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Edited by Badar-ud-Din

UNIVERSITY OF THE PUNJAB
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STUDY OF METASOMATISM ACROSS A GRANITE CONTACT, NEAR LOWER BATRASI, TEHSIL MANSEHRA, DISTRICT HAZARA, PAKISTAN.

F. A. SHAMS AND F. U. REHMAN

Abstract : Field evidence of metasomatism of the metamorphic rocks at the contact with a facies of the Mansehra granite has been followed with laboratory investigations and the results are discussed.

INTRODUCTION

The Batrasi area constitutes the eastern part of the large granite-metamorphic complex that occupies core of a major syntaxial loop of the northwest Himalayas (Wadia, 1931). The country rocks (Fig. 1) are composed of metamorphosed sedimentary sequence, while the granite at the contact is a facies of the Mansehra granite (Shams, 1961).

The Mansehra granite is a porphyritic rock containing perthitic alkali feldspar, sodic plagioclase, quartz, biotite, muscovite and accessory amounts of apatite, ore and rare garnet. In the field the rock is characterized by granitoid texture and by the ubiquitous presence of megacrysts of alkali feldspar and polygonal "shimmer aggregates" after cordierite and/or andalusite. The contact is sheared and the marginal portion of granite has developed gneissose foliation. The metamorphic rocks dip underneath the granite, while the general foliation of the granite is more or less conformable to the schistosity of the metamorphic rocks, although there is a discordency between the magnitude of dip upto 15 degrees.

The normal metamorphic sequence of the area consists of alternating pelitic and psammitic units of varying thickness. In order of abundance, these are composed of quartz, muscovite, biotite, chlorite, feldspar and small amounts of tourmaline, sphene and ore grains; rare red garnet has developed to mark the highest grade of metamorphism attained in this area. Towards the contact, but about 400 feet away, narrow hornfels zone is met with and is traceable towards the contact upto a thin body of soda aplite. Between the latter and the contact, the rocks show appreciable coarsening and development of feldspar porphyroblasts, particularly within 10 feet of the contact; this field evidence of possible feldspathisation was made basis of the present study.

The margin of the metamorphic rocks at the contact carry slickenside lineations which show that the plane of contact had acted as plane of movement along which granite body had up-thrusted and consequently rocks on both the sides were sheared. A diagramatic sketch of the contact zone is given (Fig. 2)

Petrochemistry of the Contact Zone Metamorphic Rocks :

Due to the presence of well marked feldspathized zone, the metamorphic rocks were collected systematically away from the contact till the aplite body. Considering the possible effects of feldspathisation, specific gravity of each rock sample was determined by powder method using CCl_4 in sp. gravity bottle. The entire data are given in Table No. 1, while the variation of sp. gravity of rocks with regard to distance from the contact is shown in Fig. 3.

Table No. 1

Sr. No.	Catalogue No. of rock (MAS)	Distance from the contanct	Specific Gravity	G.ions/100 c.c. of rock			
				Si^{4+}	Na	K	
1.	6479	0′-10″	2.465	2.944	0.1661	0.1657	0.3318
2.	6478	4′-10″	2.507	2.939	0.1812	0.1231	0.3043
3.	6480	9′0″	2.506	2.934	0.1996	0.0992	0.2918
4.	6481	395′	2.580	2.911	0.0973	0.1218	0.2191

The gradual decrease of the sp. gravity of rocks towards the contact means either an increase in the specific volume or in the lighter constituents of the rocks. It is possible that the two vary simultaneously because the appearance of feldspar porphyroblasts in the schist is invariable

attended by the distinct coarsening effect. In order to decide whether the coarsening was produced due to recrystallization under thermal effects or through metasomatic feldspathisation, investigation of chemical composition of the rocks was undertaken. The rocks were analyzed for Si, Na and K as oxides and the data recasted into gr. ions per 100 c.c. of rock. In Fig. 4 is shown the variation of total alkali ions (Na+K) with respect to distance away from the contact.

The systematic increase in the content of Si^{+4} and alkalies ($Na^{+}+K^{+}$) towards contact with the granite is clearly brought out so that the influence of granite to produce feldspathisation is well supported. The sympathetic increase in the content of Si^{4+} as well (Fig. 5) shows that the alkalies were not introduced as alkali ions, but were being made available in the form of alkali silicates or at least to develop such chemical combinations during fixation in the metamorphic rocks. This sympathetic variation of alkalies and silicon ions is even better shown in Fig. 6. In order to understand the behaviour of individual alkali metals, the data of Na^{+} and K^{+} over the 10 feet zone from contact, have been plotted on a larger scale separately (Fig. 7). The diagram shows clearly the antipathetic attitude of Na versus K so that while the amount of sodium decreased towards contact, that of potassium increased simultaneously. This shows that during metasomatism the tendency was to achieve chemical equilibrium comparable to granitic composition.

Presence of the hornfels zone shows that the granitic area was not only supplier of metasomatizing fluids, but of heat energy as well. It is probable that these two factors acted together in the form of a hot hydrothermal fluids capable of producing thermal as well as metasomatic effects. The fact that the hornfels zone is preserved further away from the contact as compared with the metasomatic zone may mean that either the heat preceeded the metasomatism or that the latter became effective only when the thermal status of the heated rocks fell down to a certain critical level. The metasomatism ceased when the physico-chemical conditions within the aureole were no more suitable for chemical reactions to take place. This might have happened due to orogenic uplift or due to gradual drop of the geothermal gradient of the region. It is believed, therefore, that persistence of suitable physico-chemical conditions over longer period of time could have extended to zone of metasomatism.

The evidence collected from a small part of the Mansehra-Amb State area, is consistant with the senior author's theory (Shams, in press) that the granitic complex originated through permeation and granitization of the metasedimentary strata through the agency of hot fluids of ultimately magmatic origin.

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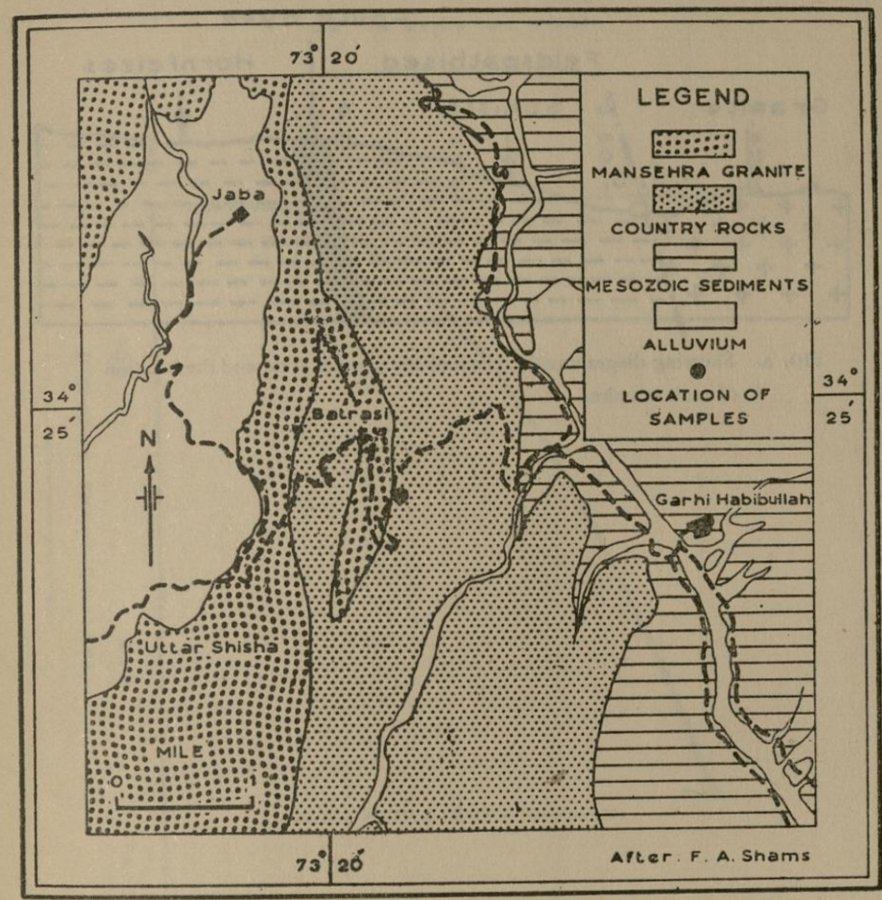


FIG. 1. Map of the granite—metamorphic contact area near lower Batrasi.

