

tion methods; systems involving the $^{16}\text{O}(n, p)^{16}\text{N}$ reaction, and others dependent on the liberation of the gases by means of a d.c. arc followed by gas chromatographic or spectrographic measurements.

We have been interested in the development of a device which would be relatively inexpensive and at the same time simple enough to allow of some degree of automation to speed up the process. In the past we have used the high-temperature hollow cathode successfully for the determination of trace metals in refractory oxides, and in these analyses we have noticed the presence of the oxygen line at 7772 Å in the spectra, and this suggested a convenient method for the determination of oxygen in metals. Rosen^{1,2} has used this type of spectrographic source for the determination of oxygen extracted into argon atmospheres and he made use of the intensity of various carbon monoxide bands in emission and absorption. In our experience more reliable results are obtained by using the atomic line for oxygen in emission. In principle our method consists in using a high-temperature hollow cathode discharge to melt the sample and excite the atomic spectrum of oxygen. A compact grating monochromator with two red-sensitive photomultipliers is used to record the intensity of the oxygen line at 7772 Å and that of the adjacent background, and the line/background ratio is presented on a chart. Provision is made for nine samples to be fed in succession into the hollow cathode from a turret head; the helium gas-scavenging train is fitted with electromagnetically operated valves and the whole sequence of operations is electronically controlled on an automatic cycle taking 4 min per sample. Recharging the sample turret and outgassing it takes 30 min. Determinations can be made on sample weights up to 200 mg, and the sensitivity is better than 1 µg of oxygen.

The potentialities of this device have not yet been fully explored and it is considered that the simultaneous determination of oxygen, hydrogen and possibly nitrogen in steel and a variety of other materials is feasible.

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CHEMISTRY

Effects of mechanically produced Capillary Waves on the Evaporation of Water through Monolayers

THE extensive measurements¹ on the retardation of evaporation by monolayers conducted during the past decade at Columbia University have been restricted to static conditions to eliminate the erratic results arising from uncontrollable turbulence induced by a current of air passed over the surface of the water. We have extended these investigations by producing capillary waves of wave-length 0.5 cm, of frequency 60 c/s, and of amplitudes extending from 0.08 cm to 0.03 cm, by the action of a mechanical vibrator, that is, we have measured the effects of waves without the complication of wind.

Up to a surface pressure of 18 dynes cm⁻¹, the pressure-area diagram follows closely that of the static monolayer surface, corrected for a small increase in area of a rippled surface. At pressures above 20 dynes cm⁻¹ considerable deviations occur; for the shorter chain alcohol (C₁₄OH) we were unable to produce surface pressures exceeding 28 dynes cm⁻¹ at any compression. These deviations were progressively less marked with the longer chain alcohols,

but still amount to an area 25 per cent less than for the static surface at 40 dynes cm⁻¹ for C₁₄OH and C₂₀OH. The decrease in surface pressure due to the wave action for a given molecular area decreased progressively as the initial wave amplitude was increased from zero to 0.08 cm. Our experiments suggest that monolayer molecules at pressures exceeding 20 dynes cm⁻¹ are being submerged by the wave rather than being collapsed into islands of 'Duflex' film.

As might be expected, the rate of transfer of water through the monolayer increased as the static surface was disturbed, the specific resistance to evaporation decreasing roughly to 60 per cent of the static value for the alcohols of chain-length 14, 16, 18 and 20. These investigations indicate that a disturbed condition of the monolayer, even for such small amplitudes as 0.03–0.08 cm, interferes with the retardation of evaporation so that effects in the field, as compared with the ideal conditions observed in the laboratory under static conditions, can never be achieved. Nevertheless, it is remarkable the extent to which a fragile monolayer will reduce evaporation under field conditions when proper precautions have been taken in respect to purity of material spread, absence of solvents, and proper spreading methods such as dusting the material as a fine solid powder¹⁻³.

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Concerning the Isokinetic Relationship

IN contemporary kinetic studies, the values of rate constants are often expressed by means of activation parameters, either by the activation energy E^* and the pre-exponential factor A , or by the activation enthalpy ΔH^\ddagger and entropy ΔS^\ddagger . For further discussions in terms of substituent or solvent effects and similar theories of organic chemistry, many authors¹ prefer the free activation energy ΔG^\ddagger (that is, the logarithm of the rate constant) at an arbitrary temperature before the activation energy E^* or enthalpy ΔH^\ddagger . If the results of such discussions have to be independent of the arbitrary temperature, a functional dependence must exist between the activation parameters in a series of related reactions. This dependence is also the necessary condition² for the validity of various linear free-energy relationships (for example, Hammett equation) at different temperatures. In fact, linear relationships obtained by plotting E^* versus $\log A$ or ΔH^\ddagger versus ΔS^\ddagger have been described many times²⁻⁶. They are referred to as the isokinetic relationship² or the compensation law⁴ (equations 1a and b). The proportionality factor β , called the isokinetic temperature, has been also discussed theoretically^{2,5}:

$$\Delta H^\ddagger = \Delta H^0 + \beta \Delta S^\ddagger \quad (1a)$$

$$\text{or} \quad E^* = E^0 + 2,303 R \beta \log A \quad (1b)$$

In this communication we wish to show that the method by which these relationships were established is incorrect and the correlations obtained fallacious. Some authors^{2,4,5,7} were aware of a certain danger in such correlations, but the proper essence of the problem, that is, the mutual dependence of the quantities correlated, was not grasped.