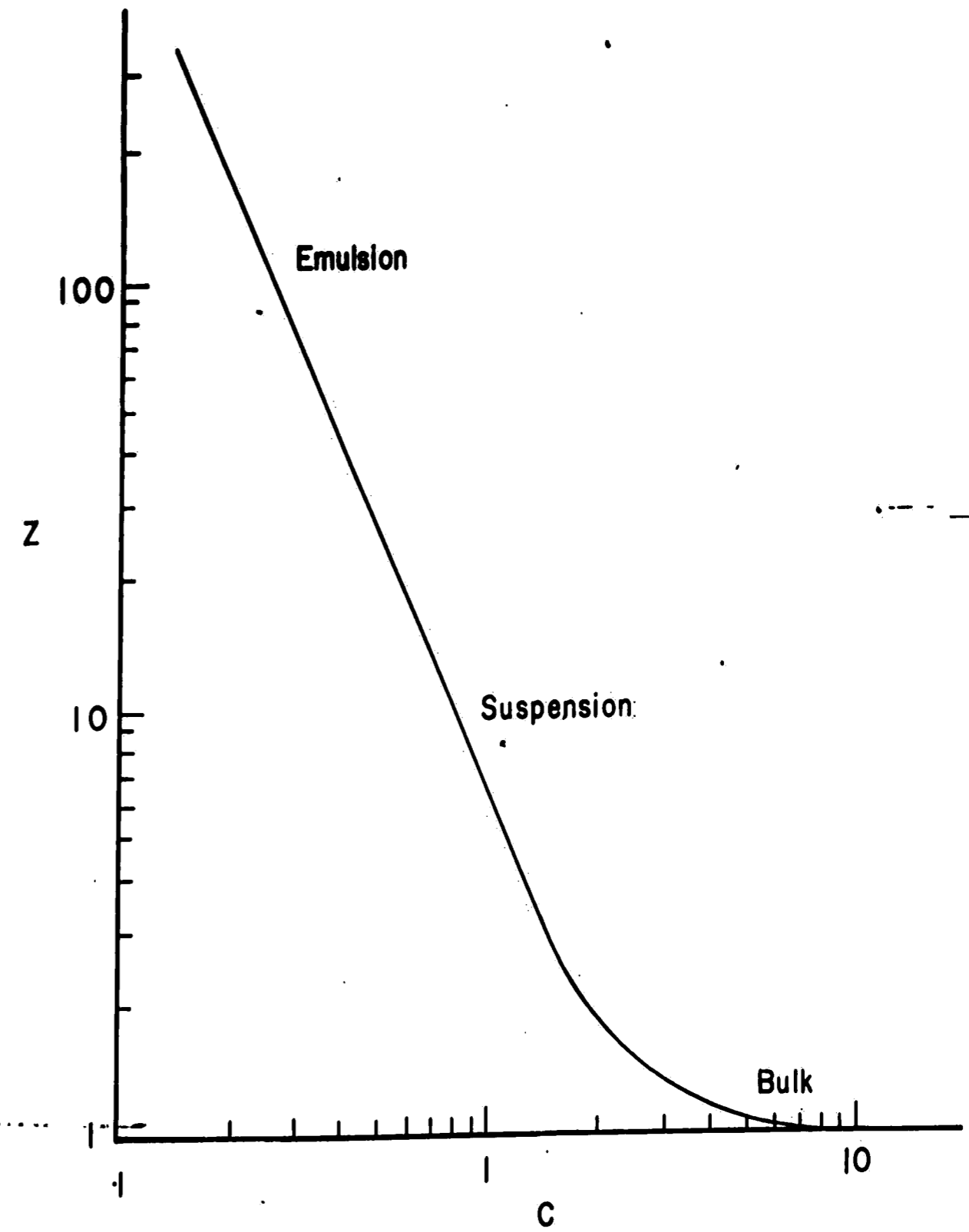


Fig. 2. Subdivision Factor 'Z' as a function of 'C'

## MOLECULAR WEIGHT DISTRIBUTION

### IN BULK POLYMERISATION

The probability of the formation of a polymer molecule of a given molecular weight is given by the relative probabilities of propagation and termination. If the probability of propagation is given by 'p', the probability of termination is '1-p'. If it is assumed that the basic unit of polymerisation is the active monomer molecule  $M_1$  and that the termination step involves only deactivation (ie. disproportionation) of a polymer chain, then the probability of the formation of a polymer chain containing 'n' monomer units is,

$$p^{n-1}(1-p) \quad (5.1)$$

and 
$$\sum_1^{\infty} p^{n-1}(1-p) = 1 \quad (5.2)$$

The number and weight average degrees of polymerisation are :

$$\bar{M}_n = \sum_1^{\infty} np^{n-1}(1-p) = 1/(1-p) \quad (5.3)$$

$$\bar{M}_w = \frac{\sum_1^{\infty} n^2 p^{n-1}(1-p)}{\sum_1^{\infty} n p^{n-1}(1-p)} = (1+p)/(1-p) \quad (5.4)$$

$$\frac{\bar{M}_w}{\bar{M}_n} = 1+p \quad (5.5)$$

For the formation of high polymers,  $p \approx 1$

$$\bar{M}_w/\bar{M}_n \approx 2$$

The probability of propagation is,

$$p = \frac{\text{Rate of propagation}}{(\text{Rate of propagation} + \text{Rate of Termination})}$$

$$= \frac{k_p(M)(q/N_a v)}{k_p(M)(q/N_a v) + 2k_{tc}(q/N_a v)(q-1/N_a v)}$$
$$= \frac{(M)}{(M) + (2k_{tc}/k_p N_a)(q-1/v)} \quad (5.7)$$

With reference to emulsion polymerisation the following critical factors make the above approach to molecular weight distribution rather complex,

1.  $p = f(q, v)$
2.  $q = q(t)$
3.  $v = v(t)$

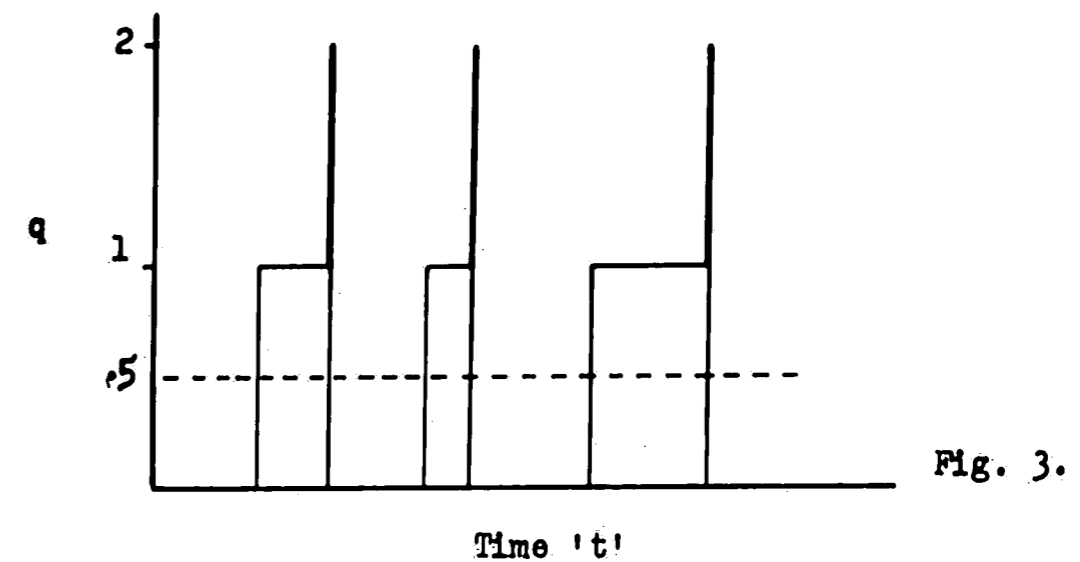
It is impossible to predict the number of free radicals as a function of time in the particle of volume 'v' ; only ' $\bar{q}$ ' can be estimated.

MOLECULAR WEIGHT DISTRIBUTION IN

IDEAL EMULSION POLYMERISATION

Ideal emulsion polymerisation mathematically means  $\bar{q} = 0.5$ , i.e. a particle containing one growing free radical terminates instantly when stung by another free radical.

Fig. 3 illustrates an ideal emulsion system.



Consider a single particle and let  $t_1, t_2, t_3, \dots$   
 $\dots t_n \dots$  be the times at which the free radicals  
enter the particle. The number of free radicals arriving  
at the latex particle is a random phenomenon obeying  
"Poisson's Probability Law" because it satisfies the  
following axioms (16) :

1. Since the counting of events ( i.e. arrival of free  
radicals ) begin at time '0', we define  $N(0) = 0$  .

$N(t) =$  Total number of free radicals that have

arrived between time '0' and 't'.

2. For any  $t > 0$

$0 < P( N(t) > 0 ) < 1$  ie., in any interval however small there is a positive probability that an event will occur, but it is not certain that an event will occur, ie.  $P( N(t) > 0 ) \neq 1$ .

3. For any  $t \geq 0$

$$\lim_{h \rightarrow 0} \frac{P( N(t+h) - N(t) \geq 2 )}{P( N(t+h) - N(t) = 1 )} = 0$$

In sufficiently small intervals, at most one event can occur; ie. it is not possible for events to happen simultaneously.

Poisson's probability law can be expressed by the following equation,

$P_N(t)$  = Probability that in time '0' to 't', exactly 'N' free radicals will arrive.

$$= \frac{e^{-\mu t} (\mu t)^N}{N!} \tag{6.1}$$

$\mu$  = Average rate of arrival of free radicals.

If  $\Delta t_1 = t_2 - t_1$ ,  $\Delta t_2 = t_3 - t_2$ , .....  
 $\Delta t_n = t_{n+1} - t_n$  ..... and if the stochastic process obeys poisson's probability law, then the ' Inter - Arrival Time ' between successive arrivals of free radicals ie.

$\Delta t_1, \Delta t_2, \Delta t_3, \dots, \Delta t_n \dots$  is an independent 'Exponentially' distributed random variable following the exponential distribution (15,16) ,

$$f(\Delta t_1) = \mu e^{-\mu \Delta t_1} \quad 0 < \Delta t_1 < \infty \quad (6.2)$$

Ideal emulsion polymerisation thus is based on the assumption that a free radical that arrives at time  $t_1$  can grow only till time  $t_2$  when the second free radical comes. Therefore growth time of the first polymer chain is ,

$$\Delta t_1 = t_2 - t_1$$

In general growth time of  $i^{\text{th}}$  chain is

$$\Delta t_i = t_{i+1} - t_i$$

and follows the distribution given by (6.2) .

The kinetic chain length 'n' of the polymer molecule at termination is,

$$n = \beta \Delta t_i \quad (6.3)$$

$\beta =$  Rate of propagation (addition of a monomer) per chain per second.

$$= k_p (M) \quad (6.4)$$

$$\therefore \Delta t_i = n/\beta$$

$$f(n/\beta) = \mu e^{-\mu(n/\beta)}$$

$$f(n) = \frac{\mu}{\beta} e^{-\mu(n/\beta)} \quad (6.5)$$

Expression (6.5) is the distribution of kinetic chain lengths 'n' and is developed further depending whether the process is batch or continuous.

In emulsion polymerisation the rate of free radical arrival ' $\lambda$ ' varies with the size of the latex particle and thus is a function of time.

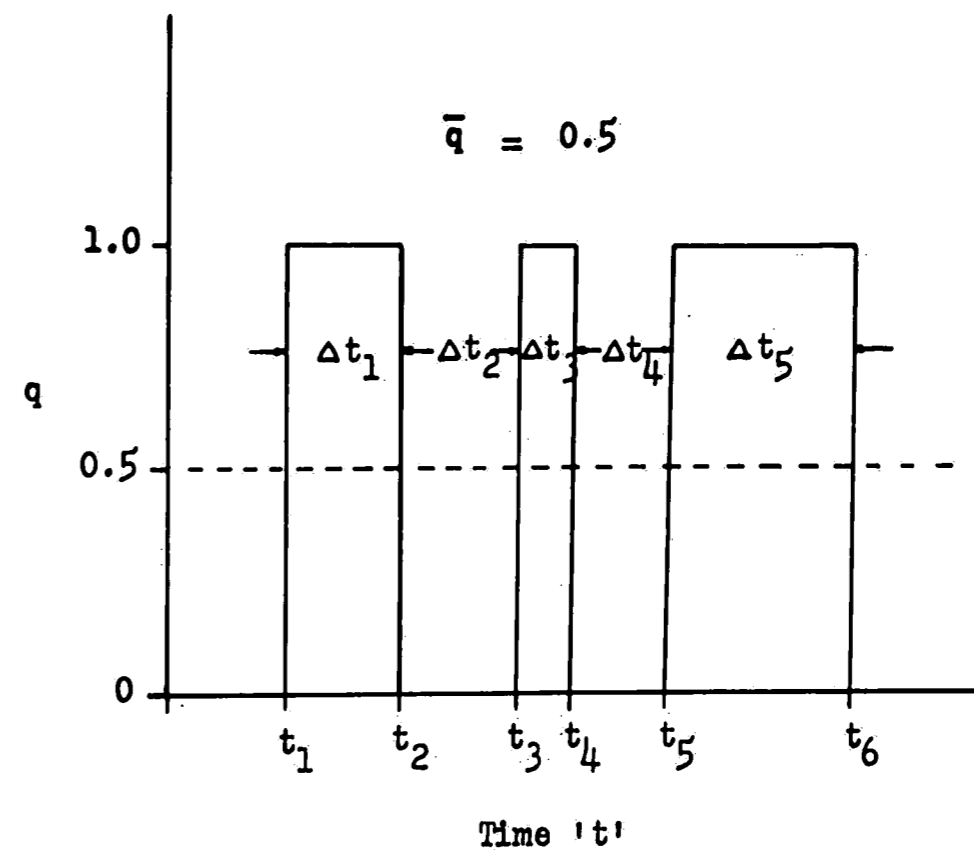


Fig. 4 Schematic representation of Ideal Emulsion Polymerisation showing 'Inter-Arrival Time' between Free Radical entries.