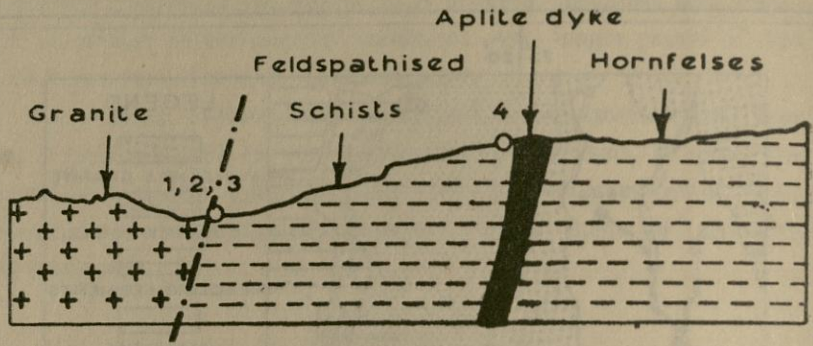


FIG. 2. Showing diagrammatic sketch of the contact zone and the location of rock samples.

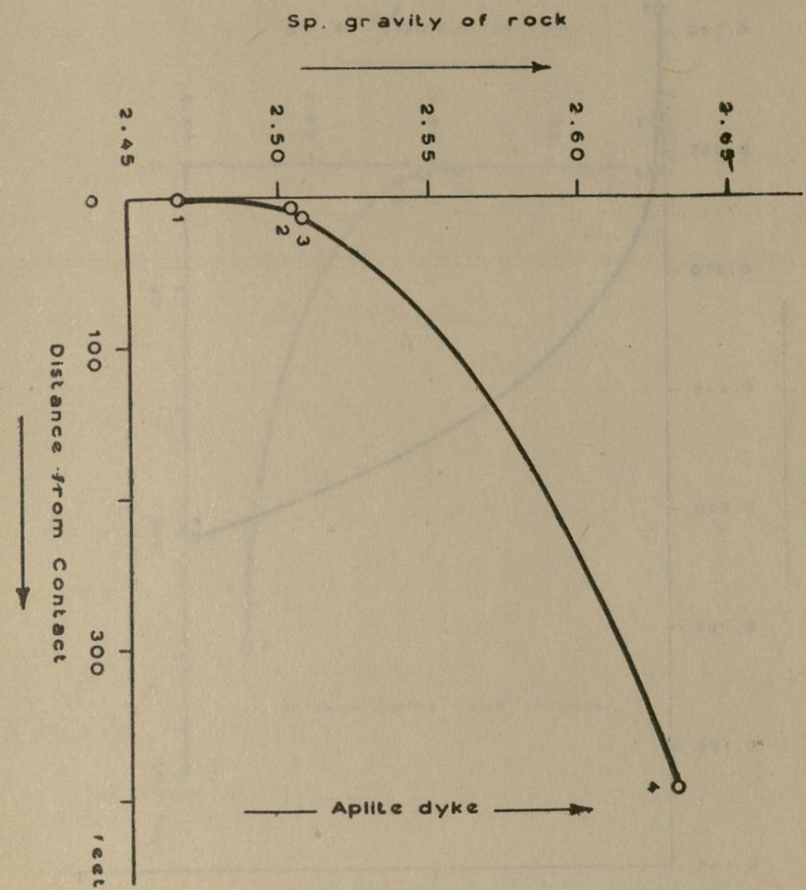


FIG. 3. Showing variation of sp. gravity of rocks with distance away from the contact.

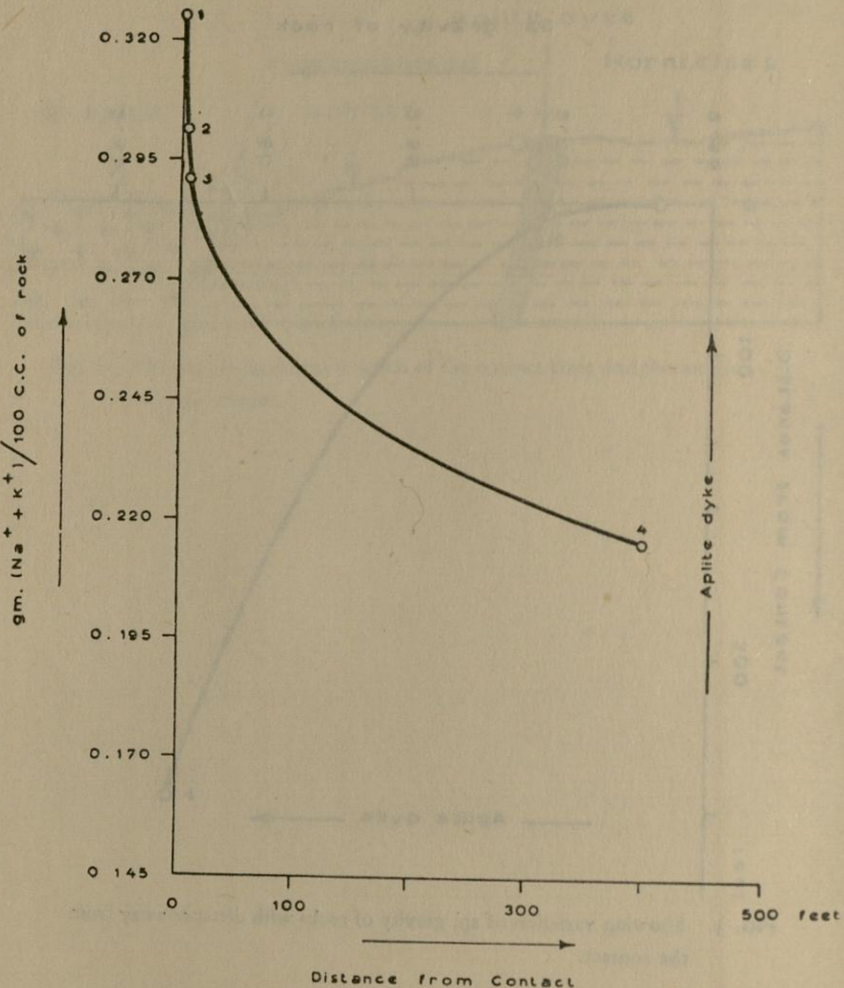


FIG. 4. Showing variation of (Na+K) content of rocks with distance away from the contact.

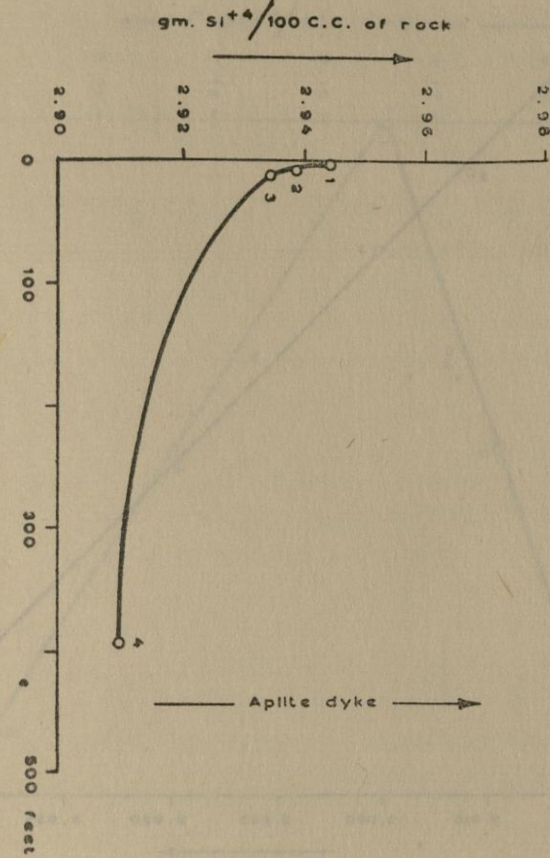


FIG. 5. Showing variation of Si^{4+} content of rocks with distance away from the contact.

