methane on these surfaces. It appears from Kemball's researches[8] that methane permits a similar differentiation between metal surfaces and their capacity to chemisorb gases.

Acknowledgment.—This work has been made possible by a generous grant from Baker and Co. to the James Forrestal Research Center at Princeton which is being used for work in catalysis by platinum metals and for studies in the metal science of these elements. Our thanks are due especially to Mr. Chas. W. Engelhard for financial support, and to Dr. E. F. Rosenblatt and to Dr. W. Cohn for assistance in the preparation and provision of catalytic materials. We express our thanks also to Dr. M. Boudart for supervision and criticism of this work.

(8) C. Kemball, *Proc. Roy. Soc. (London)*, **A217**, 376 (1953).

PRINCETON, N. J.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Reduced Equation for Viscoelastic Behavior of Amorphous Polymers in the Transition Region[1]

BY A. V. TOBOLSKY AND E. CATSIFF

RECEIVED FEBRUARY 6, 1954

A law of corresponding states is proposed for the viscoelastic properties of amorphous polymers in the transition region. Tables are presented from which the modulus–temperature curve (modulus measured after any fixed time t_1) can be constructed for many polymers.

Introduction

In previous publications,[2,3] it was proposed that the composite stress–relaxation curves of amorphous polymers in the transition region could be adequately reproduced by the equation

$$\frac{\log E_r(t/K) - \frac{1}{2}\log E_1E_2}{\frac{1}{2}\log (E_1/E_2)} = -\operatorname{erf}\,(h \log t/K) \quad (1)$$

where

$E_r(t/K) = E_{r,T}(t)$ = stress/strain in a sample maintained at a constant small strain for a time t at a temp. T

K = characteristic relaxation time, a function of temp. only for a given polymer

E_1 = quasistatic glassy modulus (usually about $10^{10.5}$ dynes/cm.^{2})

E_2 = quasistatic rubbery modulus (usually between 10^7 and 10^8 dynes/cm.^{2})

h = a parameter characteristic of each polymer

$\operatorname{erf} x = 2\pi^{-1/2}\int_0^x \exp(-x^2)\,dx$, the error integral[4]

Furthermore, it was shown that the temperature dependence of K for the polymers studied to date was

$$h \log K_R = f(T_R)$$

with $f(T_R)$ very nearly the same for all polymers. $f(T_R)$ is tabulated in Table I.

$K_R = K/K_d$

$K_d = K$ at T_d

$T_R = T/T_d$

T_d = distinctive temp. which is related to, if not equal to, the glass transition temp.

The Reduced Equation of Viscoelastic Behavior.—Just as it is very convenient to express compressibility data of fluids in terms of reduced temperature, pressure and volume, it would also be very desirable to express the viscoelastic properties of amorphous substances in terms of reduced variables. In this case, the most important reduced variable is the reduced temperature $T_R = T/T_d$. Qualitatively, the viscoelastic properties of amorphous polymers (in the transition region) are very similar at the same value of the reduced temperature. It is the purpose of this paper to establish this relation in a quantitative sense.

TABLE I

REDUCED-TEMPERATURE DEPENDENCE OF $f(T_R)$

T_R	$f(T_R)$	T_R	$f(T_R)$
0.940	1.62	1.000	0.00
.945	1.55	1.005	− .18
.950	1.46	1.010	− .34
.955	1.36	1.015	− .50
.960	1.25	1.020	− .63
.965	1.11	1.025	− .78
.970	0.98	1.030	− .92
.975	.84	1.035	−1.06
.980	.69	1.040	−1.18
.985	.52	1.045	−1.31
.990	.36	1.050	−1.43
.995	.18		

Equation 1 is essentially a five-parameter reduced equation for viscoelastic behavior of amorphous polymers in the transition region. However, it is not the simplest reduced equation possible. By comparing the values of h and T_d obtained in papers I and II on six amorphous polymers, it becomes clear that $hT_d = 100$ (± 3.7) (in °K.). Also $\log K_d = -1.45$ (± 0.12) (in hours).

If these values are substituted in equation 1 the following is obtained

$$Y = \frac{\log E_{r,T}(t) - \frac{1}{2}\log E_1E_2}{\frac{1}{2}\log (E_1/E_2)} = -\operatorname{erf}\left[\frac{100}{T_d}(\log t + 1.45) - f(T/T_d)\right] \quad (2)$$

(1) Part III of a series on elastoviscous properties of amorphous polymers in the transition region.

(2) J. Bischoff, E. Catsiff and A. V. Tobolsky, THIS JOURNAL, **74**, 3378 (1952), hereinafter called paper I.

(3) E. Catsiff and A. V. Tobolsky, *J. Appl. Phys.*, in press, hereinafter called paper II.