### BATCH POLYMERISATION

The rate of free radical arrival ' $\mu$ ' is constant and is not dependent on particle size for ideal batch emulsion polymerisation, since the rate of initiation ' $R_1$ ' and the number of particles ' $N$ ' are constant after interval I.

$$\mu = R_1/N \quad (6.6)$$

The molecular weight of a polymer molecule of chain length ' $n$ ' is given by,

$$M_n = M_o n \quad (6.7)$$

Substituting (6.6) , (6.7) into (6.5) and simplifying, the molecular weight distribution is given by,

$$f(M_n) = (R_1/k_p(M)NM_o) \cdot \exp(-R_1 M_n/k_p(M)NM_o) \quad (6.8)$$

$M_n$  = Molecular weight of polymer of chain length ' $n$ '.

$M_o$  = Molecular weight of monomer

$$\int_0^{\infty} f(M_n) dM_n = 1.0 \quad (6.9)$$

The molecular weight distribution given by equation (6.8) yields the following expressions for number and weight average molecular weights,

$$\begin{aligned} \bar{M}_n &= \int_0^{\infty} M_n f(M_n) dM_n \\ &= k_p(M)NM_o/R_1 \end{aligned} \quad (6.10)$$

$$\bar{M}_w = \frac{\int_0^{\infty} M_n^2 f(M_n) dM_n}{\int_0^{\infty} M_n f(M_n) dM_n}$$

$$= 2k_p(M)M_0/R_1 \quad (6.11)$$

$$\bar{M}_w/\bar{M}_n = 2 \quad (6.12)$$

Fig. 5 shows the molecular weight distribution for ideal batch emulsion polymerisation. The physical constants used are :

$$R_1 = 0.87 \times 10^{14} \text{ Number of initiator molecules/cm}^3 \cdot \text{sec.}$$

$$N = 2.5 \times 10^{15} \text{ Number of latex particles/cm}^3 \cdot$$

$$k_p = 0.125 \times 10^6 \text{ cm}^3/\text{gmole} \cdot \text{sec.}$$

$$(M) = 0.55 \times 10^{-2} \text{ gmole/cm}^3 \cdot$$

The predicted number and weight average molecular weights are,

$$\bar{M}_n = 1.9 \times 10^6$$

$$\bar{M}_w = 3.8 \times 10^6$$

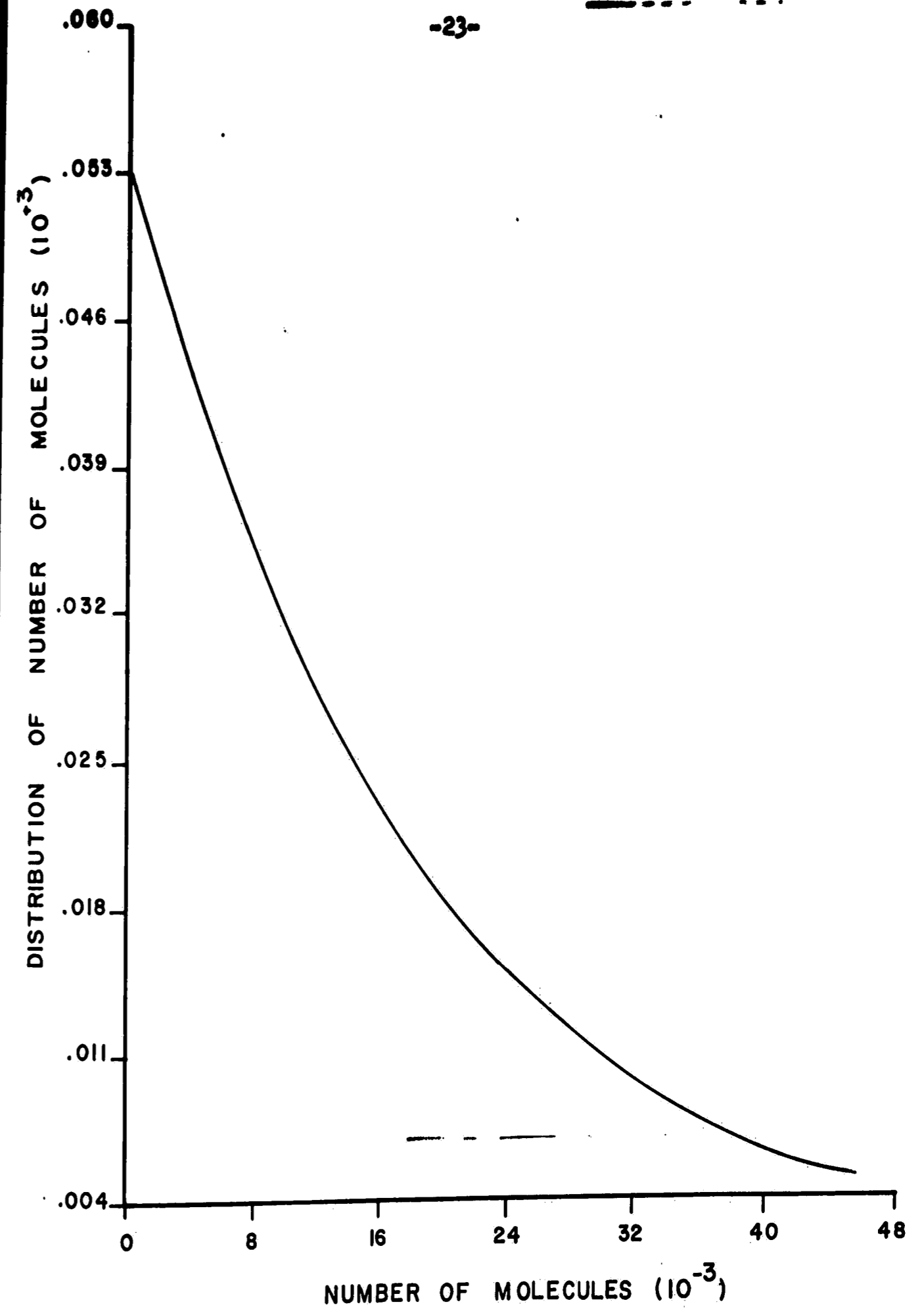


Fig. 5. Distribution of Degree of Polymerisation in Ideal Batch System

### CONTINUOUS POLYMERISATION

The steady state particle size distribution in continuous emulsion polymerisation is broad and has a definite effect on the molecular weight distribution.

The rate of free radical arrival at a particle is no longer constant but is a function of the radius 'r' of the particle.

$$\mu(r) = R_1 r / (\bar{r}) \quad (6.13)$$

r = Radius of the particle

$\bar{r}$  = Average radius of particles at steady state particle size distribution.

The derivation of equation (6.13) is given by De Graff (22) and is listed in appendix 1.

Consider a latex particle of radius 'r' at time 't'. In the interval 't' and 't+dt' the rate of free radical arrival  $\mu(r)$  is constant and so the distribution of chain lengths in the time interval t and t+dt is given by equation :

$$f_r(n) = \frac{\mu(r)}{\beta} \cdot \exp(-\mu(r)n/\beta) \quad (6.14)$$

The distribution of chain lengths in a particle which grows from 'r<sub>m</sub>' to 'r' in time t=0 to t=t becomes,

$$S_r(n) = \frac{\int_{r_m}^r 4\pi r^2 f_r(n) dr}{(4/3)\pi(r^3 - r_m^3)} \quad (6.15)$$

$r_m$  = Radius of the micelle

$$S_r(n) = \frac{\int_{r_m}^r 3\mu(r)r^2 e^{-\mu(r)n/\beta} dr}{(r^3 - r_m^3)} \quad (6.16)$$

Substituting (6.13) in (6.16) and integrating gives,

$$S_r(n) = \frac{A}{(r^3 - r_m^3)} \left\{ e^{nrB} \left( \frac{r^3}{nB} - \frac{3r^2}{n^2 B^2} + \frac{6r}{n^3 B^3} - \frac{6}{n^4 B^4} \right) - e^{nr_m B} \left( \frac{r_m^3}{nB} - \frac{3r_m^2}{n^2 B^2} + \frac{6r_m}{n^3 B^3} - \frac{6}{n^4 B^4} \right) \right\}$$

$$A = 3R_1 / N\bar{r}k_p(M)$$

$$B = -R_1 / N\bar{r}k_p(M) \quad (6.17)$$

Expression (6.17) gives the chain length distribution in a particle of radius 'r'. To obtain the distribution of the whole system it has to be weighted with the steady state particle size distribution.

$$\bar{S}_r(n) = \frac{\int_m^r S_r(n) f_r(r) dr}{\int_m^r f_r(r) dr} \quad (6.18)$$

$\bar{S}_r(n)$  = Distribution of number of molecules in continous emulsion polymerisation.

$f_r(r)$  = Steady state particle size distribution in continous ideal emulsion polymerisation.

A continous emulsion polymerisation experiment of styrene monomer was conducted by De Graff (22). The recipe was,

- Monomer = 32.4 wt. %
- Water = 67.6 wt. %
- Initiator = 1.5 wt. % of water  
( $K_2S_2O_8$ )
- Emulsifier = 2.79 wt. % of water  
(Na-Lauryl Sulphate)

The physical conditions and constants were,

- $\theta$  = 3600 secs.
- $N_o^m$  =  $1.29 \times 10^{18}$  No. of micelles/cm<sup>3</sup>.
- $R_i$  =  $.87 \times 10^{14}$  Initiator molecules/cm<sup>3</sup>.sec.
- $k_p$  =  $.125 \times 10^6$  cm<sup>3</sup>/gmole.sec.

The particle size distribution obtained is listed in table 1.

Table 1.

Particle Radius (A )	Fraction
84.5	0.038
169.5	0.149
255.0	0.243
338.5	0.211
423.5	0.196
505.0	0.100
595.0	0.048
675.0	0.008
760.0	0.007

The average radius  $\bar{r} = 335 \text{ A}^\circ$ . The above particle size distribution was curve fitted and expressed as,

$$f_r(r) = \frac{85.0}{133.865 (2\pi)^{\frac{1}{2}}} \cdot \exp\left\{ -\frac{1}{2} \frac{(r - 334.692)^2}{(133.865)^2} \right\}$$

.....(6.19)

Fig. 6., shows the above curve fit and the experimental points.

Expressions (6.17), (6.18) and (6.19) were numerically solved on the computer and the molecular weight distribution obtained is shown in Fig.7. The number and weight average molecular weights predicted are :

