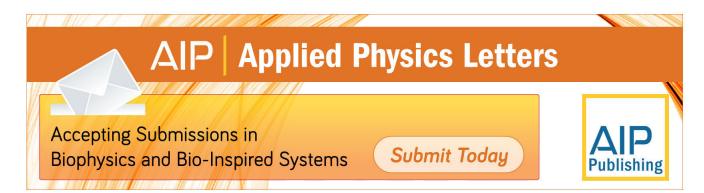TABLE IV. Thermodynamic functions of sulfur trioxide (hypothetical ideal gas at 1 atmos. pressure).

$T(°K)$	$-(F^0-H_0{}^0)/T$ cal./deg./mole	S^0 cal./deg./mole	$(H^0-H_0{}^0)$ kcal./mole	$C_p{}^0$ cal./deg./mole
298.16	51.94	61.24	2.77	12.10
300	52.00	61.32	2.80	12.13
400	54.81	65.07	4.10	14.05
500	57.17	68.36	5.60	15.66
600	59.31	71.35	7.22	16.89
700	61.23	74.03	8.96	17.85
800	62.98	76.46	10.78	18.61
900	64.61	78.69	12.67	19.22
1000	66.12	80.75	14.63	19.75
1100	67.54	82.65	16.63	20.20
1200	68.87	84.42	18.67	20.59

TABLE V. Contributions of vibrational anharmonicity to thermodynamic functions of $SO_3(g)$.

$T(°K)$	$-F_e$ (cal./mole)	H_e (cal./mole)	S_e (cal./deg./mole)	C_e (cal./deg./mole)
300	2.4	18	0.07	0.16
600	56	153	0.35	0.79
1000	310	628	0.94	1.56

compared with those of previous investigators in Table III.

By combination of our results for reaction (1) with the accurate thermochemical heat of formation of sulfur dioxide[19] and the accurate entropy

[19] F. R. Bichowsky and F. D. Rossini, *Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936), pp. 27–28.

values for sulfur[20] and oxygen,[17] the following constants for the formation of sulfur trioxide from the elements are obtained:

$$S(rh)+\tfrac{3}{2}O_2(g)=SO_3(g); \qquad (10)$$

$$\Delta F^o_{298.16}=-88.48\pm0.20 \text{ kcal.};$$

$$\Delta H^o_{298.16}=-94.43\pm0.15 \text{ kcal.};$$

$$\Delta S^o_{298.16}=-19.95\pm0.20 \text{ E. U.}$$

These figures are more trustworthy than those tabulated by Yost and Russell,[6] who give the early free-energy value of Lewis and Randall[4] and the rather uncertain thermochemical[19] heat of formation.

The calculated thermodynamic properties of sulfur trioxide in the ideal gas state are presented in Table IV, for the temperature range 298°–1200°K. The magnitudes of the anharmonic contributions to these figures can be judged from the several representative values given in Table V. The standard entropy of $SO_3(g)$ can be taken as $S^o_{298.16}=61.2\pm0.2$ E. U.

It is a pleasure to acknowledge helpful discussions with Drs. C. C. Stephenson and L. Tisza.

[20] E. D. Eastman and W. C. McGavock, J. Am. Chem. Soc. **59**, 145 (1937).

Effect of Deformation on the Swelling Capacity of Rubber

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(Received July 3, 1944)

Elongation of swollen vulcanized rubber, or other polymeric materials possessing random network structures, should increase the amount of liquid absorbed (dissolved) at equilibrium with an excess of the swelling agent. According to a previously published equation relating to the thermodynamics of stretching and swelling of rubber, the relative volume of the swollen rubber at equilibrium should equal the square root of the relative stretched length. Experiments with butyl rubber vulcanizates in xylene support these predictions of theory.

