

The energy levels rise very steeply and eventually for some value  $\pi > p$  a state will be reached for which

$$\zeta(T, \pi, p) = \zeta'(T, p),$$

where these quantities are as before.

If this condition becomes fulfilled failure will then take place by plastic deformation or "plastic shear." In other words, a substance under axial compression will become not only stronger elastically but also more malleable with increasing hydrostatic confining pressure. This is shown very clearly from the experimental results of F. D. Adams and Coker.<sup>17</sup> Their results were not duplicated by Griggs but the reason for it should be fairly obvious. Adams and Coker's confining pressure was obtained by means of a pliable steel wall, Griggs' by means of a thin liquid. As soon as incipient melting takes place along, say, a

<sup>17</sup> F. D. Adams and E. G. Coker, *An Investigation into the Elastic Constants of Rocks* (Carnegie Inst. Washington, Publ. No. 46, 1906). F. D. Adams and J. A. Bancroft, *J. Geol.* 25, 597-658 (1917).

shear plane the substance is relatively free to shear in Griggs' case because the only work involved is (a) that of breaking the remaining cohesive bonds across this plane and (b) that of exchanging regions with the pressure fluid, since the resistance to flow of the pressure fluid, for a finite rate, is a simple function of its viscosity. For Adams and Coker's case we have, in addition to (a), the work of pushing aside the supporting steel wall which is here the total lateral support. Release of strain energy can take place rapidly in the former case but only at a slow rate in the latter case.

Thus, although Griggs has expressed the belief that his results are more applicable to problems of geological deformation in depth and that rocks do not flow in the dry state, the conclusions arrived at herein do not support this contention as a general conclusion. These two apparently dissimilar experimental results are special cases of the same physical hypothesis described in this paper.

## An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures

### I. Methane, Ethane, Propane and *n*-Butane

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An empirical equation is given for the isothermal variation with density of the work content of pure hydrocarbons in the gaseous or liquid state. From this fundamental equation are derived (a) an equation of state, (b) an equation for the fugacity, and (c) an equation for the isothermal variation of the enthalpy. These equations summarize P-V-T properties of the gaseous or liquid phase, critical properties, vapor pressures, and latent heats of evaporation. A procedure is suggested for determining numerical values of the parameters in the equation. Such values are given for methane, ethane, propane, and *n*-butane. A comparison is made between observed properties of these hydrocarbons and those predicted by the equations.

#### A. INTRODUCTION

RECENT experimental studies of pure light hydrocarbons by Sage and Lacey and co-workers and by Beattie and co-workers are useful in developing an equation to represent the thermodynamic properties of these substances. An equation for this purpose has several advantages:

it permits interpolation of experimental data; it facilitates thermodynamic calculations involving integration and differentiation; it provides a concise summary of a large mass of data; and it provides a point of departure for the treatment of the thermodynamic properties of mixtures.

Concurrent with this advance in experimental