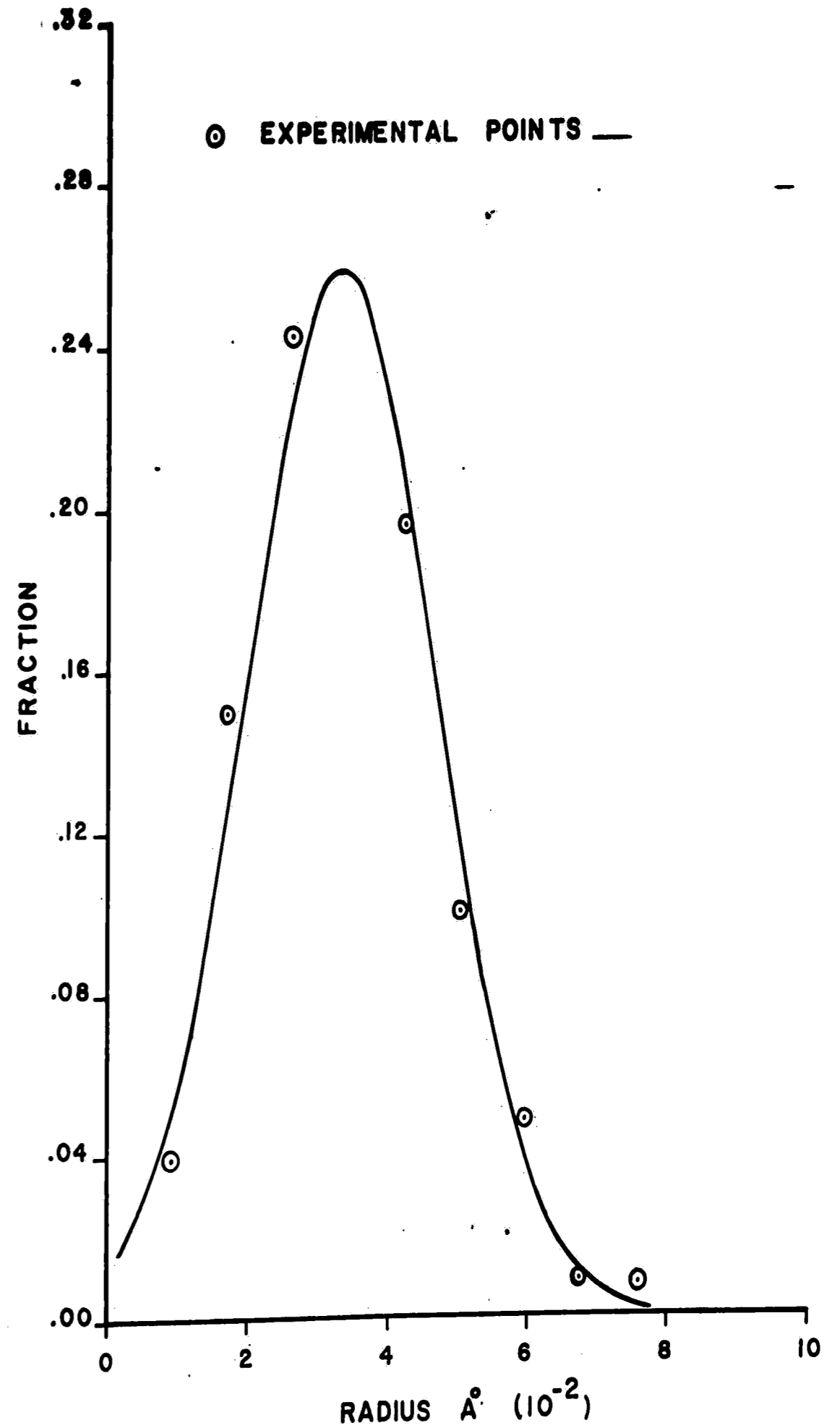


Fig. 6. Particle Size Distribution in Continuous Emulsion Polymerisation



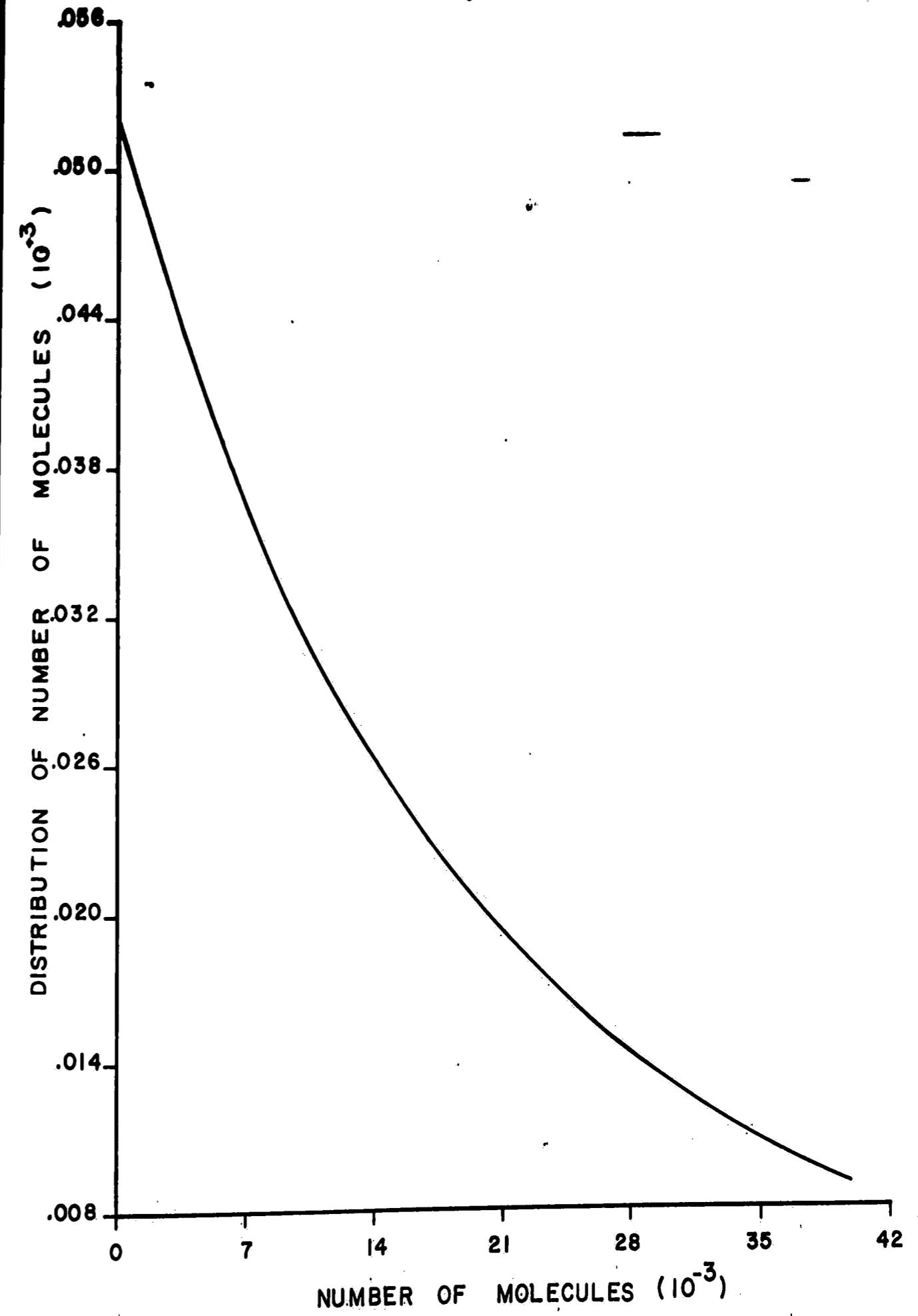


Fig. 7. Distribution of Degree of Polymerisation in Continuous Ideal Emulsion Polymerisation

$$\bar{M}_n = 1.7043 \times 10^6$$

$$\bar{M}_w = 2.5505 \times 10^6$$

$$\bar{M}_w / \bar{M}_n = 1.496$$

The number and weight averages obtained experimentally by 'Gel Permeation Chromatograph' techniques without the correction factor are,

$$\bar{M}_n = 1.11254 \times 10^5$$

$$\bar{M}_w = 9.28689 \times 10^5$$

$$\bar{M}_w / \bar{M}_n = 8.32$$

The reason for these high discrepancies are, . . . . .

1. The experimental numbers have to be corrected by the calibration constants for  $\bar{M}_n$  and  $\bar{M}_w$  of the gel permeation chromatograph.
2. The conditions assumed to lead to a continuous ideal emulsion system are far from ideal. Fig. 8, gives the probability of existence of 'q' free radicals as a function of time. For an average residence time of 3600 secs. we see that there is a finite probability of existence of  $q = 2, 3$ . The exact numbers on these probabilities for  $\theta = 3520$  secs. are :

$$P_0(0) = 0.419058$$

$$P_1(0) = 0.49511$$

$$P_2(0) = 0.08079$$

$$P_3(0) = 0.004887$$

$P_q(t)$  = Probability of finding 'q' free radicals in  
a particle at time 't'. —

The mathematical expressions for determining these  
probabilities are formulated in chapter 8 - 'Emulsion  
Polymerisation as a Birth and Death stochastic process'.

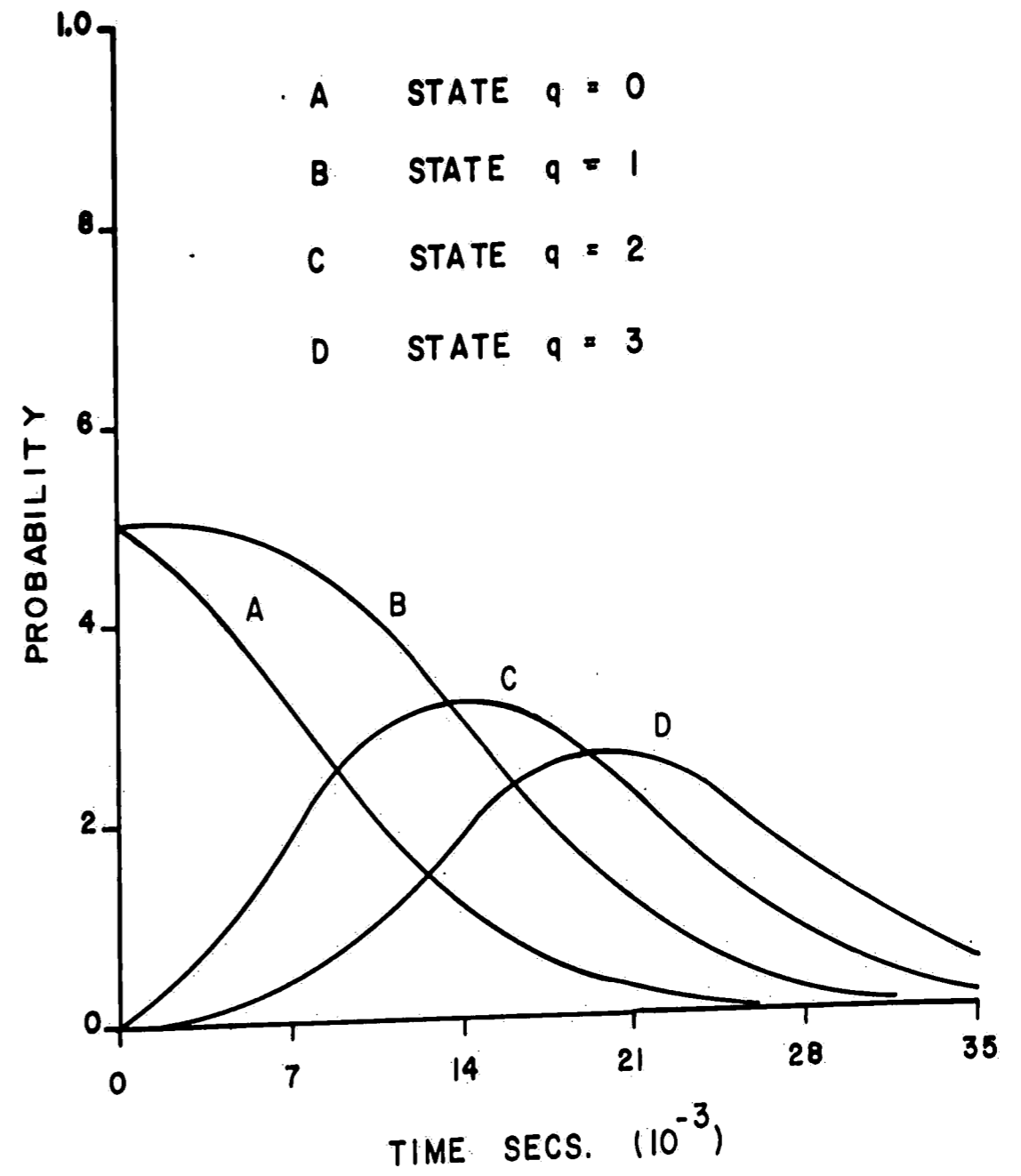


Fig. 8. Absolute Probability of States for conditions of De Graff's continous ideal emulsion polymerisation system

MOLECULAR WEIGHT DISTRIBUTION IN SEMI-IDEAL

EMULSION POLYMERISATION

Semi - Ideal emulsion polymerisation is a simple extension of ideal emulsion polymerisation.  $\bar{q}$  is no longer 0.5 but  $\bar{q} > 0.5$ , ie. there is a definite possibility of  $q=2$  for finite times,  $P_2(t) > 0$ . The assumption that  $P_q(t) = 0$  for  $q=3,4, \dots$  etc. is still invoked.

A typical  $q$  vs. time plot for semi-ideal polymerisation looks like,

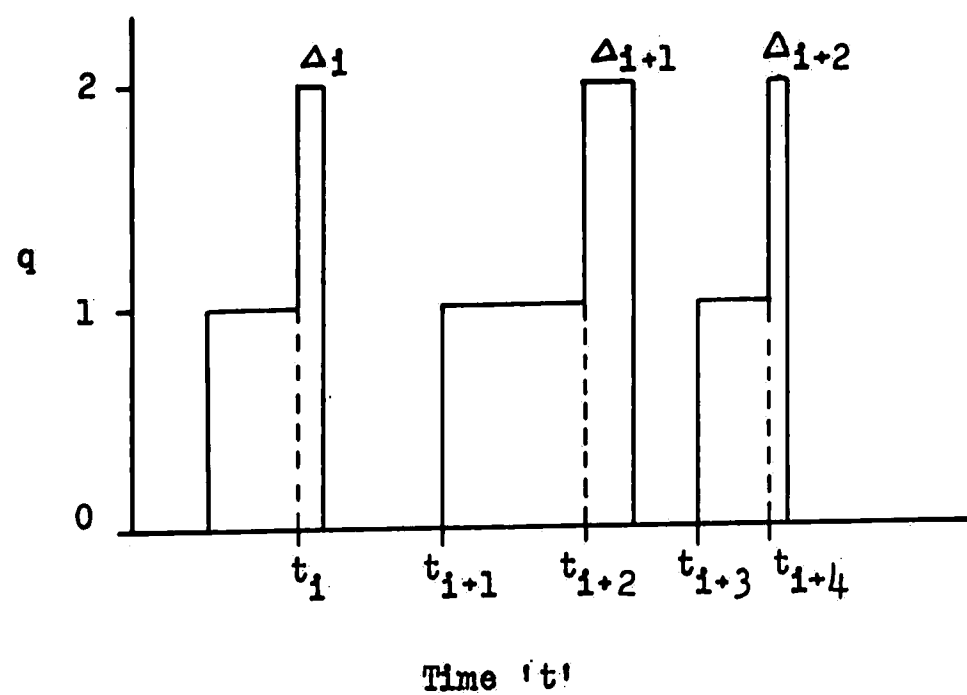


Fig. 9.

For the above system,

1. The inter-arrival times between free radicals ie.  $\tau_i = t_{i+1} - t_i$  etc. are exponentially distributed (as stated in chapter 6) and are given by the distribution

function,

$$f_{\tau}(\tau) = \mu \exp(-\mu\tau) \quad (7.1)$$

$$2. \quad \sum_{q=0}^2 P_q(t) = 1.0 \quad (7.2)$$

$$\text{ie. } P_0(t) + P_1(t) + P_2(t) = 1.0$$

3. The average number of free radicals is given by

$$\bar{q} = P_1(t) + 2P_2(t) \quad (7.3)$$

4. The arrival of even free radicals causes instantaneous termination for ideal emulsion polymerisation. The second free radical in semi-ideal polymerisation lives for a while before it terminates. Its life time  $\Delta_1, \Delta_{1+1}, \dots$  etc. ( Fig. 9 ) are parts of the time in which 'q' would have been zero if instant termination had indeed occurred. The life time of  $q=1$  is not altered in semi-ideal polymerisation. Thus we can say that

$$P_1(t) = 0.5 \quad (7.4)$$

From (7.2) , (7.3) , and (7.4) we obtain

$$P_0(t) + P_2(t) = 0.5 \quad (7.5)$$

$$P_2(t) = \frac{1}{2}(\bar{q} - 0.5) \quad (7.6)$$

For further analysis we assume ,

1. The system is at steady state ie. the probabilities  $P_0(t), P_1(t), \dots$  etc. are not functions of time.
2. The process is a batch process ie.

$$\mu = R_1 / N$$

3. Termination occurs by coupling only.

The chain length 'x' of the polymer molecule formed is given by ,

$$x = (\tau + 2\Delta)\beta \quad (7.7)$$

$\tau$  = Life time for  $q=1$  , given by the distribution (7.1).