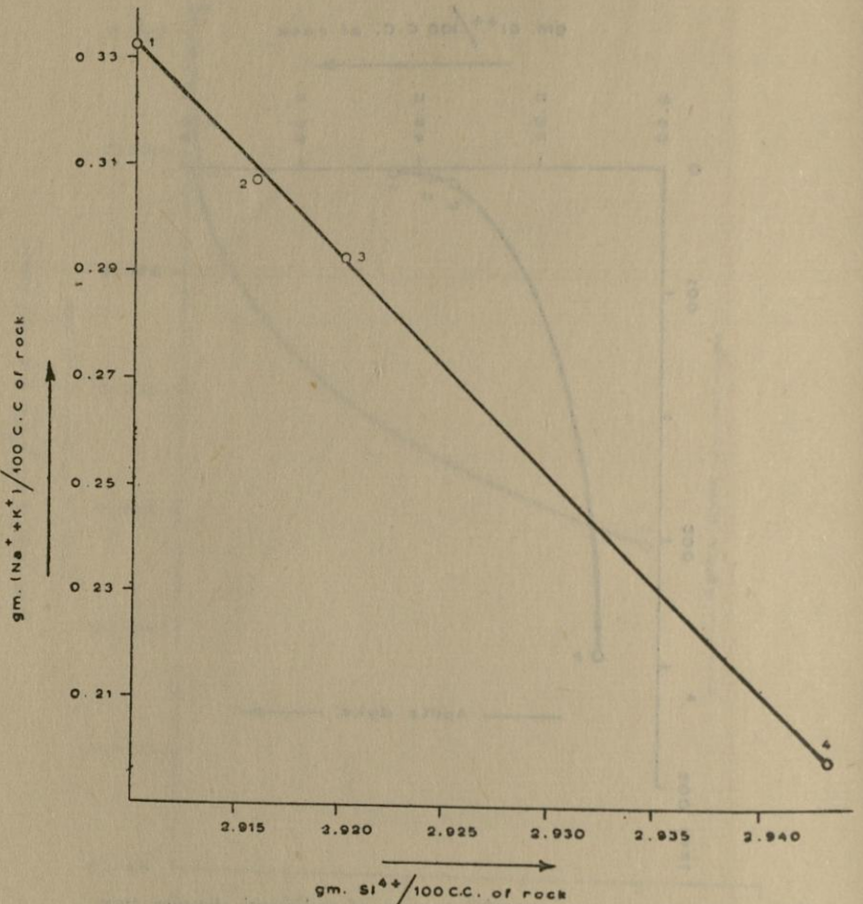


FIG. 6. Showing variation of total (Na+K) vs. Si^{4+} in rocks away from the contact.

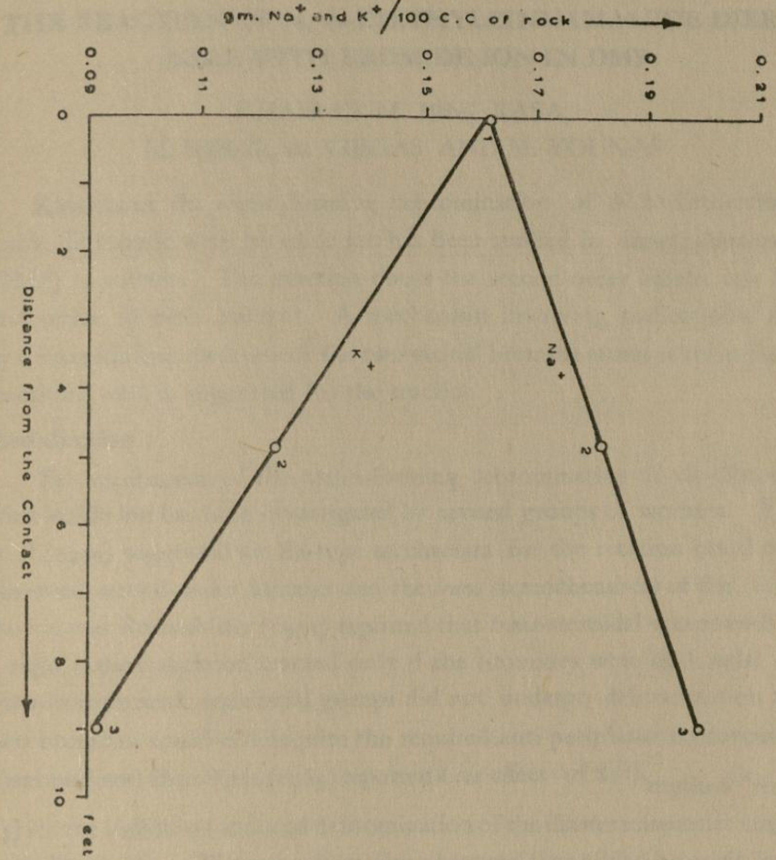


FIG. 7. Showing variation of Na and K content of rocks with distance away from the contact.

THE REACTION OF N, N-DIETHYLCINNAMAMIDE DIBROMIDE WITH BROMIDE ION IN DMF

KHAIRAT M. IBNE-RASA,
M. IQBAL, A. VIEGAS AND M. YOUNAS

Kinetics of the olefin-forming debromination of N,N-diethylcinnamamide dibromide with bromide ion has been studied in dimethylformamide (DMF) as solvent. The reaction obeys the second-order kinetic law being first order in each reactant. A mechanism involving nucleophilic attack by a bromide ion upon one of the two vicinal bromine atoms with an E2-type transition state is suggested for the reaction.

Introduction :

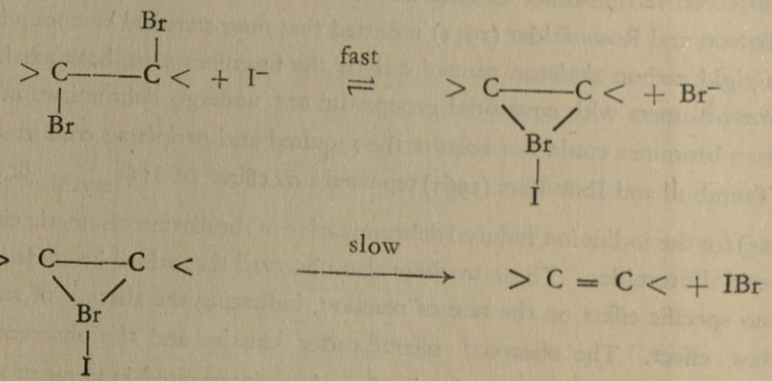
The mechanism of the olefin-forming debromination of vic-dibromides with iodide ion has been investigated by several groups of workers. Young et al (1939) suggested an E2-type mechanism for the reaction based on the observed second-order kinetics and the *trans* stereochemistry of the reaction. Barton and Rosenfelder (1951) reported that *trans*-steroidal compounds with a rigid carbon skeleton reacted only if the bromines were both axial. The *trans*-isomers with equatorial groups did not undergo debromination as the two bromines could not acquire the required anti-periplanar conformation. Trumbull and Ibne-Rasa (1963) reported a *cis* effect of 85 ($k_{erythro}/k_{threo}$ = 85) for the iodide ion induced debromination of the diastereoisomeric cinnamic acid dibromides. These workers also observed that added bromide ion had no specific effect on the rate of reaction, indicating the absence of any mass law effect. The observed second-order kinetics and the observed *trans*-stereospecificity of debromination have been interpreted in terms of a direct mechanism involving nucleophilic attack of iodide ion on bromine in a typical E2 manner resulting in *trans* elimination.

$$>\underset{\displaystyle Br}{\underset{|}{C}}\text{——}\overset{\displaystyle Br}{\overset{|}{C}}< \;+\; I^- \longrightarrow\; >C=C< \;+\; Br^- \;+\; IBr$$

The E2 mechanism operates in dibromoalkanes in which the two bromines are bonded to highly substituted carbon atoms.

The effect of substituents on the debromination of cinnamic acid dibromides has been investigated by Ibne-Rasa, A, Ahmad and Amiruddin (1968). Electron donating substituents accelerate the rate of reaction while electron-withdrawing groups decrease the rate. The accelerative effect of the *p*-mehoxy substituent is abnormally large. These authors have suggested that the elimination of the two-bromine atoms from *erythro*-cinnamic acid dibromide and its *p*-nitro, *p*-chloro, and *m*-nitro analogues, occurs by a synchronous mechanism, whereas the debromination of *p*-methoxy cinnamic acid dibromide is non-synchronous although concerted and is nearly El-type.