(4) Tables of the error integral may be found in Jahnke and Emde, "Tables of Functions," B. G. Teubner, Leipzig and Berlin, 1933; J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., London, 1909.

TABLE II

VALUES OF $X = (100/T_d)(\log t + 1.45)$

T_d, °C / t, hr.	−70	−60	−50	−40	−30	−20	−10	0	10	20
10^{-6}	−2.24	−2.13	−2.04	−1.95	−1.87	−1.80	−1.73	−1.665	−1.605	−1.55
$10^{-5.5}$	−1.99	−1.90	−1.82	−1.74	−1.66	−1.60	−1.54	−1.48	−1.43	−1.38
10^{-5}	−1.745	−1.66	−1.59	−1.52	−1.46	−1.40	−1.35	−1.30	−1.25	−1.21
$10^{-4.5}$	−1.50	−1.43	−1.37	−1.31	−1.25	−1.20	−1.16	−1.12	−1.08	−1.04
10^{-4}	−1.25	−1.195	−1.14	−1.09	−1.05	−1.01	−0.97	−0.93	−0.90	−0.87
$10^{-3.5}$	−1.01	−0.96	−0.92	−0.88	−0.84	−0.81	−.78	−.75	−.725	−.70
10^{-3}	−0.76	−.725	−.695	−.665	−.64	−.61	−.59	−.57	−.55	−.53
$10^{-2.556}$	−.545	−.52	−.495	−.47	−.455	−.44	−.42	−.405	−.39	−.38
$10^{-2.5}$	−.52	−.49	−.47	−.45	−.43	−.415	−.40	−.38	−.37	−.36
0.0100	−.27	−.26	−.25	−.24	−.23	−.22	−.21	−.20	−.19	−.19
.0316	−.025	−.02	−.02	−.02	−.02	−.02	−.02	−.02	−.02	−.02
.100	.22	.21	.20	.19	.185	.18	.17	.165	.16	.15
.316	.47	.445	.43	.41	.39	.375	.36	.35	.335	.32
1.000	.71	.68	.65	.62	.60	.57	.55	.53	.51	.495
3.162	.96	.91	.87	.835	.80	.77	.74	.715	.69	.665
10.00	1.205	1.15	1.10	1.05	1.01	.97	.93	.895	.865	.835
31.62	1.45	1.38	1.32	1.26	1.21	1.16	1.12	1.08	1.04	1.01
100.0	1.695	1.62	1.55	1.48	1.42	1.36	1.31	1.26	1.22	1.18
316.2	1.94	1.85	1.77	1.69	1.62	1.56	1.50	1.445	1.39	1.35
10^{3}	2.185	2.08	1.99	1.91	1.83	1.76	1.69	1.63	1.57	1.52
$10^{3.5}$	2.43	2.32	2.22	2.12	2.04	1.955	1.88	1.81	1.75	1.69
10^{4}	2.68	2.56	2.44	2.34	2.24	2.15	2.07	1.99	1.92	1.86
$10^{4.5}$	2.92	2.79	2.67	2.55	2.44	2.35	2.26	2.18	2.10	2.03
10^{5}	3.17	3.02	2.89	2.76	2.65	2.545	2.45	2.36	2.28	2.20
$10^{5.5}$	3.42	3.26	3.12	2.98	2.86	2.74	2.64	2.54	2.45	2.37
10^{6}	3.66	3.49	3.34	3.19	3.06	2.94	2.83	2.72	2.63	2.54