$\Delta$  = Life time spans for  $q=2$  .

The distribution of molecular sizes of the polymer chains can be calculated if the distribution of  $\Delta_1$  is known , since all the other quantities in (7.7) are known.

The frequency of appearance of periods of  $q=2$  is ,

$$\mu/2 \text{ periods/ unit time} \quad (7.8)$$

and  $P_2 = \mu \bar{\Delta} / 2 \quad (7.9)$

$\bar{\Delta}$  = Average life span of the second free radical - average time/ period.

$$= 2 P_2 / \mu \quad (7.10)$$

The distribution of kinetic chain lengths 'y' which propagates by adding one monomer molecule at a time obeys the " Geometric Probability Law " , ie. ,

$$h(y) = p^y (1 - p) \quad (7.11)$$

p = Probability that the free radicals in the particle when  $q=2$  will propagate in the next reaction.

$(1 - p)$  = Probability that they will terminate in the next reaction.

$h(y)$  = Probability distribution function of chain length 'y'.

$y$  = Number of monomer additions for each free radical during time interval ' $\Delta$ ' when  $q = 2$ .

Equation (7.11) can be rewritten as a distribution for ' $\Delta$ ' by noting that ,

$$\Delta = y/\beta \quad (7.12)$$

From (7.11) and (7.12) ,

$$p_{\Delta}(\Delta) = p^{\Delta\beta}(1 - p) \quad (7.13)$$

$\bar{\Delta}$  is given by

$$\begin{aligned} E(\Delta) = \bar{\Delta} &= \sum_{\Delta\beta=0}^{\infty} \Delta p_{\Delta}(\Delta) \\ &= \frac{(1 - p)}{\beta} \sum_{\Delta\beta=0}^{\infty} (\Delta\beta) p^{\Delta\beta} \\ &= \frac{(1 - p)}{\beta} \left\{ \sum (\Delta\beta + 1) p^{\Delta\beta} - \sum p^{\Delta\beta} \right\} \\ &= p/(1 - p)\beta \quad (7.14) \end{aligned}$$

$$\text{and } p = \beta \bar{\Delta} / (1 + \beta \bar{\Delta}) \quad (7.15)$$

Equation (7.10) and (7.15) enable us to calculate 'p'.

Equation (7.7) gives the expression of chain length

formed i.e. ,



$$x = \tau\beta + 2\Delta\beta \quad (7.16)$$

$\tau\beta$  obeys the continuous exponential distribution (7.1) i.e. ,

$$f_{\tau}(n') = (\mu/\beta) \cdot \exp(-\mu n'/\beta) \quad (7.17)$$

$n'$  = Chain length

$2\Delta\beta$  obeys the discrete distribution given by ,

$$h_{2\Delta\beta}(y) = (1-p) p^{(y-2)/2}, \quad y=2,4,6,8,\dots$$

$$y = 2\Delta\beta \quad \text{Chain length} \quad (7.18)$$

To make (7.18) continuous we write it as ,

$$f_{2\Delta\beta}(y) = (1-p) p^{(y-2)/2} \delta(y/2) \quad (7.19)$$

where  $\delta$  = Dirac Delta Function

In order to obtain an expression for the distribution of 'n' in (7.16), in which the distribution of  $\tau\beta$  and  $2\Delta\beta$  is known and given by (7.17) and (7.19) respectively, we use the theory of characteristic functions and laplace transforms. Details are given by Parzen (15) and Wylie (24). The laplace transform of (7.17) is ,

$$\bar{F}_{\tau}(s) = \frac{(\mu/\beta)}{s + (\mu/\beta)} \quad (7.20)$$

and the transform of (7.19) is ,

$$\bar{F}_{2\Delta\beta}(s) = \int_0^{\infty} \frac{(1-p)}{p} p^{y/2} \delta(y/2) e^{-sy} dy$$

for  $y = 0, 2, 4, 6, \dots$

$$\begin{aligned}
 &= \frac{(1-p)}{p} (1 + pe^{-2s} + p^2e^{-4s} + \dots) \\
 &= \frac{(1-p)}{p} \cdot \frac{1}{(1 - pe^{-2s})} \quad (7.21)
 \end{aligned}$$

The distribution of (8.16) in laplace domain is ,

$$\bar{F}_x(s) = (\mu/\beta) \frac{(1-p)}{p} \frac{1}{(1 - pe^{-2s})} \frac{1}{(\mu/\beta + s)} \quad (7.22)$$

On laplace inverting (7.22) we get the distribution of chain lengths 'n' in time domain. The inversion was done by the theory of residues and is ,

$$f_x(x) = \frac{\mu}{\beta} \frac{(1-p)}{p} \left\{ \frac{(e^{-\mu x/\beta})}{(1-pe^{2\mu/\beta})} \frac{p^{x/2}}{(\mu/\beta + \frac{1}{2}lmp)} \right\} \quad (7.23)$$

- x = Chain length 'x' of polymer molecule
- $f_x(x)$  = Distribution of chain length 'x' in time domain.
- $\bar{F}_x(s)$  = Distribution of chain length 'x' in laplace domain.

The distribution of chain lengths 'x' and given by expression (7.23) is plotted in Fig. 10. , for various values of 'q'.

The number and weight average molecular weights are given by ,

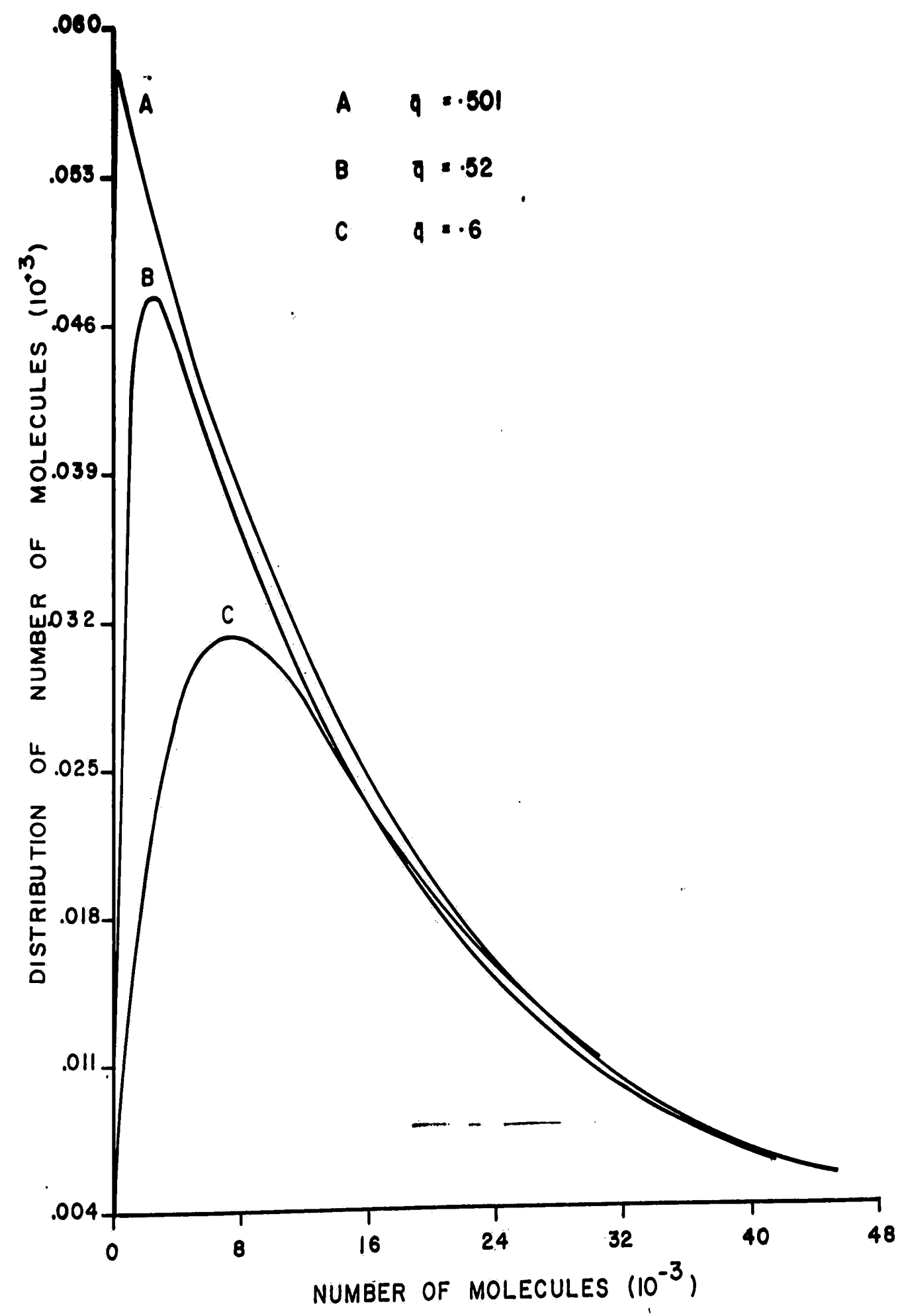


Fig.10. Distribution of Degree of Polymerisation as a function of average number of free radicals in Semi-Ideal Batch Emulsion Polymerisation

$$\bar{M}_n = (A + B)/(C - D) \quad (7.24)$$

$$\bar{M}_w = (E - F)/(A + B) \quad (7.25)$$

$$A = 1/(\mu/\beta)^2 (1 - pe^{2\mu/\beta})$$

$$B = 1/(\frac{1}{2} \log p)^2 (\mu/\beta + \frac{1}{2} \ln p)$$

$$C = 1/(\mu/\beta) (1 - pe^{2\mu/\beta})$$

$$D = 1/(\frac{1}{2} \log p) (\mu/\beta + \frac{1}{2} \ln p)$$

$$E = 2/(\mu/\beta)^3 (1 - pe^{2\mu/\beta})$$

$$F = 2/(\frac{1}{2} \log p)^3 (\mu/\beta + \frac{1}{2} \ln p)$$

Table 2. gives values of  $\bar{M}_n$ ,  $\bar{M}_w$  and their ratio for various values of ' $\bar{q}$ ', obtained anatically.

Table 2.

$\bar{q}$	$\bar{M}_n * 10^{-6}$	$\bar{M}_w * 10^{-6}$	$\bar{M}_w / \bar{M}_n$
0.500	1.903000	3.806000	2.0
0.501	1.922934	3.8076366	1.98011
0.502	1.939130	3.808919	1.96383
0.503	1.957078	3.808919	1.94622
0.504	1.975204	3.810021	1.92892
0.510	2.087956	3.822985	1.83090
0.520	2.293977	3.867208	1.68580
0.550	3.154549	3.920495	1.24280

Molecular weight distribution obtained by Schulz et.

al. , (23) is compared in Fig. 11. with the proposed theory

for semi-ideal emulsion polymerisation for the following  
recipe and physical constants ,

Styrene/Water = 1 : 2.6  
Emulsifier = 0.285 wt. % of water  
Initiator =  $1.31 \times 10^{-2}$  gmol/l.  
 $R_1$  =  $2.68 \times 10^{-8}$  gmols/l.secs.  
N =  $1.4 \times 10^{14}$  particles/cm<sup>3</sup>.

The number and weight averages are,

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w / \bar{M}_n$
Experimental	$0.583 \times 10^6$	$2.014 \times 10^6$	3.45
Theoretical	$1.007 \times 10^6$	$1.355 \times 10^6$	1.35

Physically it is hard to accept the hump in Schulz et.  
al.'s (23) experimental curve. He postulates that it is  
due to the ' Tomsdroff Gel Effect '.