For the less alkylated dibromoalkanes such as 1, 2-dibromo-propane, 2, 3-dibromopropane and 1, 2-dibromo-2-methyl propane, the debromination has been reported by Mulders and Nasielski (1963) to be subject to the mass law effect. They have, therefore, proposed the following mechanism for such cases :



Hine and Brader (1953) have suggested a different mechanism, but that does not account for the observed mass law effect.

Nucleophiles other than the iodide ion have also been reported to lead to olefin-forming debromination. Thus Ibne-Rasa, N. Muhammad and Hasibullah (1966) have shown that thiourea and the thiocyanate ion give

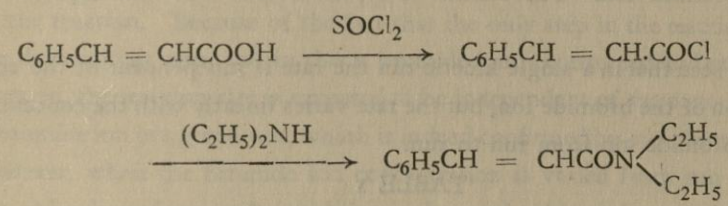
high yields of olefins when reacted with vic-dibromides. Similarly thiosulphate ion has been found to be an excellent debrominating agent in DMSO as solvent (Ibne-Rasa, H. Bano, A. Niazi and A.R. Tahir).

At the time that this work was completed (M. Iqbal, M.Sc. thesis, Punjab University, 1966) there was no report in the literature in which bromide or chloride ion had been used for debromination. In fact in the hydroxylic solvents usually used for debrominations the vic-dibromides are recovered unchanged after being heated with bromide or chloride ion for several hours.

These ions, however, have been found to react with vic-dibromides, when dipolar aprotic solvents (A.J. Parker, 1960) such as DMF or DMSO are used. The yields of olefins are high. The kinetics of the debromination of certain vic-dibromides by bromide and chloride in DMSO and DMF has recently been reported in the literature by other workers also (1969).

Results :

N, N-Diethylcinnamamide was prepared through the following reaction sequence.



The dibromide was then prepared by adding bromine to N, N-diethyl cinnamamide in chloroform.

A sample of N, N-diethylcinnamamide dibromide was reacted with 8 equivalents of LiBr in DMF and the mixture heated for 6 hours at 60°. The reaction yielded N, N-diethylcinnamamide in 78.5% yield.

erythro-Cinnamic acid dibromide when reacted with LiBr in DMF as solvent gave cinnamic acid (88%), and when the dibromide was reacted with LiCl in DMSO, cinnamic acid was obtained in 90% yield. The yield of *p*-methoxy cinnamic acid from the corresponding dibromide was 96% when the latter was reacted with LiCl in DMF.

The kinetics were followed by mixing known solutions of the dibromide and LiBr in DMF at the desired temperature. Aliquotes were pipetted out at recorded intervals and poured into ice-water mixture containing excess potassium iodide to quench the reaction and to react the liberated bromine with the iodide ion. The iodine, thus formed, was then titrated against standard thiosulphate using starch as indicator.

The first order rate constants were calculated by using the differential rate equation

$$\text{Rate} = k\ (a - x)$$

where *a* is the initial concentration of the dibromide and *x* the amount of dibromide reacted at time t.

Plots of log $(a-x)$ versus time were made and the first order rate constants calculated by multiplying the slope of the straight line with 2.303.

In a set of runs the initial concentrations of the bromide ion were varied from run to run keeping the initial concentration of the dibromide constant. The first order rate constant was found to vary linearly with the concentration of the bromide ion. The results of typical kinetic runs are displayed in Table 1.

It is seen that in a single kinetic run the rate is independent of the concentration of the bromide ion, but the rate varies linearly with the concentration of bromide ion from run to run.

TABLE 1

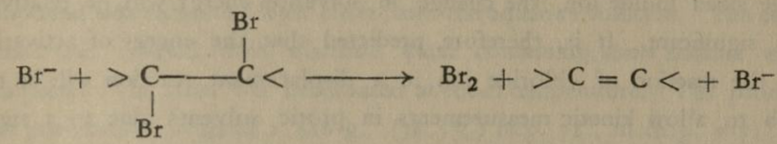
RATE CONSTANTS FOR THE DEBROMINATION OF N, N-DIETHYLCINNAMAMIDE DIBROMIDE WITH Br^- IN DMF

a	b	T°	$10^4 \times k_1$ sec^{-1}	$10^{-4} \times k_2$ l mole^{-1} sec^{-1}
0.03	0.24	60°	1.11	4.63
0.03	0.24	70°	3.00	12.5
0.03	0.36	70°	4.30	11.9
0.03	0.18	70°	2.24	12.40

Discussion :

It is seen from the data of table I that the reaction of N, N-diethyl cinnamamide dibromide with bromide ion is kinetically first order in the concentration of each reactant.

Since the mechanism for debromination with iodide ion is known to involve a nucleophilic attack by the iodide ion upon one of the two vicinal bromines, it is suggested that the bromide ion in DMF performs an analogous nucleophilic attack on one of the two bromines in the dibromide. The reaction then would be as follows.



The fact that the reaction follows the first order kinetic law and the fact that in our kinetic technique iodine is liberated quantitatively by treatment of the reaction product with excess iodied ion, seem to support the above mechanism for the reaction. Because of the fact that the only step in the reaction is the rate determining step, and in this a bromide ion is consumed and another is liberated, the reaction rate is expected to be independent of the concentration of bromide ion in a given run, which is indeed confirmed by our observations. However, when the bromide ion concentration is varied from run to run first-order dependence on bromide ion is observed, which is in accord with the above mechanism.

It is of particular interest that in DMF as solvent, the chloride and bromide ions have been found to be debrominating agents of general application during the present investigations.

These ions are ineffective as debrominating agents in conventional solvents such as ethanol, acetic acid, and their aqueous mixtures. A vicinal dibromide is usually recovered unchanged when treated with bromide or chloride ions in hydroxylic solvents.

It has been pointed out by Parker (1960) that anions are solvated by hydroxylic solvents mostly due to hydrogen bonding and this type of solvation is most serious for small sized, low polarizability anions, whereas high polarizability (large size) anions, such as the iodide ion, are not so well solvated by hydrogen bonding solvents. When the solvent is of an aprotic nature solvation of anions is essentially due to polarizability-polarizability interactions and not due to hydrogen bonding. The large-sized (high polarizability) anions are solvated to a greater extent than the small sized anions.

Thus, for example, if solvent for the small sized chloride ion is changed from protic to aprotic, the difference in solvation energies in these two media would be serious. For the same change in solvent for the large sized iodide ion, the change in solvation energy will be relatively less significant. It is, therefore, predicted that the energy of activation for the reaction of chloride ion in a displacement reaction will be too high to allow kinetic measurements in protic solvents due to a significant contribution of desolvation energy to the energy of activation. However, when the solvent is DMF (aprotic) the contribution of desolvation energy to the energy of activation will be diminished. In other words, the chloride ion will be partially deprived of its solvation shell in DMF and less energy will be needed to strip off its solvation shell before it can bond with the electrophilic atom in the substrate. Furthermore, the E2 transition state for the debromination in the present system is expected to be large and highly polarizable. Solvation of such a transition state in the aprotic DMF will be more serious than in hydrogen bonding solvents, reducing the energy of activation.

In brief, the change from conventional hydrogen bonding solvents to DMF raises the energy of the ground state and lowers that of the transition state. These two effects cummulatively decrease the energy of activation.

EXPERIMENTAL :

ISOLATION OF THE PRODUCT OF THE REACTION OF N, N-DIETHYLCINNAMAMIDE DIBROMAMIDE WITH LITHIUM BROMIDE IN DMF.