IN a recent paper[1] dealing with the thermodynamics of swelling of vulcanized rubber in solvents, the following equation was derived to express the entropy change in passing from the

[1] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. **11**, 521 (1943).

unstressed, unswollen state to the *stretched, swollen* state,

$$\Delta S_{d,s}=-kn\ln\left[n/(n+Zv)\right]$$
$$-(3/2)kv\left[\left(\frac{n+Zv}{Zv}\right)^{\frac{2}{3}}(\alpha^2+2/\alpha)/3-1\right], \quad (1)$$

where k is Boltzmann's constant, n is the number of solvent molecules, ν is the number of "chains" or portions of rubber molecules between cross linkages of the vulcanizate network, Z is the ratio of the volume of a chain to the volume of a solvent molecule, and α is the ratio of the length of the *elongated, swollen* sample to its length in the *unstressed, swollen* condition. From this equation the effects of swelling on elastic properties and the influence of stretching on swelling capacity can be predicted.

In our previous paper[1] we drew the incorrect conclusion from the above equation that the rubber gel, in equilibrium with excess solvent, should de-swell when stretched. In obtaining this result, Eq. (1) was differentiated with respect to n to obtain a partial molal entropy at constant α, instead of at constant absolute length. The equilibrium condition so introduced applies only to the rather artificial situation in which the rubber is stretched such that its length is always α times the length it would assume at the same degree of swelling in the absence of stress (recalling the definition of α). In other words, the length L of sample is to be adjusted in conformity with

$$L = \alpha L_0 V^{\frac{1}{3}},$$

where L_0 is the unstressed, unswollen length and V is the volume swelling ratio (volume of gel/volume of dry rubber), and α is fixed. It is the purpose of this note to show, contrary to a statement which occurs in our preceding paper,[2] that Eq. (1) predicts an *increase* in equilibrium swelling volume with increase in the absolute length to which the swollen sample is stretched. Experimental results are included below in support of this deduction.

Introducing a new stretch factor α' defined as the ratio of the *stretched, swollen* length to the *unstretched, unswollen* length

$$\alpha' = L/L_0 = \alpha V^{\frac{1}{3}},$$

where the volume swelling ratio V is given alternatively by

$$V \equiv (n+Z\nu)/Z\nu \equiv 1/v_2,$$

where v_2 is the volume fraction of rubber in the

swollen gel. Substituting

$$\alpha = \alpha'[Z\nu/(n+Z\nu)]^{\frac{1}{3}}$$

in Eq. (1) and differentiating with respect to n at constant α', there is obtained for the partial molal free energy of solvent

$$\Delta \bar{F}_1(\text{const. } \alpha')$$
$$= RT[\ln (1-v_2)+v_2+Kv_2^2/2+1/\alpha'Z], \quad (2)$$

the third term of which represents a van Laar heat of mixing term.[3] For equilibrium with excess solvent to prevail at constant length, $\Delta \bar{F}_1$ (const. α') must equal zero. At equilibrium, therefore,

$$-[\ln (1-v_2)+v_2+Kv_2^2/2)] = 1/\alpha'Z. \quad (3)$$

Taking v_2 to be small (large swelling), expansion of the logarithmic term in series yields the approximate expression

$$1/V = v_2 \cong [2/\alpha'Z(1-K)]^{\frac{1}{2}}. \quad (3')$$

In the unstretched, swollen sample $\alpha' = V^{\frac{1}{3}}$. Hence, writing V_0 for the swelling volume in the unstretched, swollen condition

$$V/V_0 = (\alpha'/V_0^{\frac{1}{3}})^{\frac{1}{2}} = (\alpha'/\alpha_0')^{\frac{1}{2}}. \quad (4)$$

Thus, the swelling volume is predicted to increase in proportion to the square root of the length. These same equations may be applied to simple compression, where $\alpha' < \alpha_0'$.