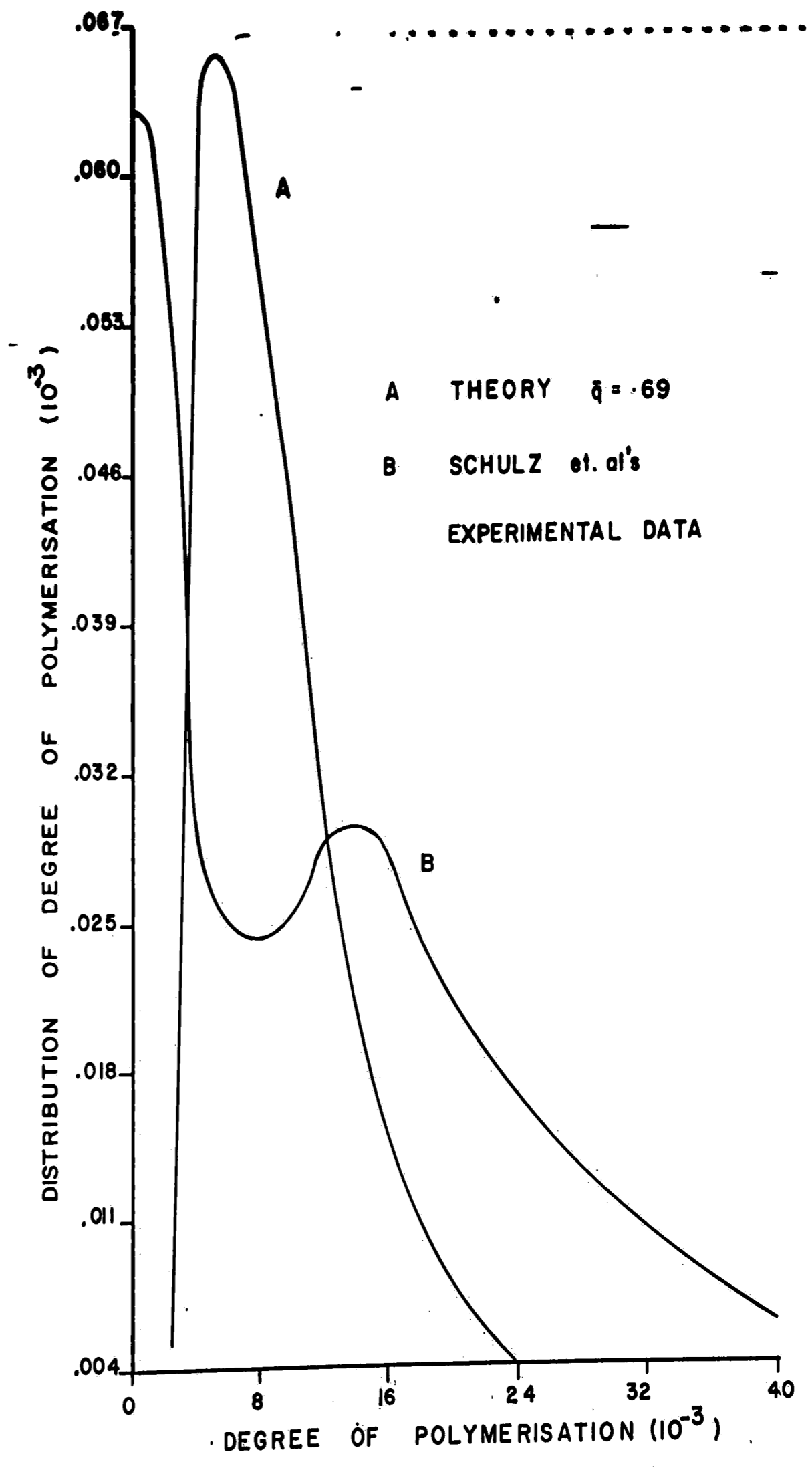


Fig.11. Comparison of Schulz's data and Semi-Ideal Batch theory

EMULSION POLYMERISATION AS A BIRTH

AND DEATH STOCHASTIC PROCESS

Emulsion polymerisation can be considered as a birth and death stochastic process. If we consider one latex particle as the system then the continuous random arrival of free radical molecules to this particle is a birth process. When the free radical arrives the population of free radicals inside the particle increases. Inside the latex particle itself two phenomena take place. The free radicals either propagate by reacting with the monomer present in the latex particle or they react among themselves and terminate either by disproportionation or coupling mechanism. This assumes no termination by chain transfer reactions. Termination by disproportionation yields two dead polymer chains and termination by coupling gives one polymer chain. In either case two free radicals die. This process of termination is a death stochastic process. It is to be noted that on one death event the population of free radicals in the particle decreases by two, since two free radicals are involved in one termination.

A mathematical description of the birth and death stochastic process requires a knowledge of birth and death rates.

In continuous emulsion polymerisation the birth rate is

given by ,

$$\mu(r) = R_p r / (N \bar{F}) \tag{8.1}$$

Refer to appendix 1. for the derivation of (8.1).

The expression for death rate is ,

$$\theta_q(r) = k_{to} q(q-1) / (N_a v(r) ) \tag{8.2}$$

ie. death rate is a function of 'q', the population of free radicals in a particle and 'r'.

$\theta_q(r)$  = Rate of termination of free radical -s in a particle of radius 'r' and containing 'q' free radicals (free radical molecules terminated per second)

$v(r)$  = Volume of a latex particle of radius 'r' and assumed to be spherical.

Refer to appendix 2. for details of equation (8.2)

A latex particle will be the system of our analysis.

The random variable X(t) defines the state of the system,

ie.

X(t) = q ; means that the system (ie. particle) has 'q' free radicals in it at time 't'. 'q' can take only discrete values , q = 0,1,2,3, .....



Assumptions for Birth and Death Process :

1. If at time 't' the system is in state 'q' ( $q=0,1,2\dots$ ) the probability of the transition  $q \rightarrow q+1$  in the interval  $(t, t+\Delta t)$  is

$$\mu(r)\Delta t + o(\Delta t)$$

2. If at time 't' the system is in state 'q' ( $q=0,1,2\dots$ ), the probability of the transition  $q \rightarrow q-2$  in the interval  $(t, t+\Delta t)$  is

$$\theta_q(r)\Delta t + o(\Delta t)$$

3. The probability of no change in the interval  $(t, t+\Delta t)$  is

$$1 - (\mu(r) + \theta_q(r))\Delta t + o(\Delta t)$$

The above assumptions lead to the following relation ,

$$P_q(t+\Delta t) = \mu(r)P_{q-1}(t)\Delta t + \theta_{q+2}(r)P_{q+2}\Delta t +$$

$$(1 - (\mu(r) + \theta_q(r))\Delta t)P_q(t) \quad (8.3)$$

$P_q(t), P_{q-1}(t) \dots$  etc. are the probability of the system being in state  $q, q-1, \dots$  respectively.

Expression (8.3) states that the only ways, in view of the above assumption, the system can be in state 'q' at time 't+\Delta t' are :

1. The system at time 't' was in state 'q' and did not change in the interval (t, t+Δt).
2. The system was in state 'q-1' at time 't' and a free radical arrived in the interval (t, t+Δt).
3. The system was in state 'q+2' and a death (ie. termination) occurred in the interval (t, t+Δt).

The first term on the right hand side of expression (8.3) arises because of the first assumption, the second term because of the second and the third term because of the third assumption.

Transposing the term  $P_q(t)$  on the right hand side to the left hand side, dividing by  $\Delta t$  and taking the limit  $\Delta t \rightarrow 0$ , we get the differential difference equation,

$$\frac{dP_q(t)}{dt} = \mu(r)P_{q-1}(t) + \theta_{q+2}(r)P_{q+2}(t) - (\mu(r) + \theta_{q+2}(r))P_q(t) \quad (8.4)$$

$\mu(r)$  and  $\theta_q(r)$  are both functions of the radius of the particle, which itself is a function of time. Thus we can write  $\mu(t)$  and  $\theta_q(t)$  instead of  $\mu(r)$  and  $\theta_q(r)$  respectively. Equation (8.4) becomes,

$$\frac{dP_q(t)}{dt} = \mu(t)P_{q-1}(t) + \theta_{q+2}(t)P_{q+2}(t) - (\mu(t) + \theta_{q+2}(t))P_q(t) \quad (8.5)$$

The equation for  $q=0$  reduces to,

$$\frac{dP_0(t)}{dt} = -(\mu(t) + \theta_0(t))P_0(t) + \theta_2(t)P_2(t) \quad (8.6)$$

The initial conditions are,

$$P_0(0) = 1.0$$

$$P_q(0) = 0.0 \quad \text{for } q=1,2,3, \dots$$

A relation between 'r' and 't' for a latex particle was obtained by De Graff (22) by the solution of the equation,

$$\frac{dr}{dt} = c_2 \frac{I_0(c_1 r^2)}{I_1(c_1 r^2)} \quad (8.7)$$

$$c_1 = (10.67 * 3.14 R_1 / (k_t N \bar{r}))^{1/2}$$

$$c_2 = k_p(M)M_0 c_1 / 16000 * 3.14 N_a \rho \quad (8.8)$$

$$(M) = 5 * 10^{-3} \text{ gmoles/cm}^3$$

$$M_0 = 106.0$$

$$\rho = 1.06 \text{ gms/cm}^3$$

The solution thus obtained was curve fitted by the equation ,

$$r = A + Bt + Ct^2 \quad (8.9)$$

For  $t \leq 1017.5$  secs.

$$A = 55.53702$$

$$B = 0.32815$$

$$C = -0.00014$$

For  $t > 1017.5$

$$A = 200.4799$$

$$B = 0.04325$$

$$C = 0.0$$

Fig. 12. shows the curve 'r' vs. 't'.

An analytical solution of equation (8.5) coupled with (8.6), (8.1), (8.2) and (8.9) is physically impossible, instead a numerical solution was obtained for the following physical constants :

$$k_{to} = 0.1 \times 10^9 \text{ cm}^3/\text{gmole}\cdot\text{sec. at } 50^\circ\text{C.}$$

$$C_I = 0.82 \text{ wt. \%}$$

$$R_1/C_I = 5.8 \times 10^{13}$$

$$N = 2.344 \times 10^{14} \text{ particles/cm}^3.$$

$$\bar{r} = 453.56 \text{ A}^\circ$$

Two techniques were used, ( Ref. appendix 4. )

1. Finite first order difference approximation of the derivative ie.

$$\frac{dP_q(t)}{dt} = \frac{P_q(t+\Delta t) - P_q(t)}{\Delta t} \quad (8.10)$$

The equation (8.5) and (8.6) were solved for  $q=0, 1, 2, 3, 4$ .

2. Equation (8.5) was written as a system of simultaneous first order coupled linear ordinary differential equations and was solved using ' Lehigh University Analog Simulation (LEANS) ' version of digital computation.

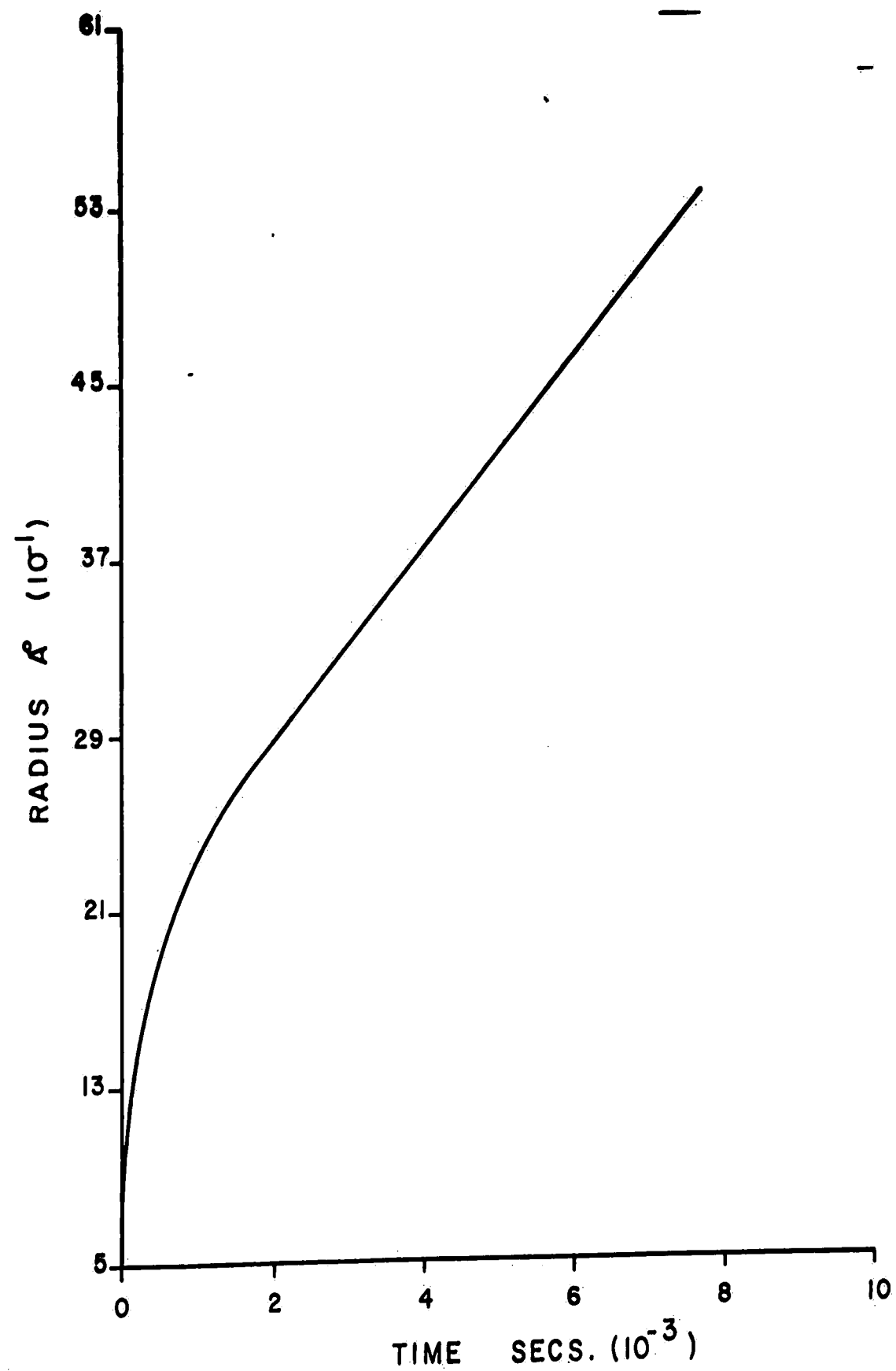


Fig.12 Radius as a function of Time for a latex particle

The solution obtained by both methods are listed in appendix 3.

Integration intervals of the order of  $10^{-4}$  to  $10^{-5}$  secs. had to be used otherwise both the above numerical techniques exploded. This was a very good indication that the derivative in equation (8.5) was very small and tending to zero i.e. the differential equation (8.5) was at steady state. The steady state and unsteady state solutions are also listed in appendix 3.

From tables A, B, and C of appendix 3. we note,

1. Unsteady state solution of equation (8.5) obtained by both finite difference numerical integration and LEANS are in very good agreement.
2. The system is unsteady only for about 100 seconds, after that the steady state and unsteady state results are in fairly good agreement.

The steady state solution is shown in Fig. 13.

