of a heat engine is a matter of common observation, with which, presumably, even Dr. Haldane agrees. Carnot summed up the situation in the converse statement: "Wherever there exists a difference of temperature, motive power can be produced." Carnot went on to show that the efficiency of a thermo-dynamically reversible cycle is proportional to the temperature range solely, and that for a given temperature range no heat engine cycle can possibly be more efficient than a thermo-dynamically reversible one.

Now Dr. Haldane's cycle is not thermo-dynamically reversible. Carnot's cycle is thermo-dynamically reversible; therefore, Dr. Haldane's cycle cannot possibly be more efficient than Carnot's cycle. Further, since, by definition, efficiency $= \dfrac{\text{work done}}{\text{heat supplied}}$, it is evident that efficiency is a ratio independent of the actual magnitudes of the quantities involved, so that to base a comparison of efficiencies on a given quantity of heat is valueless.

In his second published reply to his critics, Dr. Haldane abandons this point of view and attacks the particular theorem, that is, he tries to prove that Carnot wrongly assessed the efficiency of a reversible cycle as $1 - (T_2/T_1)$.

The real thermal efficiency, as Dr. Haldane correctly says, is given by the fraction $(H-h)/H$, when H is the total heat communicated to the working substance and h the heat energy or heat equivalent of the work lost in recompression, but, by total heat communicated, Dr. Haldane says he means the heat supplied from the source during isothermal expansion, *plus* the heat accumulated in the working substance during adiabatic compression. This reasoning leads for the efficiency of the Carnot cycle to

$$\left\{ \dfrac{T_1 - T_2}{T_1 + \dfrac{(K_v T_1 - T_2)}{R \log_e x}} \right\}.$$

Since, however (as Dr. Haldane himself admits on p. 394 of his original paper), the work done by the engine during adiabatic expansion is exactly equal to the negative work done during adiabatic compression, it is evident that the only source from which the engine receives its heat is the external source. This is the accepted view, and it leads to Carnot's expression for the efficiency, namely, $1 - (T_2/T_1)$.

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Chemical Effects produced by Resonance Radiation.

DR. RIDEAL having started an investigation of reactions which we discovered last spring, and which one of us (H. S. T.) stated publicly in Oxford so late as last October were being further studied, it seems desirable to place on record some of the results to which such further studies have led, especially as they show a marked divergence from the results of Hirst and Rideal (NATURE, **116**, 899, December 19, 1925).

We are quite unable to subscribe to the conclusion of Hirst and Rideal that hydrogen and oxygen combine very slowly both in the absence and presence of mercury vapour, and only combine rapidly in the presence of a layer of liquid mercury. Our experiments show that hydrogen and oxygen, with the concentration of mercury vapour obtained by bubbling these gases through liquid mercury at room temperatures, will combine rapidly in the presence of the resonance radiation from the cooled mercury arc. Furthermore, we have shown that hydrogen peroxide

is a prior product of reaction appearing in marked quantities at high rates of gas flow, whereas with slower rates of flow the peroxide formed decreases and the water formed increases. In this manner we have been able to cause the gases to react to produce either exclusively hydrogen peroxide or mixtures of this with water. We have further shown that many hundred molecules of hydrogen peroxide are produced for every mercury atom passing through the zone of radiation, and that mercuric oxide is formed. The removal of mercury vapour in this manner may have given rise to the anomalous results of Hirst and Rideal. In the absence of mercury vapour, no peroxide or water is formed under our experimental conditions, but the shorter wave-lengths in the mercury arc do produce a certain amount of ozonisation, which also occurs even when mercury vapour is present.

The quantity of hydrogen peroxide produced varies with several factors; the rate and composition of gas flow, the temperature, the concentration of mercury vapour, and the intensity of illumination. We shall record in more detail elsewhere the experimental data thus obtained.

Since hydrogen peroxide is demonstrably present in the gas phase, it is obvious that a liquid mercury surface must influence the velocity in some manner, since it has long been known that hydrogen peroxide is readily decomposed at a mercury surface. We have, however, no data, in a very considerable body of experimental work, which would assign any of the *photosensitised* process to the liquid mercury. Nor does there appear to be any sound theoretical reason why mercury atoms in a liquid surface should be more effective than those in the gas phase. Cario and Franck showed also that the quenching of the fluorescence of mercury vapour by hydrogen was proportional to the chemical reaction which could thereby be produced. Secondary effects similar to that just mentioned in the presence of hydrogen peroxide will also effect the velocity in the combination of hydrogen and ethylene and in the combination of hydrogen and carbon monoxide, in these cases, however, adversely. For we have shown that the resonance radiation causes a polymerisation of ethylene with the formation of liquid condensation products, and formaldehyde polymerises to solid products as we pointed out in our initial communication on the subject.

We are inclined to assign the variability of reaction rate in the presence of liquid mercury at room temperature entirely to variations in the concentration of mercury vapour caused by removal as mercuric oxide and irregular renewal due to skin effects on the liquid surface. By operation at higher temperatures (60°-70° C.) such variable behaviour completely disappears, as shown by one of us (A. L. M.) in a recent paper (*J. Phys. Chem.*, **30**, 34, 1926). Our view is strengthened by actual measurements of absorption of resonance radiation by mercury in the presence of various gases, material which will also shortly be published.

We have markedly improved the technique of the study of the chemical effects produced by resonance radiation as exemplified by the apparatus already described by one of us (A. L. M.), and by a new form of apparatus, through which, by building the arc system around the quartz reaction vessel, we avoid the use of quartz-mercury arcs and can operate with Pyrex glass arcs.

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A. L. MARSHALL.
J. R. BATES.

Princeton University,
    Princeton, New Jersey,
        January 20.