Experimental measurements on the influence of stretching on swelling were conducted on molded rings of pure gum butyl rubber, 0.25 in. wide by about 0.050 in. thick and having a mean diameter of 1.00 in. These were prepared by curing a compound consisting of 100 parts B-1.5 butyl rubber, 1.0 part zinc oxide, 1.5 parts sulfur, and 1.0 part tetramethylthiuram disulfide for one hour at 153°C. The swelling liquid was reagent-grade xylene containing 0.05 percent phenyl β-naphthylamine antioxidant.

A ring was weighed to the nearest mg, and two $\frac{5}{16}$-in. glass rods of short length were inserted through it. One of these served as an upper (fixed) support; to the other a lead weight

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[2] Second line, p. 526 of reference 1.

[3] In analogous equations of previous papers we have replaced Z with $M_c/\rho V_1$ where M_c is the molecular weight per chain of relative volume Z, ρ is the density of the dry rubber, and V_1 is the molar volume of the solvent.

was attached. The assembly consisting of glass rods, rubber ring, and weight, was immersed in the xylene contained in a tall cylinder. This procedure was adopted after it had been found that stretching to an arbitrary field length followed by immersion in solvent invariably resulted in rupture. A considerable tension is required to achieve the desired elongation prior to swelling. In the presence of solvent the strength is so much reduced that rupture occurs before the tension can be sufficiently relieved by swelling. In the method adopted here elongation proceeds concurrently with swelling, and at no time is the rubber subjected to a high stress.

After allowing swelling to proceed at room temperature in darkness for 24 hours, the over-all vertical length of the loop was measured with a cathetometer. From this length, the diameters of the glass rods, and the approximate thickness of the swollen rubber, the mean circumferential length of the swollen specimen was computed (fourth column of Table I). The assembly was then removed from the xylene bath, excess solvent was blotted away with filter paper while the sample remained under tension, and the sample was immediately removed and placed in a weighing bottle and weighed. Thereafter the ring was again installed between the glass rods and replaced in the xylene under tension as before. Measurements were repeated after additional periods of 24 and 96 hours. Weights of the swollen rings for one, two, and five days immersion agreed within the experimental error— about ± 0.01 gram. Average weights are recorded in the third column of Table I.

Taking 0.93 and 0.86 for the densities of the butyl compound and the xylene, respectively, the volumes of dry rubber and swollen gel were computed. (The volume change on mixing is negligible.) Their ratio, the swelling ratio V, is given in the fifth column. The relative lengths α' were computed by dividing the absolute lengths of the fourth column by 7.98 cm, the mean circumferential length of the unstretched, unswollen ring.

The observed ratio of the V's for stretched and unstretched samples are given in the next to the last column. Values calculated from α' and α_0' using Eq. (4) are given in the last column. Comparisons between these two columns show that the observed effect of elongation on swelling is in

TABLE I. Effect of elongation on equilibrium swelling.

Load in g*	Weight of butyl ring, g	Weight of swollen ring, g	Mean circumferential length of swollen ring, cm	Swelling ratio V	α'	V/V_0 Obs.	V/V_0 Calc.
0	0.570	3.06	(14.20)**	5.72	(1.78)**		
50	0.570	3.11	15.45	5.81	1.93	1.01_6	1.04
100	0.564	3.13	16.41	5.92	2.06	1.03_5	1.07_5
150	0.568	3.44	18.15	6.46	2.27	1.13	1.13

* Uncorrected for buoyancy of xylene on submerged weight.
** Values calculated from swelling ratio; i.e., α' for zero load equals $V^{\frac{1}{3}}$, since swelling is isotropic.

the proper direction and that its magnitude approximates the predictions of theory.

The set of results shown in the table was obtained on four different rings. Some of the irregularity undoubtedly is owing to variations in cure from one ring to another, although all of these were cured from the same compound under as nearly identical conditions as possible. The increase in swelling with elongation is reversible. In an experiment to check this point, removal of the load from the ring was followed by a decrease in swelling volume to the same value obtained on another unstressed sample of the same rubber.