Table 2.

Exp.	Time after inoculation in minutes	Cold TCA-N mg per liter of culture	hot TCA-N per cell mg × 10⁻¹²	$\dfrac{\text{Cold TCA-N}}{\text{Hot TCA-N}}$ ratio
B	360	5.8	8.3	1.5
L.F.: Na-lactate	480	9.9	6.6	1.6
	540	11.3	6.6	1.6
	600	10.3	6.4	1.4
	660	10.0	6.3	1.3
	720	9.6	6.1	1.5
	721	sodium lactate added		
	780	13.1	5.9	0.7
	840	15.5	6.0	0.4

The "glycogen" was isolated and the glucose obtained from the "glycogen" as described in a paper to follow [4]. The trichloroacetic acid (TCA) extraction in experiment B was performed according to Schneider [5].

Results. The results of the "glycogen" determinations are presented in Table 1. A very rapid increase of "glycogen" per mg of dry cells, and per cell was found during the first 60—90 minutes (the lag phase). Then the "glycogen" decreased until the cell division rate began to decrease, indicating the beginning of the starvation phase. From this moment on a rapid increase in "glycogen" content was found in the nitrogen deficient cultures. In the carbon deficient culture there was also an increase during the same phase, but its rate was slower. After the addition of the limiting factors the cells began to multiply again. During this second multiplication phase the "glycogen" content immediately decreased in the nitrogen deficient cultures. In the carbon deficient one there was a short lag phase during which the "glycogen" content of the cells increased slightly, followed by a decrease.

In order to obtain a rough estimate of the relationship between the low and high molecular nucleic acid fractions, the cells were extracted with TCA according to Schneider [5]. The cold TCA fraction contains mainly low molecular and the hot TCA fraction high molecular nucleic acid derivatives.

The ratio between the nitrogen in the cold and the hot TCA extracts was higher than 1.3 during the whole carbon deficient period in experiment B, where Na-lactate was the limiting factor. After the addition of lactate the ratio rapidly decreased (Table 2).

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On the Correspondence between Thermocells and Isothermal Cells

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A theoretical relationship between the thermopotential difference of two pure thermocells and the corresponding isothermal cell has been derived recently by Holtan [1,2].

Consider for instance the thermocell

$$\text{Pt(H}_2\text{);} \quad \text{HCl}_{aq}; \quad \text{(H}_2\text{)Pt} \qquad (1)$$
$$T \qquad T + \Delta T$$
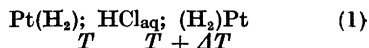
For the differential thermopotential difference of this cell we write $(\Delta\varphi/\Delta T)_1$.

Consider then the thermocell

$$\text{Ag; AgCl, HCl}_{aq}, \text{ AgCl; Ag} \qquad (2)$$
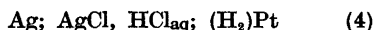$$T \qquad\qquad T + \Delta T$$
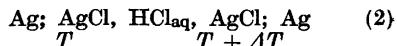
For the differential potential difference of this cell we write $(\Delta\varphi/\Delta T)_2$.

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According to the relation derived

$$(\Delta\varphi/\Delta T)_1 - (\Delta\varphi/\Delta T)_2 = (d\Delta\varphi/dT)_{is} + (\Delta\varphi/\Delta T)_m \qquad (3)$$

where $(d\Delta\varphi/dT)_{is}$ is the temperature coefficient of the isothermal cell

$$Ag; \; AgCl, \; HCl_{aq}; \; (H_2)Pt \qquad (4)$$

We have hereby used the American sign convention. Note that the German sign convention was used in references 1 and 2. $(\Delta\varphi/\Delta T)_m$ is the differential thermopotential difference of the metallic thermocouple silver-platinum.

The system (1) has been investigated experimentally for m = 1.

Two vessels connected by a siphon was used. One vessel was submerged in a Dewar vessel maintained at 0° C by means of ice. The other was submerged in an ultrathermostat. The temperature of this vessel was registered by means of a mercury precision thermometer. The potential differences were measured by means of a potentiometer from Tinsley & Co, London, 1953. The electrodes were simple of the Hildebrand type. Freshly platinized platinum electrodes from Mattey & Co., Ltd, London, were used. The platinum wires were lead all way out to the potentiometer. The hydrogen gas was generated by electrolysis and bubbled through alkaline pyrogallol solution and then through 1 M hydrochloric acid.

It is well known that the hydrogen electrode of the Hildebrand type is unstable to some degree[3], however, different sets of electrodes were tried until a set was found that showed zero potential difference at zero temperature difference.

The differential potential difference of this cell was found to be +0.60 mV/degree at 25° C (positive sign because the cold electrode was found to be positive). Owing to the difficulties mentioned, the limits of error must be considered rather large, say ±0.03 mV/degree.