To a solution of 3.00 g. (0.00826 mole) of N, N-diethylcinnamamide dibromide in 200 ml. of DMF was added 5.742 g (.06608 mole) of lithium bromide. The reaction mixture was heated at a constant temperature of 60° for 6 hours with occasional shaking. The solvent was removed by distillation under reduced pressure till a small amount of the reaction mixture was left behind. The liquid was dissolved in 150 ml. of distilled water. Then the compound was extracted with ether from the aqueous solution. The ether extract was washed with distilled water containing some sodium meta bisulphite. The ether was evaporated at room temperature. The product after purification weighed 1.316 g. (78.5%) m.p. 71°, m.m.p. =71°.

THE KINETIC METHOD :

Sodium thiosulphate solution (.01N) was prepared and standardized at frequent intervals against standard potassium bromate according to the method described by Kolthoff and Sandell. Lithium bromide (B.D.H. reagent grade) was dried in an electric oven at 120-130° for six hours and kept in a desiccator until used. A typical kinetic run is described below :

Fifty ml. of a solution of 10.89 g. (0.03 mole) of N, N-diethylcinnamamide dibromide in DMF (B.D.H. reagent grade) was taken in a 500 ml. round bottomed flask. The round bottomed flask containing this solution was immersed in a constant temperature bath. When the solution had come to the temperature of the bath, 50 ml. of DMF solution containing 20.84 g. (0.24 mole) of lithium bromide, which had previously been brought to the temperature of the bath, was added. Zero time was taken as the time when the lithium bromide solution was added. Five ml. samples were removed with a pipette at recorded intervals and poured into a crushed ice-water mixture containing 5 ml. of 5% potassium iodide to quench the reaction. The liberated iodine was quickly titrated against standard sodium thiosulphate solution using starch as indicator. A parallel blank run was taken and the volume of sodium thiosulphate corrected for this blank. The same method was used for all the runs in DMF.

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DINGLE'S PARADOX IN SPECIAL RELATIVITY

A.B. PAL *and* M. SALEEM

Dingle's paradox in special relativity has been analysed in detail and it is shown that his two equations are *not* contradictory. Also, it is shown that the three questions raised by Dingle can be answered within the framework of Einstein's special theory of relativity.

1. Dingle's Equations

We shall first consider Dingle's reasoning which leads him to two "contradictory" equations [1].

Let position and time be measured in an inertial system K by co-ordinates x, y, z, t and in another inertial system k by co-ordinates x', y', z', t'. Let the two sets of axes exactly coincide at $t=t'=0$, and the relative velocity v of system k with respect to system K be along the axes x and x', so that the position of the origin O' of co-ordinates x', y', z', t' is given by $x=vt$ for an observer sitting in system K, and the position of the origin O of the co-ordinates x, y, z, t is given by $x'=-vt'$ for an observer sitting in system k.

According to the Lorentz transformation, the following relations hold between t and t':

$$a\,t=t'+\frac{vx'}{c^2} \qquad \text{(I)}$$

$$at'=t-\frac{vx}{c^2}, \qquad \text{(II)}$$

where $a=\left(1-\frac{v^2}{c^2}\right)^{\frac{1}{2}}$ and c denotes the velocity of light.

Dingle considers four precisely similar and regularly running clocks A, B, H and N. The clock A is placed at the origin O in system K, and the clock H at some point on the positive x-axis. The clock B is placed at the origin O' in system k, and the clock N at some point on the negative x'-axis. Clock H has been synchronized with clock A in system K, and clock N with clock B in system k.

Dingle considers the following three successive events :—

(1) *Event* E_0 : At this event, A and B encounter each other, so that $t=t'=0$.

(2) *Event* E_1. At this event, B and H encounter each other (fig. 1), so that

$t'=t_1'$, the reading of B at event E_1, $x'=x_1'=0$,

$t=t_1$, the reading of H at event E_1, $x=x_1=vt_1$.

As H has been synchronized with A, the reading of A at event E_1 is also equal to t_1. Thus equation (I) gives

$$at_1=t_1' \qquad (1)$$

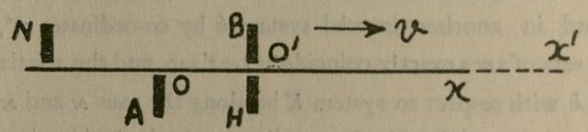

Fig. 1.

Fig. 1. Event E_1.

(3) *Event* E_2. At this event, N and A encounter each other (fig. 2), so that

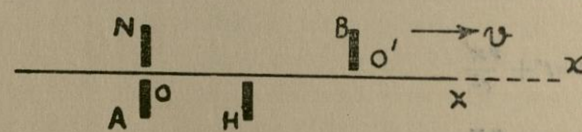

Fig. 2.

Fig. 2. Event E_2.

$t=t_2$, the reading of A at event E_2, $x=x_2=0$,

$t'=t_2'$, the reading of N at event E_2, $x'=x_2'=-v\,t_2'$.

As N has been synchronized with B, the reading of B at event E_2 is also equal to t_2'. Thus equation (II) gives

$$at_2'=t_2. \qquad (2)$$

Between events E_0 and E_1, A advances by t_1, and B by t_1'. Thus equation (1) gives

$$\left(\frac{\text{rate of } A}{\text{rate of } B}\right)=\frac{t_1}{t_1'}=\frac{1}{a}>1. \qquad (3)$$

Between events E_0 and E_2, A advances by t_2, and B by t_1'. Thus equation (2) gives

$$\left(\frac{\text{rate of } A}{\text{rate of } B}\right)=\frac{t_2}{t_2'}=a<1 \qquad (4)$$

According to Dingle, the ratios $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ in equations (3) and (4) represent *one and the same* quantity, and so he draws the following two conclusions :

(*a*) Equations (3) and (4) are *contradictory*.

(*b*) Rate of B is smaller as well as greater than rate of A, *i.e.*, B is going *slower as well as faster* than A.

Conclusion (*a*) indicates that Einstein's theory is logically unsound, and conclusion (*b*) indicates that this theory predicts an *objective* phenomenon (*i.e.*, the working of the clocks A and B) which is physically impossible. Hence, Dingle concludes that the special theory of relativity is *false*.

2. Meaning of the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$

Before pointing out the fallacy in Dingle's reasoning, we shall first carefully examine the *meaning* of the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$, which appears in equations (3) and (4).

Let us denote the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ by R. Equation (3) gives a *particular* value of R measured between the pair of events E_0 and E_1, where event E_1 occurs on the clock B. Equation (4) gives another *particular* value of R measured between the pair of events E_0 and E_2, where event E_2 occurs on the clock A. We can also find the *general* value of R measured between the pair of events E_0 and E, where event E may occur at *any* point on the x-axis. Suppose the observer in system K places a number of clocks (similar to A) at different points along the x-axis, and then synchronizes all these clocks with clock A by using light signals in system K, so that if an event occurs at any point on the x-axis and the clock placed at that point shows time t at this event, then the observer in system K can *assume* that the time by clock A at event E is also equal to t. Let the observer in system k also place a number of clocks (similar to A) at different points on the x'-axis and synchronize all these clocks with clock B by using light signals in system k, so that if the clock, where the event E occurs, shows time t' at this event, then the observer in system k can *assume* that the time by clock B at event E is also equal to t'. Between events E_0 and E, A advances by t, and B by t'. Thus the *general* value of R is given by

$$\mathrm{R}=\frac{t}{t'}. \qquad (5)$$

As $at'=t-\frac{vx}{c^2}$, by equation (II), equation (5) can be put in the form :

$$\mathrm{R}=\frac{at}{t-\frac{vx}{c^2}},$$

which clearly shows that R is not a constant but *varies* with the position x and time t of the event E.

