

## THE OXIDATION-REDUCTION POTENTIAL OF DIPHOSPHOPYRIDINE NUCLEOTIDE

by

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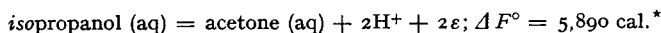
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The generally-accepted value for the oxidation-reduction potential of diphosphopyridine nucleotide (DPN) is that reported by Borsook<sup>1</sup>;  $E'_0 = -0.282$  V at pH 7.0 and 30°. This value differs from the value of  $-0.320$  V (pH 7.0 and 25°), obtained by combining data<sup>2,3</sup> for the ethanol-DPN-acetaldehyde equilibrium with reliable values for the free energy of formation of aqueous ethanol ( $-43,390$  cal.)<sup>4</sup> and acetaldehyde ( $-33,710$  cal.). The latter value is obtained from data for the gaseous substance<sup>4</sup> and the partial vapour pressure<sup>5</sup> in solution.

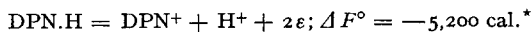
To obtain an independent value for the DPN potential, the reaction between oxidised and reduced DPN, isopropanol and acetone has been studied. This was found to be catalysed by crystalline alcohol dehydrogenase prepared according to RACKER<sup>3</sup>. The equilibrium constant is as follows (25°):

$$K = \frac{[\text{acetone}] \cdot [\text{DPN.H}] \cdot [\text{H}^+]}{[\text{isopropanol}] \cdot [\text{DPN}^+]} = 7.3 \cdot 10^{-9} M$$

Thermal data for acetone and isopropanol<sup>6,7,8</sup> are in excellent agreement with entirely independent equilibrium data for the catalytic dissociation of gaseous isopropanol into gaseous acetone and hydrogen<sup>9,10</sup>; the two  $\Delta F^\circ$  values thus obtained for this reaction differ by only 65 cal. The mean value together with vapour pressure data<sup>11,12</sup> gives at 25°:



and hence:



This corresponds to  $E'_0 = -0.320$  V (pH 7.0; 25°) which is identical with the value from the ethanol-acetaldehyde system. In view of this agreement and the reliability of the free energy data, especially those for the isopropanol system, this value of  $E'_0$  is estimated to be correct to  $\pm 0.005$  V. Full experimental and theoretical details will be submitted for publication in the *Biochemical Journal*.

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\* The standard state for dissolved reactants, including the hydrogen ion, is unit activity (1 M). Although these are hypothetical conditions for many biological reactions, their use in free energy calculations is both valid and convenient.