

are consequently in error by amounts dependent on relative physical properties and sizes of containers and specimens. Preliminary calculations indicate these errors can be several per cent of reported pressures.

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¹ Bridgman, P. W., *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1952).

² Love, A. E. H., *A Treatise on the Mathematical Theory of Elasticity* (Dover Publications, New York, 1944).

GEOCHEMISTRY

Further Isotopic Age Measurements on Rocks from North-eastern Greenland

SUBSEQUENT to the publication of our earlier communication¹ a few additional critical samples of basement rocks from north-eastern Greenland were obtained and analysed. These are given in Table 1. The rubidium-strontium determination on the potassium feldspar cogenetic with the biotite from the alkali granite (*GAA-135*) confirms the presence of an ancient basement in this region. Even this age of $2,290 \pm 70$ m.y. must be regarded as a minimum due to the possibility of earlier metamorphic events. Since the potassium-argon on the biotite from this rock gave an apparent isotopic age of $1,900 \pm 50$ m.y., it seems unlikely that the ⁸⁷Sr/⁸⁷Rb ratio of the feldspar was affected by the Caledonian orogeny.

Table 1. ISOTOPIC AGES FROM ROCKS IN NORTH-EASTERN GREENLAND

I. Pre-Cambrian Basement							
Sample No.	Rock type	Mineral	Isotopic age (m.y.)	Rb p.p.m.	Normal Sr p.p.m.	Radiogenic Sr p.p.m.	Location
<i>GAA-135</i>	Alkali Granite	Feldspar	Rb/Sr = 2290 ± 70	455	8.80	4.41	70° 20' N./29° 47' W.
II. Caledonian Infra-structural Rocks (Pre-Middle Devonian)							
Sample No.	Rock type	Mineral	Isotopic age (m.y.)	K (per cent)	⁴⁰ Ar s.c.c./gm.		Location
<i>GW-73r</i>	Schist	Muscovite	K/Ar = 410 ± 10	6.74	1.23×10^{-4}		73° 11' N./27° 40' W.
<i>JH-146</i>	Granodiorite	Biotite	R/Ar = 395 ± 10	7.29	1.27×10^{-4}		73° 20' N./26° 50' W.

The potassium-argon ages on the muscovite from the schist (*GW-73R*) which was developed during the main phase of the orogeny and the biotite from the syn-orogenic granodiorite (*JH-146*) further confirm the observation that the Caledonian activity around the North Atlantic ended by 390 m.y. ago in Lower Devonian time.

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¹ Kulp, J. L., Kologrivov, R., Haller, J., and Koch, L., *Nature*, **194**, 953 (1962).

CHEMISTRY

Kinetic Law in the Adjustment Period of Natta's Polymerization

THE Ziegler-Natta polymerization of α -olefines has been widely investigated by many workers mainly from the practical point of view. On the other hand, the details of the reaction mechanism are not yet clear. There are, of course, some basic investigations of the reaction by Natta *et al.*¹, one of which is considered here; that is, the kinetic behaviour of the polymerization of propylene in the initial stages (Natta's 'the adjustment period'), where the polymerization-rate, r , changes with the polymerization time, t , from the initial rate, r_0 , at $t = 0$, to the stationary rate, r_∞ . The phenomenon can be divided into two types, that is, the build-up type and the decay type. The decay type was observed with the ground catalysts (size $\leq 2\mu$), while the build-up type was observed with the unground ones ($1 \sim 100\mu$). Analysing the latter types of rate change, Natta *et al.* found that:

$$t_N \propto 1/P \quad (1)$$

$$\ln t_N \propto 10 \text{ kcal}/RT \quad (2)$$

where t_N is the polymerization time at which the rate equals $3/4$ of the value of the stationary rate, r_∞ , and P the pressure of propylene. Natta suggested that the stationary reaction corresponds to a definite particle size of the catalyst, and any other catalyst with a different particle size would alter to this definite size.

In order to compare the kinetic behaviours of the two types, I have carried out the polymerization with the active catalyst (titanium trichloride-'ARA' of

Stauffer Co., Ltd.) and obtained some decay curves as shown in Fig. 1. Analysing the results, we have:

$$(r - r_\infty)/(r_0 - r_\infty) = \exp(-k_K t) \quad (3)$$

$$k_K = AP \exp(-6.5 \text{ kcal}/RT) \quad (4)$$

$$r_\infty = BP \exp(-10 \text{ kcal}/RT) \quad (5)$$

$$r_0 = CP \exp(-9.8 \text{ kcal}/RT) \quad (6)$$

where A , B , and C are the frequency factors. Here, it should be noted that the rate equation of the stationary polymerization (5) is in agreement with Natta's result, except for the value of B . My value of B is larger than that reported by Natta, which may be attributed to the large surface area of 'ARA' (about $20 \text{ m}^2/\text{g}$ by BET method with nitrogen adsorption).

From equation (3) we have, denoting by t_K , the time at which the rate equals $4/3$ of r_∞ :

$$t_K = \frac{1}{k_K} \ln \frac{3(r_0 - r_\infty)}{r_\infty} = \frac{\text{const.}}{k_K} \propto \frac{1}{P} \quad (7)$$

and from equations (7) and (4):

$$\ln t_K \propto \ln \frac{1}{k_K} \propto 6.5 \text{ kcal}/RT \quad (8)$$