It must be carefully noted that the event E occurs simultaneously on *two* clocks, which encounter each other at this event[2]. One of these clocks is a K-clock (*i.e.*, a clock at rest in system K), and the other is a k-clock (*i.e.*, a clock at rest in system k). The time t' is actually the *reading of the k-clock* at event E. The k-observer *assumes* that the reading of clock B at event E is also equal to t', as this observer has synchronized the k-clock with clock B by using light signals. But the K-observer thinks that this method of *error*

synchronization is *not* correct, as seen from his system, and so he sees an error in the reading t' of the k-clock at event E. This error can be determined as follows :

Suppose the k-observer wants to synchronize a clock F, placed on the x'-axis at distance x' from the origin O', with the clock B, which is placed at O' in system k. A light signal is sent from B to F, where it is instantaneously reflected back and sent to B. If the signal starts from B at time T_1' and returns to it at time T_3', then the k-observer *assumes* that the signal reaches F at time T_2', which satisfies the relations :

$$T_2'-T_1'=\frac{x'}{c},$$

$$T_3'-T_2'=\frac{x'}{c}.$$

Thus $$T_2'=(T_1'+T_3')/2 \qquad (6)$$

and $$(T_3'-T_1')=\frac{2x'}{c}. \qquad (7)$$

The K-observer sees that light travels from B to F with velocity $(c-v)$ with respect to F, and then travels from F to B with velocity $(c+v)$ with respect to B. He thinks that the light signal reaches F at time T_{2K}' by clock B, so that

$$(T_{2K}'-T_1')\,(c-v)=(T_3'-T_{2K}')\,(c+v),$$

whence $T_{2K}'=(T_1'+T_3')/2+(T_3'-T_1')\,v/2c.$

Using equations (6) and (7) in the above relation, we get

$$T_{2K}'=T_2'+\frac{vx'}{c^2}$$

which shows that the K-observer will find an *error* in the time T_2'. As this error depends on x' only, we conclude that the K-observer will find an error $\frac{vx'}{c^2}$ in time t'. Hence, the K-observer will find that the correct value of the reading t' of clock B is t_K', where

$$t_K'=t'+\frac{vx'}{c^2}. \qquad (8)$$

Similarly, it can be shown that the k-observer will find that the correct value of the reading t of clock A is t_k, where

$$t_k = t - \frac{vx}{c^2}. \qquad (9)$$

As the time t is measured by the K-observer and the time t' is measured by the k-observer, we see from equation (5) that the ratio R means

$$\frac{\text{rate of } A \text{ measured by } K\text{-observer}}{\text{rate of } B \text{ measured by } k\text{-observer}},$$

i.e., R is calculated from t and t', wich are measured by *two* different observers, namely, the K-observer and the k-observer. It is obvious that the ratio

$$\frac{t}{t_K'} = \frac{\text{rate of } A \text{ measured by } K\text{-observer}}{\text{rate of } B \text{ measured by } K\text{-observer}}$$

can be calculated from t and t_K', which are measured by the *same* observer, namely, the K-observer. If we denote this ratio by R_K, then and by equation (8),

$$R_K = \frac{t}{t_K'},$$

$$R_K = \frac{t}{t' + \frac{vx'}{c^2}} \qquad (10)$$

It is obvious that the ratio

$$\frac{t_k}{t'} = \frac{\text{rate of } A \text{ measured by } k\text{-observer}}{\text{rate of } B \text{ measured by } k\text{-observer}}$$

can be calculated from t' and t_k, which are measured by the *same* observer, namely, the k-observer. If we denote this ratio by R_k, then

$$R_k = \frac{t_k}{t'}, \text{ and by equation (9),}$$

$$R_k = \frac{t - \frac{vx}{c^2}}{t'}. \qquad (11)$$

The values of R_K and R_k can be easily determined by using the Lorentz transformation.

As $t' + \frac{vx'}{c^2} = at$, by equation (I), we get from equation (10)

$$R_K = \frac{1}{a}. \qquad (12)$$

As $t - \frac{vx}{c^2} = at'$, by equation (II), we get from equation (11)

$$R_k = a. \qquad (13)$$

To sum up, the above analysis shows that

1. The ratio R has two *particular* values given by equations (3) and (4). Its *general* value is given by equation (5).

2. The ratio R_K has the *constant* value $\frac{1}{a}$ for *all* possible values of x and t.

3. The ratio R_k has the *constant* value a for *all* possible values of x and t.

3. Fallacy in Dingle's Reasoning

Dingle assumes that the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ appearing in equations (3) and (4) is *one and the same* quantity. We can now *test* this assumption in the light of the analysis given in section 2.

If we denote the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ appearing in equations (3) and (4) by R, then the general value of R (between events E_0 and E) is given by equation (5), namely,

$$R = \frac{t}{t'}. \qquad (5)$$

We have also defined two more ratios R_K and Rk given by equations (10) and (11), namely,

$$R_K = \frac{t}{t' + \frac{vx'}{c^2}} \qquad (10)$$

$$Rk = \frac{t - \frac{vx}{c^2}}{t'}. \qquad (11)$$

When the event E does *not* occur on clock A or clock B, then the three ratios R, R_K and Rk have *different* values, given by equations (5), (10) and (11) respectively. Using equation (II) in equation (5), we get

$$R = \frac{at}{t - \frac{vx}{c^2}},$$

which shows that R *varies* with x and t, *i.e.*, the ratio R has different values for different events. But R_K has the constant value $1/a$ for all events, and Rk has the constant value a for all events, as shown in section 2.

When the event E occurs on clock B, then E and E_1 are *one and the same* event, so that

$$x = x_1, \quad t = t_1,$$
$$x' = x_1', \; t' = t_1',$$

and equations (5), (10) and (11) become

$$R = \frac{t_1}{t_1'} \tag{5a}$$

$$Rk = \frac{t_1}{t_1' + \frac{vx_1'}{c^2}} \tag{10a}$$

$$Rk = \frac{t_1 - \frac{vx_1}{c^2}}{t_1'} \tag{11a}$$

As event E_1 occurs on clock B (fig. 1), we get $x_1' = 0$, and so equations (5a) and (10a) give the *remarkable* result

$$R = R_K,$$

which shows that the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ in equation (3) is equal to R_K defined by the relation

$$R_K = \frac{\text{rate of } A \text{ measured by } K\text{-observer}}{\text{rate of } B \text{ measured by } K\text{-observer}}$$

Hence, equation (3) gives the *point of view of the K-observer*, who finds that

$$\frac{\text{rate of } A}{\text{rate of } B} = R_K = \frac{1}{a},$$

i.e., the K-observer sees that B is going *slower* than A.

When the event E occurs on clock A, then E and E_2 are *one and the same* event, so that

$$x = x_2, \quad t = t_2,$$
$$x' = x_2', \quad t' = t_2',$$

and equations (5), (10) and (11) become

$$R = \frac{t_2}{t_2'} \tag{5b}$$

$$R_K = \frac{t_2}{t_2' + \frac{vx_2'}{c^2}}, \tag{10b}$$

$$Rk = \frac{t_2 - \frac{vx_2}{t_2}}{t_2'}. \tag{11b}$$

As event E_2 occurs on clock A (fig. 2), we get $x_2 = 0$, and so equations (5b) and (11b) give the *remarkable* result

$$R = Rk$$

which shows that the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ in equation (4) is equal to R defined by the relation

$$Rk = \frac{\text{rate of } A \text{ measured by } k\text{-observer}}{\text{rate of } B \text{ measured by } k\text{-observer}}.$$

Hence, equation (4) gives the *point of view of the k-observer*, who finds that

$$\frac{\text{rate of } A}{\text{rate of } B} = Rk = a,$$

i.e., the k-observer sees that B is going *faster* than A.

It follows that the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ in equation (3) is *not* the same quantity as the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ in equation (4). Dingle's *fallacy* is that he assumes these two ratios to be *one and the same* quantity.

As equation (3) represents the point of view of the K-observer and equation (4) represents the point of view of the k-observer, it is obvious that these two equations are *not* contradictory, and so the special theory of relativity *is* logically sound. Also, Dingle's conclusion (*b*), namely,

B is going *slower as well as faster* than A

will make *sense*, if we write it in the following correct form :

B is going *slower* than A, as seen from system K,

but B is going *faster* than A, as seen from system k.

Hence the ***objective*** phenomenon (*i.e.*, the working of the precisely similar and regularly running clocks A and B) predicted by Einstein's theory *is* physically possible.

4. Dingle's Questions

We now turn to Dingle's three interesting questions.

The *first* question is : "How is it possible for the ratio of the intervals recorded by two identically constructed, regularly running, clocks, between the same pair of events, to vary with the events chosen ?"

We see from equations (3) and (4), namely,

$$\frac{\text{rate of } A}{\text{rate of } B}=\frac{t_1}{t_1'}=\frac{1}{a} \qquad (3)$$

$$\frac{\text{rate of } A}{\text{rate of } B}=\frac{t_2}{t_2'}=a \qquad (4)$$

that the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ between the pair of events E_0 and E_1 is equal to $1/a$, but its value between the pair of events E_0 and E_2 is a. Thus equations (3) and (4) indicate that the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ *varies* with the pair of events chosen. Dingle wants to know the reason for such a *strange* variation in the ratio for the two *identically constructed and regularly running* clocks A and B.