The differential thermopotential difference of the system (2) for m = 1 has been determined by Bernhardt and Crockford[4] to −0.08 mV/degree (mean value in the temperature interval 25−35° C), whereas Hall and Crockford[5] found 0.02 mV/degree in the temperature interval 0−25° C.

We see that the thermopotential difference according to the figures listed above has an appreciable temperature dependence (especially for systems containing hydrochloric acid). As we want to consider the value at 25° C, the value −0.08 is somewhat high (probably of the order 0.01−0.02 mV/degree). Combining, however, this value with the experimental value for the thermocell (1), we get

$$(\Delta\varphi/\Delta T)_1 - (\Delta\varphi/\Delta T)_2 = 0.68 \text{ mV/degree.}$$

For the temperature coefficient of the isothermal cell (4) we calculate after data given by Eastman and Milner[5], Eucken, Clusius and Woitinek[7], Uhlich[8] and Rossini et al.[9] for m = 1 at 25° C

$$(d\Delta\varphi/dT)_{is} = 0.66 \text{ mV/degree}$$

As the thermoelectric power of the thermocouple silver-platinum is small (+0.01 mV/degree [10]), we see that relation (3) holds within the limits of experimental error.

We may get another test of equation (3) by comparing the two thermocells

$$\begin{matrix} Hg; Hg_2Cl_2, & MCl_{aq}^-; \; Hg \\ T & T + \Delta T \end{matrix} \qquad (5)$$
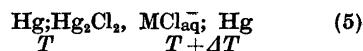
and the cell (2).

The thermopotential difference of system (5) was determined experimentally for HCl, m = 1, to 0.30 mV/degree at 25° C.

We then obtain

$$(\Delta\varphi/\Delta T)_1 - (\Delta\varphi/\Delta T)_5 = 0.30 \text{ mV/degree}$$

which favorably compares with 0.32 mV/degree calculated for the corresponding isothermal cell. In addition to data already referred to, we have used data listed by Kelly [11,12].
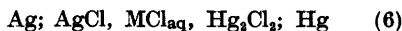
The system (5) may also be compared with system (2). Richards [13] investigated the cell (5) in the temperature interval 0−30° C. These results may then be compared with those of Crockford and Hall [5] for the temperature interval 0−25° C without introducing any large error.

In Table 1 we have listed the difference between the thermopotential differences of the systems (5) and (2).

Table 1.

Chloride		$(\Delta\varphi/\Delta T)_5 - (\Delta\varphi/\Delta T)_2$
HCl		0.31
NaCl	m = 1	0.32 Average:
KCl		0.32 0.32 mV/degree
HCl		0.33
NaCl	m = 0.01	0.32 Average:
KCl		0.30 0.32 mV/degree

For the isothermal cell

$$Ag;\ AgCl,\ MCl_{aq},\ Hg_2Cl_2;\ Hg \qquad (6)$$

we obtain $(d\Delta\varphi/dT)_{is} = 0.34$ mV/degree at 25°C.

As the thermoelectric force of the thermocouple silver-mercury is small (about 0.01 mV/degree [10]), we again find that the relation (3) holds within the limits of experimental error.

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Oxidative Stress Relaxation of Natural Rubber Vulcanized with Di-*Tertiary*-Butyl Peroxide

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It has been shown by Farmer and Moore [1] that natural rubber can be vulcanized with di-*tert.*-butyl peroxide (DTBP). Presumably the free radicals formed by the unimolecular decomposition of the peroxide abstract some of the more labile (*e. g.* α-methylenic) hydrogen atoms leading to direct C—C crosslinks between the rubber molecules, *tert.*-butanol and acetone being the main reaction products.

This preliminary communication presents some of the results of an investigation of the oxidative stress relaxation of the following types of DTBP vulcanizates: (A). First grade pale crepe, DTBP, and some carbon black (MPC) mixed on the mill and vulcanized in a press. The carbon black was added to minimize the deleterious effect of impurities. (B). Purified rubber vulcanized: 1. In aqueous heating media. 2. In the press. 3. In DTBP vapour.

(A). In Fig. 1 is plotted on a logarithmic scale the relaxation curves for a vulcanizate with 20 % MPC vulcanized for 15 minutes at 160° and relaxed in air at 90—140° (modulus 2.57 kg/cm² at an extension ratio of 1.2). A rapid initial rate of relaxation due primarily to peroxidic reaction products, was eliminated by preheating the samples *in vacuo* for 30
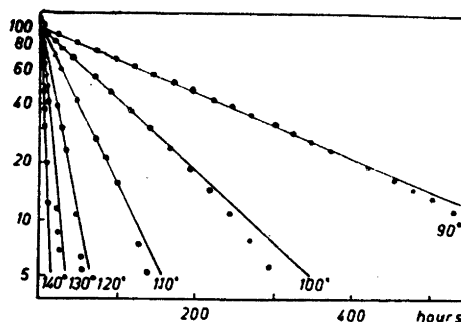

Fig. 1. Relaxation curves. Ordinate: % *of original stress. Abscissa: hours.*