Smith and Ewart's theory and Stockmayer's solution of the recursion relation (4.13) will only allow the prediction of  $\bar{q}$  under steady state conditions for various values of particle radius. Expression (8.5) now enables us to predict with a certain degree of certainty (i.e. the absolute probability) the value of 'q' and thus ' $\bar{q}$ ' as a function of time.

Inside the latex particle two phenomenon take place ,

1. The free radicals propagate by reacting with the

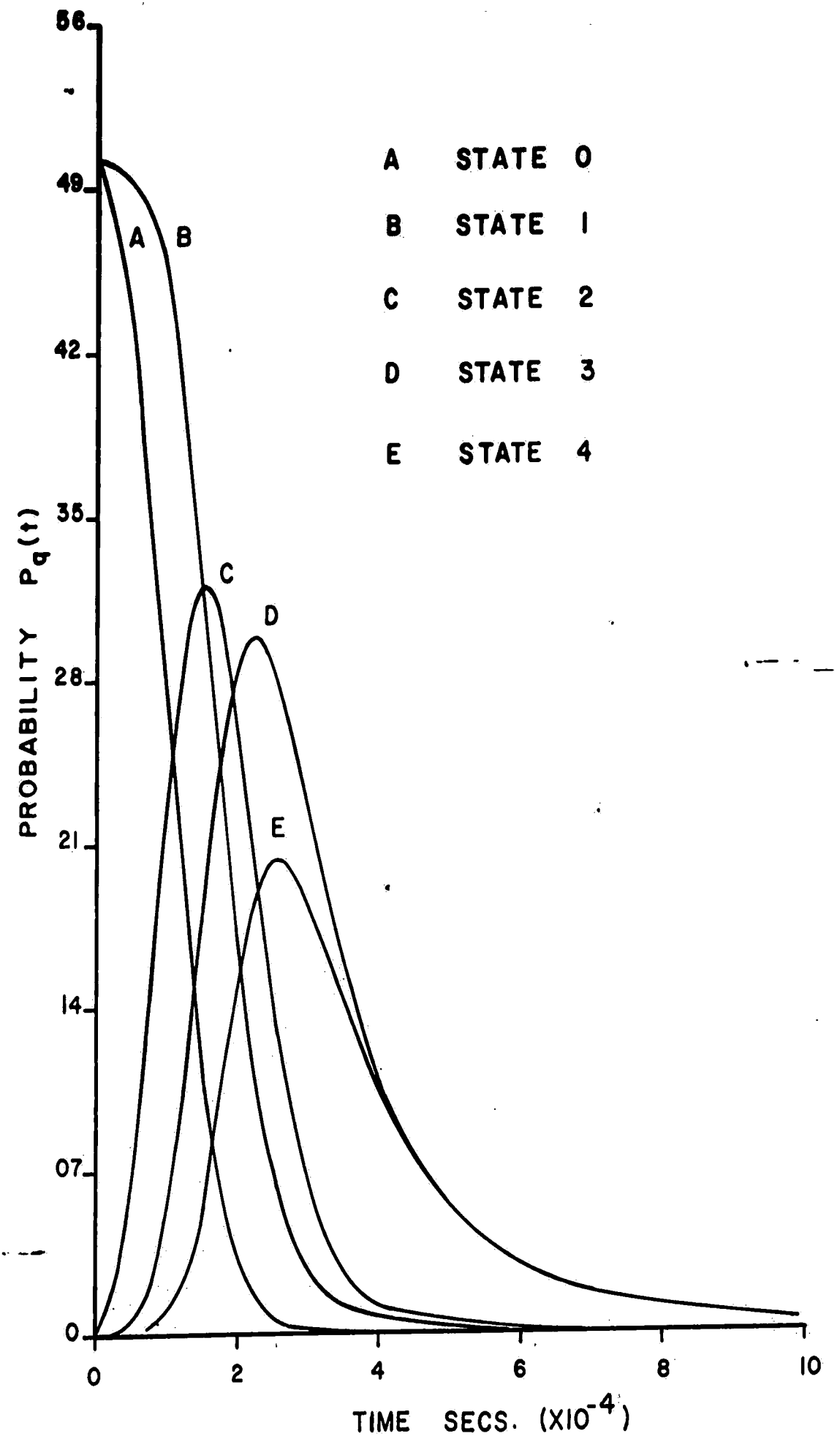
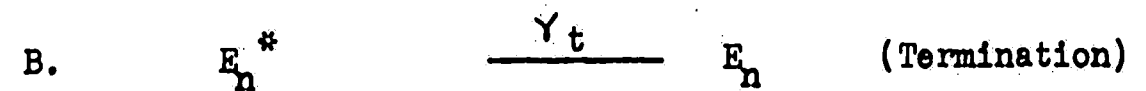
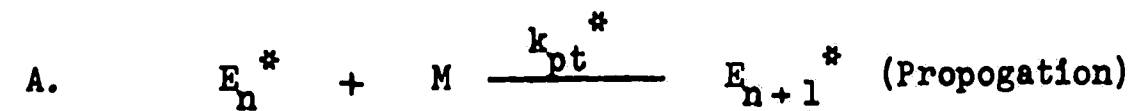


Fig.13 Probability Distribution of Free Radicals  
in a Latex Particle as a function of Time

monomer molecules present in the particle. This process is a 'Growth Process'.

2. Active free radicals react among themselves and terminate either by disproportionation or coupling, this was termed the 'Death Process'.

Further analysis will be based on termination by 'Disproportionation' only, i.e., when two active growing free radical polymer molecules come together they exchange an electron and are deactivated. Under these assumptions we can write the chemical reactions which one active free radical polymer molecule of chain length 'n' can undergo inside the latex particle,



$E_n^*, E_{n+1}^*$  = Active free radical polymer chain of length n and 'n+1' respectively (i.e. growing)

$E_n$  = Deactivated (or Dead) free radical polymer chain of length 'n'.

$k_{pt}^*$  and  $Y_t$  will be defined later.

Consider an individual polymer chain in a latex particle -e. The state of this polymer chain can be completely determined if ,

1. The chain length 'n' is specified.



2. The polymer molecule can be classified as a active (ie. growing) or inactive (ie. dead) chain.

With reference to the individual chain we have chosen in the latex particle,  $k_{pt}^*$  and  $\gamma_t$  are defined such that,

1. The probability that a randomly selected active chain undergoes reaction A in the time interval  $(t, t+dt)$  is,

$$k_{pt}^* dt + o(dt^2) \quad (8.11)$$

2. The probability that a randomly selected active chain undergoes reaction B in interval  $(t, t+dt)$  is ,

$$\gamma_t dt + o(dt^2) \quad (8.12)$$

$k_{pt}^*$  and  $\gamma_t$  are assumed to be functions of time but are independent of the chain length 'n' of the polymer molecules. Thus the expressions for  $k_{pt}^*$  and  $\gamma_t$  in the case of continuous emulsion polymerisation are ,

$$k_{pt}^* = k_p(M) \quad \text{Rate of monomer addition/free radical/} \\ \text{second.} \quad (8.13)$$

$$\gamma_t = k_{tc}(q-1) / N_a v(t) \quad \text{Rate of termination / free radical /} \\ \text{second.} \quad (8.14)$$

$\gamma_t$  is thus, also a function of number of free radicals 'q' present in the latex particle.

Now consider one latex particle containing 'q' free radicals at a certain time 't'. The absolute probability

of their existence as a function of time 't' is known. We define the following quantities ,

$F_{q,n}^*(t)$  = Fraction of active polymer chains of length 'n' monomer molecules at time 't' in a particle containing 'q' active free radical molecules.

$F_{q,n}(t)$  = Fraction of inactive polymer chains of length 'n' monomer molecules at time 't' in a particle containing 'q' active free radical molecules.

$Q_{q,n}(t)$  = Total fraction of n-mer chains irrespective of activity at time 't' in a particle containing 'q' free radicals.

With the above definition , the fraction of active and inactive polymer chains present in a latex particle containing 'q' free radicals at time 't' is given by the following differential difference equations :

$$\frac{dF_{q,n}^*(t)}{dt} = -(k_{pt}^* + \gamma_t)F_{q,n}^*(t) + k_{pt}^* F_{q,n-1}^*(t) \quad n > 1 \quad (8.15)$$

$$\frac{dF_{q,1}^*(t)}{dt} = -(k_{pt}^* + \gamma_t)F_{q,1}^*(t) \quad n = 1 \quad (8.16)$$

$$\frac{dF_{q,n}(t)}{dt} = \gamma_{t,q,n}^* F_{q,n}^*(t) \quad n > 1 \quad (8.17)$$

The initial conditions are :

$$F_{q,n}^*(0) = 1 \quad n = 1$$

$$= 0 \quad n > 1 \quad (8.18)$$

$$F_{q,n}(0) = 0 \quad n > 1 \quad (8.19)$$

The initial conditions signify that at  $t=0$ , the only permissible species in the system is either the initiator  $E_1^*$  or the monomer.

Equation (8.15) like equation (8.3) means that the only ways in which we will have a certain fraction of active polymer molecules of chain length 'n' in a particle containing 'q' free radicals at time 't+dt' is if,

1. The fraction of polymer of chain length 'n-1' at time 't' propagated and added one monomer and were still active.
2. The active fraction of polymer of chain length 'n' did not change in time interval (t,t+dt), ie. it neither propagated nor terminated.

Equation (8.17) shows that the rate of change of inactive fraction of chain length 'n' is equal to the rate at which active fraction of chain length 'n' terminates.

To obtain a analytic solution for (8.15), (8.16), (8.17), (8.18) and (8.19) we define ,

$$\psi_t = \int_0^t \gamma_t dt$$

$$\frac{d\psi_t}{dt} = \gamma_t \tag{8.20}$$

$$\theta_t = \int_0^t k_{pt}^* dt$$

$$\frac{d\theta_t}{dt} = k_{pt}^* \tag{8.21}$$

The solution for (8.15), (8.16) and (8.17) are :

$$F_{q,n}^*(t) = \frac{\theta_t^{n-1} \exp(-(\psi_t + \theta_t))}{(n-1)!} \tag{8.22}$$

$$F_{q,n}(t) = \int_0^t F_{q,n}^*(t) \gamma_t dt \tag{8.23}$$

Thus from the definition of  $Q_{q,n}(t)$ , we get

$$Q_{q,n}(t) = F_{q,n}^*(t) + F_{q,n}(t) \tag{8.24}$$

$F_{q,n}^*(t)$  being the fraction of active n-mer chains, it has significance only at instantaneous time 't'. Thus if  $F_{q,n}^*(t)$  is weighted with  $P_q(t)$ , the probability of finding 'q' free radicals at time 't', we will obtain the most probable measure of the fraction of active n-mer

chains at time 't', ie

$$F_n^*(t) = F_{q,n}^*(t) \cdot P_q(t) \quad (8.25)$$

Noticing expression (8.23) it is reasonable to say that to obtain a true weighted measure of  $F_{q,n}(t)$  ie.  $F_n(t)$  we must integrate  $F_n^*(t)$  over time ie.,

$$F_n(t) = \int_0^t F_{q,n}^*(t) \cdot P_q(t) \cdot \gamma_t \, dt \quad (8.26)$$

q can take values 0,1,2,3, ..... and  $P_0(t)$ ,  $P_1(t)$ ,  $P_2(t)$ , ..... etc. are all different functions.

Thus we obtain the total fraction of n-mer molecules at time 't' from equation (8.25) and (8.26) as ,

$$Q_{q,n}(t) = F_n^*(t) + F_n(t) \quad (8.27)$$

On summing expression (8.27) over all values of 'q' we will get the total fraction of n-mer molecules in a particle which grows from time 0 to 't', ie.

$$Q_n(t) = \sum_{q=0}^{\infty} Q_{q,n}(t) \quad (8.28)$$

Equation (8.28) gives the distribution of chain lengths in a latex particle which grows from radius ' $r_m$ ' to ' $r$ ' in time '0' to 't'.

Once the distribution of chain lengths is known in a latex particle of size ' $r$ ', the distribution of chain lengths of the entire system can be obtained by weighting

it with the particle size distribution  $f_p(r)$  i.e.,

$$\bar{M}_n = \frac{\int_0^r Q_n(r) \cdot f_p(r) dr}{\int_0^r f_p(r) dr} \quad (8.29)$$

As was stated earlier, only the analytic method is outlined above to obtain the molecular weight distribution in continuous emulsion polymerisation. No numbers were obtained to show what the distribution looks like or what the number and weight average molecular weights are.

APPENDIX 1

DERIVATION OF " $\mu$ " - RATE OF FREE RADICAL

ARRIVAL AS A FUNCTION OF RADIUS

Stockmayer's equation for ' $\bar{q}$ ' (4.16) derived ' $\bar{q}$ ' as a function of ' $\tau_\mu$ ', average time between successive free radical arrivals.

The continuous emulsion polymerisation model considers free radical diffusion into a latex particle as a function of particle radius, particle size distribution and rate of free radical initiation. Therefore the average time between free radical arrivals,  $\tau_\mu$ , is also a function of these variables.

If  $R_{1n}$  is the rate of free radical generation in the  $n^{\text{th}}$  reactor and  $p_n(r)$  is the particle size distribution then the following is true.

$$\tau_\mu(r) = \frac{\text{Number of particles of radius 'r'}}{\text{Number of free radicals entering 'r' size particles.}}$$

The number of particles of radius 'r' is :

$$\int_r^{r+dr} N_n p_n(r) dr \quad (1)$$

$$N_n = \text{Number of particles in the 'n' }^{\text{th}} \text{ reactor.}$$

If the diffusion of free radicals is proportional to the radius then the fraction of radicals entering 'r' size particles is :

$$\frac{N_n \int_r^{r+dr} 4 \cdot 3.14 D C_w r p_n(r) dr}{N_n \int_0^{\infty} 4 \cdot 3.14 D C_w r p_n(r) dr} \quad (2)$$

D = Diffusion Constant

C<sub>w</sub> = Concentration of free radicals.