As shown in section 3, equation (3) represents the point of view of the K-observer. Hence, when we determine the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ between the pair of events E_0 and E_1 by using equation (3), we adopt the point of view of the K-observer, and when we determine this ratio between the pair of events E_0 and E_2 by using equation (4), we adopt the point of view of the k-observer. It is this *change in the point of view* which produces a variation in the ratio. If we stick to the *same* point of view, then the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ does not depend upon the events chosen. This can be easily proved as follows.

Let us first adopt the point of view of the K-observer. In this case, the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ between the pair of events E_0 and E is equal to R_K,

whose value is given by equation (10), namely,

$$R_K=\frac{t}{t'+\frac{vx'}{c^2}} \qquad (10)$$

But $t'+\frac{vx'}{c^2}=at$, by equation (I).

Thus $R_K=\frac{t}{at}=\frac{1}{a}$

which shows that R_K is *not* a function of the co-ordinates t, x or t', x' of the event E, and so the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ does not depend upon the events chosen.

Now let us adopt the point of view of the k-observer. In this case, the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ between the pair of events E_0 and E is equal to Rk, whose value is given by equation (11), namely

$$Rk=\frac{t-\frac{vx}{c^2}}{t'}. \qquad (11)$$

But $t-\frac{vx}{c^2}=at'$, by equation (II),

Thus $Rk=\frac{at'}{t'}=a$,

which shows that R_K is *not* a function of the co-ordinates t, x or t', x' of the event E, and so the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ does not depend upon the events chosen.

Hence, the ratio $\left(\frac{\text{rate of } A}{\text{rate of } B}\right)$ does *not* vary with the events chosen, provided we stick to the point of view of the *same* observer.

The *second* question is : "If it is possible, why must the events that alone give the "correct" ratio be chosen from the set occurring on one and not the other of the clocks."

As shown in section 3, the "correct" ratio, *i.e.*, the ratio given by the relation

$$\frac{\text{rate of } A}{\text{rate of } B} = \frac{1}{a}$$

is obtained from the point of view of the *K*-observer, which is represented by equation (3). Hence, we must choose the set of events which occurs on clock *B* only.

The *third* question is: "If they must be chosen, how does one (consistently with a theory in which only feature in which the clocks differ—motion—can be ascribed indifferently to one or the other) discover on which clock the valid set of events occurs".

It is obvious from the analysis given in section 3, that the clock, on which the valid set of events occurs, can be easily discovered after we know the point of view which we have to adopt. For example, if we adopt the point of view of the *K*-observer and use equation (3), then the valid set of events occurs on clock *B*.

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A NEED ACHIEVEMENT SCALE AND ITS RELATIONSHIP TO ACADEMIC SUCCESS AND LEVEL OF INTELLIGENCE

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Abstract : Combined groups of male and female achievers and underachievers generally differed in need achievement. In case of males need achievements was negatively related to intelligence and unrelated to academic success, whereas in case of females it was positively related to academic success but was unrelated to intelligence.

Considerable interest has been shown in recent years in the study of achievement motivation and relationship to its academic work. However, the need for conducting the present study arose out of the realization that while a number of researches pertinent to this had been conducted under conditions prevalent in the Western cultural and educational con-texts, there were very few in which the relationship of this personality vari-able to academic performance and intellectual ability had been studied systematically within a different cultural setting like Pakistan. Even in studies conducted in the West, there is lack of concensus concerning the relationships between achievement motivation and scholastic achievement. McClelland, Atkinson, Clark, and Lowell (1953) have reported a moderate correlation of .51, while Weiss, and Groesbeck (1959) reported an r of .34. However, Lowell (1952) and Parrish and Rethlingshafer (1954) failed to find any significant relationship between these variables. The fact that sex differences are also likely to affect both these variables (McClelland, et al., 1953, pp : 172, 175) was also considered of interest in the present study. Findings so far reported in the literature have primarily been concerning male subjects, but there are a few studies which have suggested that the conditions under which achievement motivation is aroused in females differs from that of males (Veroff 1950, Field 1951).

Aims

The primary purpose of the present study was to determine whether there was a significant relationship between achievement motivation and academic success in a mixed group of post-graduate Pakistani students.* Also whether there existed any sex differences in this regard.

Secondly, it was aimed to explore, for each sex, the degree of relationship between general intellectual ability and need for achievement.

The third aim of the study concerned exploration, amongst each sex, of the degree of relationship between general intellectual ability and academic achievement.

Finally, holding the effects of intelligence, it was explored whether the relationship between achievement motivation and academic success was significant for groups of each sex.

Method

The subjects selected for this study were 40 male and 55 female post-graduate students of the Department of Applied Psychology. The scores of three consecutive annual batches of students were combined for purposes of analysis. The tests administered consisted of the Need Achievement Scale of the Edwards Personal Preference Schedule (EPPS) and the Verbal Reasoning and Numerical Ability Tests of the DAT Battery. The combined scores derived from the latter are claimed to be a fairly valid index of general intellectual ability. These tests have been adapted for use in Pakistan (Rouck 1966) and hence were regarded as fairly valid measures of general intellectual ability of Pakistani students. The results of students performance in the M.Sc. annual promotion examination formed the basis for the determination of academic success. The percentage of marks secured was aggregated from performance in four papers in Applied Psychology. The classification of achievers and under-achievers was based on those securing 45 percent or more marks (achievers) and the rest (under-achievers). The cutting point was one which roughly corresponded to the mean score. In terms of the present classifications used for examination

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purposes, this separated the second divisions and above from third divisions.

For purposes of statistical analysis male and female groups were also considered separately. The t test was applied to Need Achievement scores of achievers and under-achievers. In addition, Pearsons' product moment correlations were computed between the Need Achievement Scale and D.A.T., academic performance and D.A.T., and academic performance and Need Achievement. Finally, in order to nullify the influence of intelligence in the relationship between Need Achievement and academic performance a partial correlation was computed.

Results

The results reported in Table 1 indicate that there was a significant difference between the EPPS Need Achievement scores of achievers and under-achievers comprising the combined group of male and female students.

TABLE 1

DIFFERENCE BETWEEN MEANS OF COMBINED GROUPS OF MALE AND FEMALE ACHIEVERS & UNDERACHIEVERS ON N. ACH. SCALE OF THE EPPS.

Group	N	X	S.D	Mean Diff. Ach., U. Ach.	S.E. Mean Diff.	t
Achievers	44	15.70	3.56	.43	.2	2.15*
Underachievers	51	15.27	3.57			

*Significant at .05 level.

However, when this group was subdivided according to sex, no significant difference was revealed in EPPS Need Achievement Scores of either males or females. (Table 2).

TABLE 2

DIFFERENCE BETWEEN MEANS OF MALE AND FEMALE ACHIEVERS AND UNDERACHIEVERS ON N. ACH. SCALE OF THE EPPS.

Group	Achievers		Under achievers		Mean Diff.	S.E. Mean Diff.	t
	N	$\bar{X}$	N	$\bar{X}$			
Male	12	16.25	28	15.29	.96	.95	1.006
Female	39	15.54	16	15.25	.29	1.03	2 8

Computation of correlations between the Differential Aptitude Tests and the EPPS Need Achievement Scores yielded a significant negative correlation for male students, but an insignificant correlation for female students. (Table 3).

TABLE 3

COEFFICIENTS OF CORRELATION BETWEEN DAT SCORES AND N. ACH. SCALE OF EPPS FOR MALES AND FEMALES.

Group	N	r
Males	40	—.34*
Females	55	.12

*Significant at .05 level.

The value of correlation coefficient computed between the Differential Aptitude Tests Scores and academic performance was insignificant for males, but a positive highly significant correlation was found for the females. (Table 4).

TABLE 4

COEFFICIENTS OF CORRELATION BETWEEN DAT SCORES AND ACADEMIC RESULTS FOR MALES AND FEMALES.

Group	N	r
Males	40	.008
Females	55	.47*

* Significant at .01 level.

Further, correlations between the Need Achievement Scale scores of the EPPS and academic results did not reveal any significant relationships either for the males or females. (Table 5).

TABLE 5

COEFFICIENTS OF CORRELATION BETWEEN N. ACH. SCALE OF EPPS AND ACADEMIC RESULTS OF MALES AND FEMALES

Group	N	r
Males	40	.23
Females	55	.12

Finally, partial correlations between the Need Achievement Scale scores and academic results were computed for each sex group holding constant the Differential Aptitude Tests scores. This was done with a view to observe whether intelligence as a factor was influencing the relation between the other two variables. Both of the resultant correlations, however, were found to be insignificant. (Table 6).

TABLE 6

COEFFICIENTS OF PARTIAL CORRELATION BETWEEN N. ACH. SCALE OF EPPS AND ACADEMIC RESULTS HOLDING CONSTANT DAT SCORES.

Group	N	r 12.3
Males	40	.25
Females	55	.073

Discussion and Implications

The general trend of the results indicated that while there appeared to be a significant difference in the Need Achievement of a combined group of male and female achievers and under-achievers, this difference became insignificant when scores of each sex group were analysed separately. However, it is recognised that failure to find a substantial relationship between these two variables could be attributable to one or more of the following reasons :

Earlier studies have suggested (Atkinson 1964) that when tasks are either very easy or very difficult, the differences in tendency to succeed are slight. In the present study the degree of difficulty of our measure of academic success based on an average of results derived from four essay type examination papers was not specified, therefore it was not possible to know whether the tasks involved in pursuit of course work leading to an examination did actually succeed in arousing such an intermediate expectancy of success as is liable to elicit the greatest amount of achievement oriented behaviour. It is recognised that the students included in the sample formed a heterogenous group in terms of ability. This means that the achievement related motivation of quite a number of students might have been less strongly aroused.

Also, it is likely that two other specific situational influences, namely, the strength of expectancy or probability of success and the incentive value of success were not operating jointly with achievement motivation in an optimum way so as to affect the direction, magnitude and persistance of achievement oriented performance.

Moreover, since achievement motivation is only one of the motives which is likely to influence academic success, it is possible that other extrinsic motives or "unrelated incentives" were also at work in this situation which tended to wash out the relationship between Need Achievement and performance.

Finally, since the method of assessing achievement motivation in the present study involved verbal statements regarding activities and attitudes for which preference was indicated by the subjects, it is possible that this method did not successfully reflect differences in achievement motivation. Possibly a Thematic Apperceptive measure or Graphic measure of achievement motivation as proposed by Aronson (1958) could be used for validation of the results.

As regards the finding that a significant negative correlation was found for male students between intellectual ability and achievement motivation, it appears that while the more intelligent male students feel unmotivated to achieve, the less intelligent are desirous of making up for this deficiency by increased desire to succeed. The implications of this finding need to be explored further since there appear to be differential effects for the two sexes.

It is also of interest to note that while intellectual ability and academic performance revealed a highly significant correlation in the case of females, there existed no relationship at all for males. This again suggests that factors other than intelligence are influencing the performance of boy students. Further, viewed in conjunction with the negative correlation between intelligence and Need Achievement found in their case, it may be suggested that while those boys that are more intelligent but are poorly

motivated may be exhibiting low scholastic achievement on this accord, those possessing a higher level of motivation but inadequate intellectual ability are poor in academic work due to this factor.

It would, therefore, appear that there were differential effects to be found for males in the relationships obtaining between intelligence and achievement motivation, and intelligence and academic success. Further investigations aimed at exploring the variables associated with such sex difference amongst Pakistani students need to be conducted.

Summary

To explore the degree of relationship between achievement motivation both with academic success and intelligence, and the relation of intelligence and academic performance, the study was so designed as to throw light on differential effects, if any, of such relationships on Pakistani post-graduate students comprising 40 males and 55 females. Groups of achievers and under-achievers were compared on a Need Achievement measure of EPPS. Although the results suggested a significant difference in achievement motivation between achievers and under-achievers in a combined group of males and females, the difference became insignificant when separate analyses were done for the two sexes.

For males, intelligence and achievement motivation were negatively correlated and intelligence and academic work were not correlated at all. For females, however, while intelligence was not correlated with achievement motivation, it was significantly correlated with academic work.

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EXACTLY SOLVABLE VELOCITY-INDEPENDENT POTENTIALS

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and

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Bhattacharjie and Sudarshan[1] (BS) have evolved a method for constructing potentials for which the Schrodinger wave equation can be solved exactly. Since only a few such potentials are known, this method is very helpful in finding out new solvable potentials. Their method is based on reducing an ordinary second order linear differential equation

$$\frac{d^2u(z)}{dz^2}+p(z)\frac{du(z)}{dz}+q(z)\,u(z)=0,$$

whose exact solution is known, to

$$\frac{d^2\phi(r)}{dr^2}+A(r)\frac{d\phi(r)}{dr}+B(r)\phi(r)=0$$

by means of the transformation

$$z=f(r),\; u(z)=g(r)\,\phi(r),\; g(r)\neq 0.$$

In order to identify this differential equation with $l=0$ radial wave equation

$$\frac{d^2\phi(r)}{dr^2}+(k^2-V)\,\phi(r)=0$$

a suitable choice of the transforming functions is made so that the coefficient $A(r)$ of $\frac{d\phi(r)}{dr}$ is zero and B, the coefficient of $\phi(r)$, is equal to k^2-V*. By this process, velocity-independent and velocity-dependent potentials can be constructed. However, in practice, the construction of velocity-independent potentials, for which the Schrodinger wave equation can be solved exactly, is very cumbersome as the presence of k^2 is a hurdle. We shall give two examples for the construction of velocity independent potentials.

*In Ref. 1, the authors have inadvertently used k^2+V instead of k^2-V almost throughout the paper.

Let us first consider the confluent hypergeometric differential equation[2]

$$\frac{d^2u(z)}{dz^2}+\frac{c-z}{z}\frac{du(z)}{dz}-\frac{a}{z}u(z)=0.$$

The transformation

$$z=f(r),\ u(z)=g(r)\phi(r),\ g(r)\neq 0,$$

gives

$$gM=e^{\frac{f}{2}}f^{-\frac{c}{2}}\left(\frac{df}{dr}\right)^{\frac{1}{2}}$$

and

$$k^2-V=\frac{\frac{d^2g}{dr^2}}{g}-\frac{a}{f}\left(\frac{df}{dr}\right)^2-\left[\frac{c-f}{f}\frac{df}{dr}-\frac{\frac{d^2f}{dr^2}}{\frac{df}{dr}}\right].$$

Let us choose

$$f=r^2.$$

Then

$$g=\sqrt{2}\,M e^{\frac{r^2}{2}}r^{-c+\frac{1}{2}}=N e^{\frac{r^2}{2}}r^{-c+\frac{1}{2}}.$$

This gives

$$\frac{\frac{dg}{dr}}{g}=r+(-c+\tfrac{1}{2})\frac{1}{r},\quad \frac{\frac{d^2g}{dr^2}}{g}=r^2-2c+2+(c^2-\tfrac{1}{4})\frac{1}{r^2}:$$

Equation (1), then, gives

$$k^2-V=-r^2+2c-4a+\left(-c^2+2c-\frac{3}{4}\right)\frac{1}{r^2}.$$

Associating k^2 with $-4a$, we get

$$V=r^2-2c+\left(c^2-2c+\frac{3}{4}\right)\frac{1}{r^2},$$

which is a velocity-independent potential.

Another velocity-independent potential can be obtained by considering Bessel's differential equation of order n[2]. This equation is

$$\frac{d^2u(z)}{dz^2}+\frac{1}{z}\frac{du(z)}{dz}+\left(1-\frac{n^2}{z^2}\right)u(z)=0.$$

The transformation

$$z=e^r,\ u(z)=\phi(r)$$

reduces it to

$$\frac{d^2\phi(r)}{dr^2}+(e^{2r}-n^2)\phi(r)=0,$$

which on identification with the Schrodinger equation gives

$$V=k^2+n^2-e^{-2r}$$

For $n^2=-k^2$, this reduces to a velocity-independent potential

$$V=-e^{-2r}.$$

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