Therefore the number of free radicals entering 'r' size particles per unit volume per second is :

$$\frac{R_{in} \int_r^{r+dr} r p_n(r) dr}{\bar{r}} \quad (3)$$

Therefore :

$$\tau_{\mu}(r) = N \bar{r} / R_{in} r \quad (4)$$

and  $\mu(r) = 1/\tau_{\mu}(r) = R_{in} r / N \bar{r} \quad (5)$



APPENDIX 2

DERIVATION OF  $\theta_q(r)$  - RATE OF TERMINATION  
OF FREE RADICALS AS A FUNCTION OF THE  
NUMBER OF FREE RADICALS AND RADIUS

The rate of termination of free radicals in a particle of radius 'r' and containing 'q' free radicals is (4.12) ,

$$R_t = k_{tc} (q/N_a v(r)) ((q-1)/N_a v(r)) \quad (1)$$

The units of  $R_t$  are :

gmoles of free radicals terminated/  
 $\text{cm}^3 \cdot \text{sec}.$

Therefore,

$$\theta_q(r) = R_t N_a v(r) \quad (2)$$

= Number of free radical molecules  
terminated per sec.

$$= k_{tc} ( q(q-1)/N_a v(r) ) \quad (3)$$

APPENDIX 3

A. The unsteady - state solution of equation (8.5)  
obtained by ' Finite Difference Approximation '.

Integration Interval =  $5.0 \times 10^{-5}$  secs.

<u>TIME</u> (secs)	<u>ABSOLUTE PROBABILITY OF STATES</u>			
t	$P_0(t)$	$P_1(t)$	$P_2(t) \times 10^7$	$P_3(t) \times 10^{12}$
0.1	.99752089	.002478979	1.3050	2.3234
1.0	.97569187	.024306790	13.3296	24.4025
2.0	.95243265	.047564678	26.7304	50.1118
5.0	.88857456	.111418727	67.1491	134.9425
7.0	.85057863	.149411940	94.2424	198.1976
10.0	.79977825	.200208236	135.0502	303.7201
12.0	.76967643	.230307327	162.3439	381.5220
15.0	.72959298	.270386670	203.3900	510.0586
50.0	.51818624	.481555615	2580.9194	46126.2609
100.0	.49995479	.499777280	2678.6880	47874.2349
150.0	.49973469	.499997260	2679.8684	47895.3337
200.0	.49973200	.499999910	2679.8826	47895.5918
300.0	.49973200	.499999949	2679.8828	47895.5949
650.0	.48743006	.499892868	12569.4828	$1.0712 \times 10^4$

B. Unsteady - State solution of equation (8.5) obtained by ' Lehigh University Analog Simulation ' (LEANS) technique.

Integration Interval =  $3.91 \times 10^{-5}$  secs.

Degree of Accuracy =  $5.0 \times 10^{-5}$  secs.

<u>TIME(secs.)</u>	<u>ABSOLUTE PROBABILITY OF STATES</u>			
t	$P_0(t)$	$P_1(t)$	$P_2(t)$ * $10^7$	$P_3(t)$ * $10^{12}$
0.1	.99752	.002482	1.3053	2.32
1.0	.97566	.024342	13.331	24.37
2.0	.95237	.047631	26.733	50.05
5.0	.88843	.111560	67.148	134.76
7.0	.85040	.149590	94.234	197.92
10.0	.79955	.200430	135.03	303.27
12.0	.76663	.230370	162.18	380.63
15.0	.72672	.270270	203.04	508.51
18.0	.69224	.304740	244.01	651.34

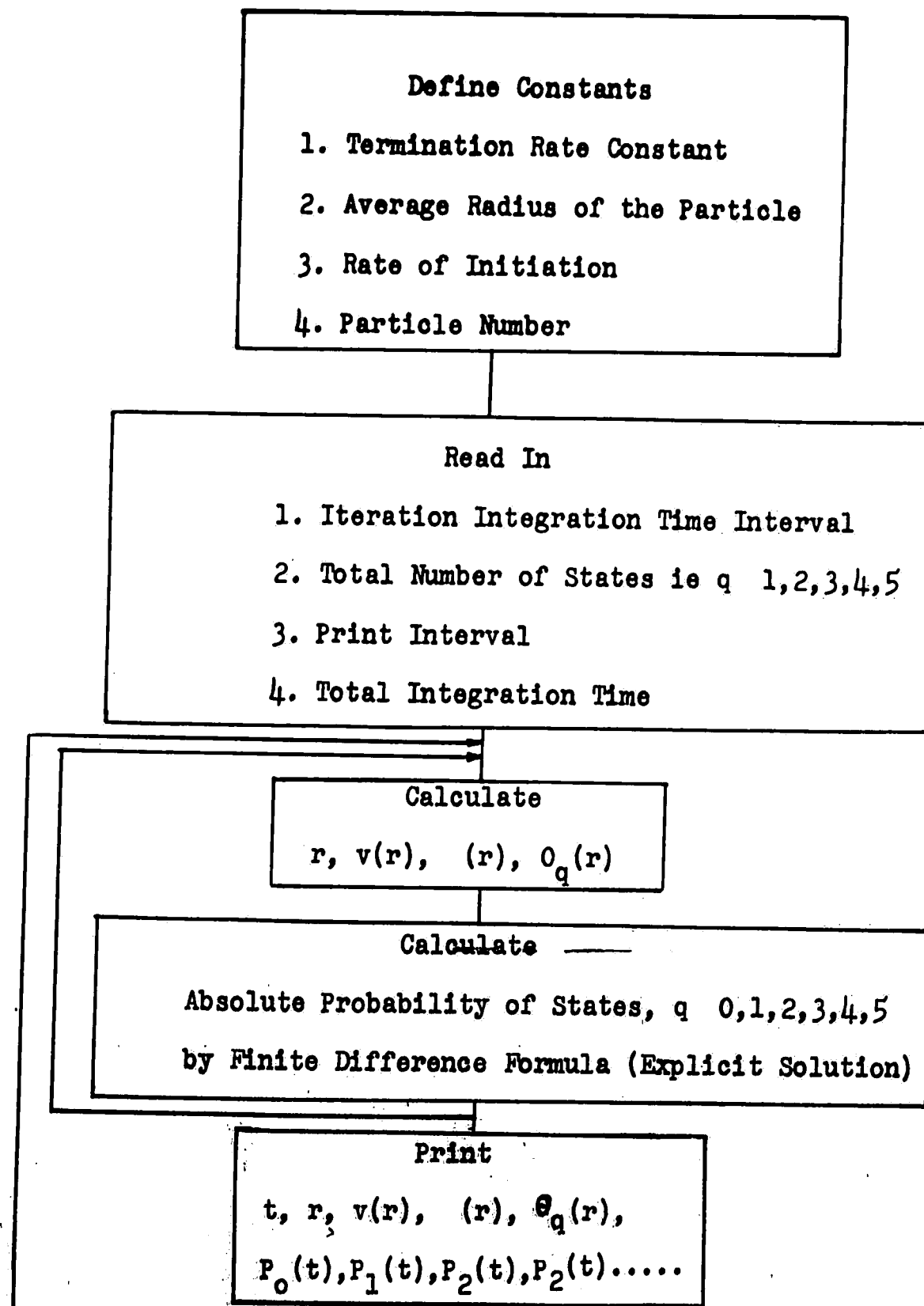
C. Steady - State solution of equation (8.5) by considering it as a system of algebraic equations whose coefficients vary with time.

<u>TIME.</u> (secs)	<u>ABSOLUTE PROBABILITY OF STATES</u>			
t	P <sub>0</sub> (t)	P <sub>1</sub> (t)	P <sub>2</sub> (t)	P <sub>3</sub> (t)
100	0.499839	0.5	1.61235*10 <sup>-4</sup>	1.7335*10 <sup>-8</sup>
200	0.499497	0.5	5.02783*10 <sup>-4</sup>	1.6864*10 <sup>-7</sup>
300	0.498875	0.49999	1.12481*10 <sup>-3</sup>	8.4473*10 <sup>-7</sup>
600	0.495344	0.49998	4.65646*10 <sup>-3</sup>	1.4545*10 <sup>-5</sup>
1000	0.490244	0.49993	9.75559*10 <sup>-3</sup>	6.4285*10 <sup>-5</sup>
10000	0.258441	0.44350	2.34117*10 <sup>-1</sup>	5.5880*10 <sup>-2</sup>
20000	3.511510*10 <sup>-2</sup>	1.43722*10 <sup>-1</sup>	0.255380	0.263287
30000	1.64275*10 <sup>-3</sup>	0.00129583	0.0466775	0.107174
50000	1.02424*10 <sup>-6</sup>	2.46992*10 <sup>-5</sup>	1.80199*10 <sup>-4</sup>	1.3884*10 <sup>-3</sup>

Beyond t = 50,000 secs. , states q = 4, 5, 6, 7, 8, 9, ..... have an appreciable probability of existence, as can be seen from Fig. 13.

APPENDIX 4

A 1. The block diagram for the unsteady state digital solution of equation (8.5) by ' Finite Difference Approximation ' is :



A2.

LISTING OF THE PROGRAMME

```
DIMENSION P(20), Q(20)
TKC = 0.10E+09
PAI = 3.1415927
AVO = 6.023E+23
AVGRAD = 453.6
CONIN = 0.82
RICI = 5.8E+13
PTNO = 2.344E+14
ALP = (4./3.)*PAI
Z = (RICI*CONIN)/PTNO
RMU = Z/AVGRAD
BETA = (TKC/AVO)*(1.0E+24)
PRINT 421, TKC, Z, AVGRAD, RMU, BETA
421 FORMAT(1H1, 5X, * TERMINATION RATE CONSTANT = *,
1 E20.3, //, 5X, * INITIATION RATE / PARTICLE NUMBER *,
2 E20.5, //, 5X, * AVERAGE RADIUS = *, E20.4, //,
3 5X, * R/(N*AVG RADIUS) = *, E20.5, //,
4 5X, * KTC / AVOGADROS NO = , E20.5, //)
READ 31, DELT, N1, PTINT, TOTIME
31 FORMAT(F10.2, I5, 2F10.2)
N = N1 + 1
DO 101 J = N, 20
P(J) = 0.0
101 CONTINUE
READ 430, (P(I), I=1, N1), T
430 FORMAT(5E16.4)
T = 0.0
NP = INT(TOTIME/PTINT + 0.001)
M = INT(PTINT/DELT + 0.001)
DO 113 L = 1, NP
DO 102 I = 1, M
T = T + DELT
CALL RADIUS(T, R)
VOL = ALP*R*R*R
ARRIVE = RMU*R
DEPART = BETA/VOL
TOTAL = 0.0
DO 108 J = 1, N1
GONE = DEPART*FLOAT(J)*FLOAT(J+1)*P(J+2)
200 IF(J-2) 109, 99, 110
109 Q(J) = P(J) + (GONE - (ARRIVE*P(J)))*DELT
GO TO 50
99 Q(J) = P(J) + ((ARRIVE*(P(J-1)-P(J))) + GONE)*DELT
GO TO 50
```

```
110 COME = DEPART*FLOAT(J-1)*FLOAT(J-2)
ARRATE = ARRIVE + COME
Q(J) = P(J) + ((ARRIVE*P(J-1))-(ARRATE*P(J)) + GON
1 E)*DELT
50 TOTAL = TOTAL + Q(J)
108 CONTINUE
DO 111 J = 1,N1
P(J) = Q(J)
111 CONTINUE
102 CONTINUE
PRINT 397, T, R, VOL, ARRIVE, DEPART
397 FORMAT(///,5X, * TIME = *,E20.5,/,
1 5X, * RADIUS = *,E20.5,/,
2 5X, * VOLUME = *, E20.5,/,
3 5X, * BIRTH RATE = *, E20.5,/,
4 5X, * DEATH RATE = *, E20.5,/)
DO 112 J = 1,N1
PRINT 501, P(J)
501 FORMAT(5X,5E20.8,///)
112 CONTINUE
IF(ABS(TOTAL - 1.0) .GT. 0.0001) GO TO 230
IF(P(N1) .GT. 1.0E-12) N1 = N1 + 1
IF(N1 .GT. 20) N1 = 20
PRINT 502, N1
502 FORMAT(120X,*N1 = *, I3)
GO TO 113
113 CONTINUE
CALL EXIT
230 PRINT 240
240 FORMAT(//,5X,* ABS(TOTAL) .GT.. 1 *)
CALL EXIT
END
```

B1.

LEANS UNSTEADY - STATE SOLUTION

The six simultaneous , unsteady-state, coupled, linear O.D.E. to be solved are :

$$1. \quad \frac{dP_0(t)}{dt} = -\mu(t)P_0(t) + \frac{2k}{v(t)} P_2(t)$$

$$2. \quad \frac{dP_1(t)}{dt} = -\mu(t)P_1(t) + \mu(t)P_0(t) + \frac{6k}{v(t)} P_3(t)$$

$$3. \quad \frac{dP_2(t)}{dt} = -\left(\mu(t) + \frac{2k}{v(t)}\right) P_2(t) + \mu(t)P_1(t) + \frac{12k}{v(t)} P_4(t)$$

$$4. \quad \frac{dP_3(t)}{dt} = -\left(\mu(t) + \frac{6k}{v(t)}\right) P_3(t) + \mu(t)P_2(t) + \frac{20k}{v(t)} P_5(t)$$

$$5. \quad \frac{dP_4(t)}{dt} = -\left(\mu(t) + \frac{12k}{v(t)}\right) P_4(t) + \mu(t)P_3(t)$$

$$6. \quad \frac{dP_5(t)}{dt} = -\left(\mu(t) + \frac{20k}{v(t)}\right) P_5(t) + \mu(t)P_4(t)$$



$$k = k_{tc} / N_a$$

$$\mu(t) = R_1 r / (N \bar{F})$$

B2.

LISTING OF LEANS PROGRAMME

ELEMENT TYPE	BLOCK NO.	INPUT 1.	INPUT 2.	INPUT 3.	I/C, CONSTANT, GAIN
IND	1	0	0	0	0.
CON	8	0	0	0	1.6650E-16
FOO	2	1	0	0	0.
GAIN	3	2	0	0	4.4800E-04
MULT	4	2	2	0	0.
MULT	5	2	4	0	0.
GAIN	6	5	0	0	4.1890E-24
DIV	7	8	6	0	0.
GAIN	9	7	0	0	2.0000E+00
MULT	10	17	9	0	0.
MULT	12	11	3	0	0.
INT	11	10	-12	0	1.0000E+00
MULT	14	13	3	0	0.
GAIN	16	7	0	0	6.0000E+00
MULT	15	23	16	0	0.
INT	13	12	15	-14	1.0000E-11
GAIN	19	7	0	0	2.0000E+00
SUM	18	3	19	0	0.
MULT	20	18	7	0	0.
GAIN	21	7	0	0	1.2000E+01
MULT	22	21	30	0	0.
INT	17	14	22	-20	1.0000E-11
MULT	24	17	3	0	0.
GAIN	25	7	0	0	2.0000E+01
MULT	26	25	39	0	0.
GAIN	27	7	0	0	6.0000E+00
SUM	28	3	27	0	0.
MULT	29	28	23	0	0.
INT	23	24	26	-29	1.0000E-11
MULT	31	3	23	0	0.
GAIN	32	7	0	0	1.2000E+01
SUM	33	3	32	0	0.
MULT	34	33	30	0	0.
INT	30	31	-34	0	1.0000E-11
MULT	35	30	3	0	0.
GAIN	36	7	-0	0	2.0000E+01
SUM	37	3	36	0	0.
MULT	38	37	39	0	0.
INT	39	35	-38	0	1.0000E-11

01.

STEADY - STATE SOLUTION

The equations to be solved simultaneously are :

$$1. \quad \frac{dr(t)}{dt} = C2 I_0 (C1 r^2) / I_1 (C1 r^2)$$

$$C1 = (10.67 * 3.14 R_1 / (k_{tc} N \bar{r}))^{1/2}$$

$$C2 = C1 (k_p (M) M_0) / (16000.0 * 3.14 \rho N_a)$$

$$2. \quad v(t) = (4./3.) * 3.14 r^3$$

$$3. \quad \mu(t) = R_1 r(t) / (N \bar{r})$$

$$4. \quad k = k_{tc} / N_a$$

$$5. \quad P_0(t) = \frac{2k}{v(t)\mu} P_2(t)$$

$$6. \quad P_1(t) = P_0(t) + \frac{6k}{v(t)\mu} P_3(t)$$

$$7. \quad P_2(t) = \frac{\mu}{(\mu + \frac{2k}{v(t)})} P_1(t) + \frac{12k P_4(t)}{v(t) (\mu + \frac{2k}{v(t)})}$$

$$8. \quad P_3(t) = \frac{(\mu(t) P_2(t) + \frac{20k P_5(t)}{v(t)})}{(\mu(t) + \frac{6k}{v(t)})}$$

$$9. \quad P_4(t) = \frac{\mu(t)}{(\mu(t) + \frac{12k}{v(t)})} P_3(t)$$

$$10. \quad P_5(t) = \frac{\mu(t)}{(\mu(t) + \frac{20k}{v(t)})} P_4(t)$$

$$11. \quad 1.0 = P_0(t) + P_1(t) + P_2(t) + P_3(t) + P_4(t) + P_5(t)$$

C2. LISTING OF THE PROGRAMME

```
DIMENSION X(2),Y(2),DERY(2),PRMT(5),AUX(8,1)
DIMENSION XT(1000),YR(1000)
DIMENSION Q(6,6),R(6)
DIMENSION P1OUT(1100),P2OUT(1100),P3OUT(1100),
1 P4OUT(1100),P5OUT(1100),P6OUT(1100),TOUT(1100)
COMMON/GP1/NDIM,C1,C2
COMMON/GP2/ICOU
COMMON/GP3/XT,YR
COMMON/GP4/IZT
EQUIVALENCE (TOUT,XT)
EXTERNAL FCT,OUTP
READ 10, PARTN
10 FORMAT(E10.5)
READ 20, TEMP, CI, CE
20 FORMAT(3E10.5)
READ 10, PARTNO
READ 10, PI
READ 10, SURCON
READ 30, RKT, RM
30 FORMAT(2E10.5)
READ 40, SMC, SMW, RHO, AVAG
40 FORMAT(4E10.5)
READ 10, RBAR
READ 10, Y(1)
READ 10, RNI
READ 10, RKP
READ 10, SMC0
ALP = (4./3.)*PI
Z = RNI/PARTN
RMU = Z/RBAR
BETA = (RKT/AVAG)*(1.0E+24)
PRINT 420
420 FORMAT (1H1,10X,* PHYSICAL CONSTANTS OF THE
1 EMULSION SYSTEM *,//)
PRINT 421, RKT, RKP, RNI, PARTN, CI, CE, RBAR
421 FORMAT(5X,* TERMINATION RATE CONSTANT = *,E20.5,/,
1 5X,* PROPAGATION RATE CONSTANT = *, E20.5,/,
2 5X,* RATE OF INITIATION = *, E20.5,/,
3 5X,* PARTICLE NUMBER = *, E20.5,/,
4 5X,* INITIATOR CONCENTRATION = *, E20.5,/,
5 5X,* EMULSIFIER CONCENTRATION = *, E20.5,/,
6 5X,* AVERAGE RADIUS = *, E20.5,////)
READ 200, NK
200 FORMAT(I10)
ICOUNT = 1.0
```

```
P1OUT(ICOUNT) = 1.0
P2OUT(ICOUNT) = 0.0
P3OUT(ICOUNT) = 0.0
P4OUT(ICOUNT) = 0.0
P5OUT(ICOUNT) = 0.0
P6OUT(ICOUNT) = 0.0
TOUT(ICOUNT) = 0.0
C1 = SQRT(10.67*PI*RNI/(RKT*PARTN*RBAR))
C2 = (RKP*SMC*SMW/(16000.*PI*RHO*AVAG))*C1*(1.0E+2
1 4)
PRINT 50, C1, C2
50 FORMAT(/////,5X,* C1 = *,E20.5,/,5X,* C2 = *,E20.5
1 ,/////)
PRMT(1) = 0.0
PRMT(2) = 4.0E+04
PRMT(3) = 640.0
PRMT(4) = 5.0E-06
PRMT(5) = 0.0
DERY(1) = 1.0
NDIM = 1
ICOU = 1
CALL RKGS(PRMT,Y,DERY,NDIM,IHLF,FCT,OUTP,AUX)
DO 102 IL = 1,IZT
VOL = ALP*YR(IL)*YR(IL)*YR(IL)
ARRIVE = RMU*YR(IL)
DEPART = BETA/VOL
DO 1 J = 1,NK
DO 2 I = 1,NK
IF(I .EQ. J) Q(I,J) = -(ARRIVE + DEPART*FLOAT(I-1)
1 *FLOAT(I-2))
IF((I-1) .EQ. J) Q(I,J) = ARRIVE
IF((I+2) .EQ. J) Q(I,J) = DEPART*FLOAT(I+1)*FLOAT(
1 I)
IF(J .GT. (I+2)) Q(I,J) = 0.0
IF(J .LT. (I-1)) Q(I,J) = 0.0
IF(J .EQ. (I+1)) Q(I,J) = 0.0
Q(NK,J) = 1.0
2 CONTINUE
1 CONTINUE
DO 3 K = 1,NK
IF(K .LT. NK) R(K) = 0.0
IF(K .EQ. NK) R(K) = 1.0
3 CONTINUE
NP = NK
KK = 0
CALL SIMQ(Q,R,NP,KK)
PRINT 333, XT(IL),R
333 FORMAT(7E18.5)
ICOUNT = ICOUNT + 1
P1OUT(ICOUNT) = R(1)
```

```
P2OUT(ICOUNT) = R(2)
P3OUT(ICOUNT) = R(3)
P4OUT(ICOUNT) = R(4)
P5OUT(ICOUNT) = R(5)
P6OUT(ICOUNT) = R(6)
102 CONTINUE
ICOUNT = ICOUNT - 1
CALL QIKPLT(TOUT,P1OUT,ICOUNT,6H*TIME*,13H*PROBABI
1 LITY*,31H*ABSOLUTE PROBABILITY OF STATE*)
CALL PLOT(-7.0,1.0,-3)
CALL QLINE(TOUT,P2OUT,ICOUNT,-0)
CALL QLINE(TOUT,P3OUT,ICOUNT,-1)
CALL QLINE(TOUT,P4OUT,ICOUNT,-2)
CALL QLINE(TOUT,P5OUT,ICOUNT,-3)
CALL QLINE(TOUT,P6OUT,ICOUNT,-4)
CALL PLOT(12.0,0.0,-3)
CALL ENDPLT
CALL EXIT
END
```

```
SUBROUTINE FCT(X,Y,DERY)
DIMENSION X(1),Y(1),DERY(1)
DO 1 I = 1,NDIM
XBES = C1*Y(1)*Y(1)
N = 0
CALL BESI(XBES,N,BI,IER)
YO = BI
N = 1
CALL BESI(XBES,N,BI,IER)
Y1 = BI
DERY(1) = C2*(YO/Y1)
1 CONTINUE
RETURN
END
```

```
SUBROUTINE OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
DIMENSION X(1),Y(1),DERY(1),PRMT(5)
DIMENSION XT(1000),YR(1000)
COMMON/GP2/ICOU
COMMON/GP3/XT,YR
COMMON/GP4/IZT
XT(ICOU) = X(1)
YR(ICOU) = Y(1)
ICOU = ICOU + 1
```

```
IF(ABS(X(1) - PRMT(2) .LE. 1.0E-08) 12,11
12 PRINT 40
40 FORMAT(/////,12X,* TIME *,13X,* RADIUS *,//)
   IZT = ICOU - 1
   DO 20 II = 1,IZT
   PRINT 30, XT(II),YR(II)
30 FORMAT(5X,2E20.5)
20 CONTINUE
11 RETURN
END
```

Note : RKGS, SIMQ, BESI are I.B.M. Scientific Subroutines.



### BIBLIOGRAPHY

1. Billmeyer, F.W., Textbook of Polymer Science, Interscience, New York, 1962.
2. Gardon, J.L. "Emulsion Polymerisation I. Recalculation and Extension of Smith - Ewart Theory", Journal of Polymer Science, 6(Part A-1) : 623-641 (1968).
3. Gardon, J.L. "Emulsion Polymerisation II. Review of Experimental Data in the context of the revised Smith - Ewart Theory", Journal of Polymer Science, 6(Part A-1) : 634-664 (1968).
4. Gardon, J.L. "Emulsion Polymerisation III . Theoretical Predictions of the effects of slow termination rate within latex particles", Journal of Polymer Science, 6(Part A-1) : 665-685 (1968).
5. Gardon, J.L. "Emulsion polymerisation IV. Experimental verification of the theory based on slow termination rate within latex particles", Journal of Polymer Science, 6(Part A-1) : 687-710 (1968).
6. Gardon, J.L. "Emulsion Polymerisation V. Concentration of Monomers in Latex Particles", (To be published)
7. Harkins, W.D. "A General Theory of the Mechanism of Emulsion Polymerisation", Journal of Amer. Chem. Society, 69 : 1428-1444 (1947).
8. Haward, R.N. "Polymerisation in a system of Discrete Particles", Journal of Polymer Science, 4 : 273-287 (1949).

9. Morton, M., Kaiserman, S., Altier, M.W. "Swelling of Latex Particles", Journal of Colloid Science, 9 : 300-312 (1954).
10. Smith, W.V. "The Kinetics of Styrene Emulsion Polymerisation", Journal of Amer. Chem. Soc., 70 : 3695-3702 (1948).
11. Smith, W.V., Ewart, R.H. "Kinetics of Emulsion Polymerisation", Journal of Chemical Physics, 16,#6 : 592-599 (1948).
12. Stockmayer, W.H. "Note on the Kinetics of Emulsion Polymerisation", Journal of Polymer Science, 24 : 314 (1957).
13. Van der Hoff, B.M.E. "On the Mechanism of Emulsion Polymerisation of Styrene", Journal of Physical Chemistry, 60 : 1250-1254 (1965).
14. O'Toole, J.T. "Kinetics of Emulsion Polymerisation", Journal of Applied Polymer Science, 9 : 1291-1297 (1965).
15. Parzen, E., "Modern Probability Theory and its Applications", Wiley, New York, 1960.
16. Parzen, E., "Stochastic Processes", Holden-Day Inc., San Francisco, 1962.
17. Coleman, B.D., "Statistics of Irreversible Termination in Homogenous Anionic Polymerisation", Journal of Chemical Physics, 39, # 12 : 3233-3239 (1963).

18. Bharucha-Reid, A.T., "Elements of the Theory of Markov Processes and their Applications", McGraw-Hill, 1960.
19. Mc Quarrie, D.A., "Stochastic Approach to Chemical Kinetics", Methuen's Review Series in Applied Probability, v.8 , 43-46 (1967).
20. Lapidus, L., "Digital Computation for Chemical Engineers", Mc Graw Hill, 1962.
21. Flory, P.J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1963.
22. De Graff, A., "Emulsion Polymerisation in C.S.T.R.", Master's Thesis, Lehigh University, Bethlehem (1968).
23. Jovanovic, V.S., Romatowski, J., and Schulz, G.V., "Molecular Weight Distribution in Emulsion Polymerisation", The Makromolekulare Chemie, 85 , 187-194 (1965).
24. Wylie, C.R., "Advanced Engineering Mathematics", Mc Graw Hill, N.Y., 1966.

Vita

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