T_d, °C / t, hr.	30	40	50	60	70	80	90	100	110	120	130
10^{-6}	−1.50	−1.45	−1.41	−1.36	−1.32	−1.29	−1.25	−1.22	−1.19	−1.15	−1.13
$10^{-5.5}$	−1.34	−1.29	−1.25	−1.21	−1.18	−1.145	−1.11	−1.09	−1.06	−1.03	−1.00
10^{-5}	−1.17	−1.13	−1.10	−1.06	−1.03	−1.005	−0.975	−0.95	−0.925	−0.90	−0.88
$10^{-4.5}$	−1.01	−0.97	−0.94	−0.915	−0.89	−0.86	−.84	−.82	−.795	−.775	−.755
10^{-4}	−0.84	−.815	−.79	−.765	−.74	−.72	−.70	−.68	−.665	−.65	−.63
$10^{-3.5}$	−.675	−.655	−.635	−.615	−.60	−.58	−.565	−.55	−.535	−.52	−.51
10^{-3}	−.51	−.495	−.48	−.465	−.45	−.44	−.43	−.415	−.40	−.39	−.38
$10^{-2.556}$	−.365	−.35	−.34	−.33	−.32	−.31	−.305	−.295	−.29	−.28	−.27
$10^{-2.5}$	−.35	−.335	−.325	−.315	−.305	−.30	−.29	−.28	−.27	−.265	−.26
0.0100	−.18	−.175	−.17	−.165	−.16	−.16	−.15	−.15	−.14	−.14	−.135
.0316	−.02	−.02	−.015	−.015	−.015	−.01	−.01	−.01	−.01	−.01	−.01
.100	.15	.14	.14	.135	.13	.13	.12	.12	.12	.115	.11
.316	.31	.30	.29	.285	.28	.27	.26	.255	.25	.24	.235
1.000	.48	.46	.45	.435	.42	.41	.40	.39	.38	.37	.36
3.162	.64	.62	.60	.585	.57	.55	.535	.52	.51	.495	.485
10.00	.81	.78	.76	.735	.71	.69	.675	.655	.64	.62	.61
31.62	.97	.94	.91	.885	.86	.835	.81	.79	.77	.75	.73
100.0	1.14	1.10	1.07	1.03	1.00	.975	.95	.925	.90	.87	.855
316.2	1.30	1.26	1.22	1.18	1.15	1.12	1.09	1.06	1.03	1.00	0.98
10^{3}	1.47	1.42	1.37	1.33	1.295	1.26	1.22	1.19	1.16	1.13	1.10
$10^{3.5}$	1.63	1.58	1.53	1.48	1.44	1.40	1.36	1.33	1.29	1.26	1.23
10^{4}	1.80	1.74	1.68	1.63	1.585	1.54	1.50	1.46	1.42	1.38	1.35
$10^{4.5}$	1.96	1.90	1.84	1.78	1.73	1.68	1.64	1.60	1.55	1.51	1.47
10^{5}	2.13	2.06	1.99	1.93	1.875	1.82	1.77	1.73	1.68	1.64	1.60
$10^{5.5}$	2.29	2.22	2.15	2.08	2.02	1.97	1.91	1.86	1.81	1.76	1.72
10^{6}	2.46	2.38	2.30	2.23	2.16	2.11	2.05	1.99	1.94	1.89	1.85

Equation 2 is the reduced equation for viscoelastic behavior of the six polymers studied thus far; the relaxation modulus at any time and temperature, $E_{r,T}(t)$, can be obtained from equation 2 and Table I provided that T_d, E_1 and E_2 are known. Since E_1 and E_2 do not differ very much from one polymer to another, the variation of $E_{r,T}(t)$ from one polymer to another should depend mainly on T_d. From $E_{r,T}(t)$ all other viscoelastic properties can be derived.

The extent to which equation 2 is a valid one for the six polymers studied thus far is shown in Fig. 1. In this figure the new variable Z, related to Y of equation 2 as shown below, was plotted as ordinate on probability paper (*e.g.*, Codex 32,451) in the form

$$Z = \frac{1}{2}(1 + Y) \times 100 = \frac{\log E_{r,T}(t) - \log E_2}{\log E_1 - \log E_2} \times 100 \quad (2a)$$

The argument of the error integral function in equation 2 was plotted as abscissa using the experimentally determined values of T_d. The ordinate scale of probability paper is so designed that such a plot should give a straight line of fixed slope if the experimental data are described by equation 2. This is shown by a heavy black line in the figure.

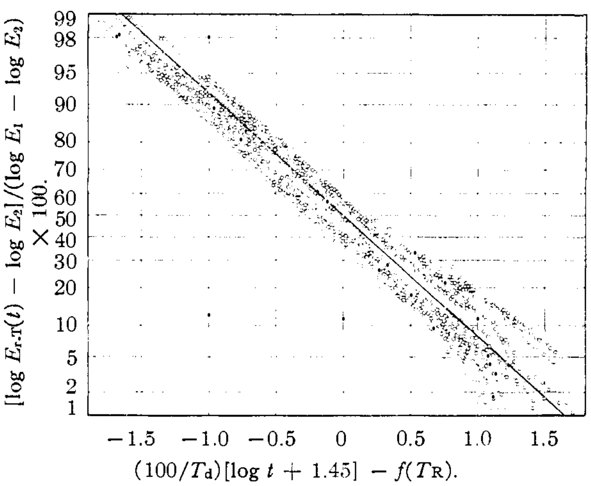

Fig. 1.—Test of validity of three-parameter reduced equation for viscoelastic behavior of amorphous polymers in transition region.

Figure 1 indicates that equation 2 represents a fairly good approximation for the properties of the polymers studied thus far. It is interesting to ask whether this same equation will be applicable to other polymers as well. For this purpose we show how the modulus–temperature curves (measured at constant strain after a fixed period of time, *e.g.*, 10 seconds) can be simply obtained from equation 2 for a polymer of distinctive temperature T_d, or conversely, how the experimental modulus–temperature curves for any polymer can be compared with equation 2.

Modulus–Temperature Curves.—In order conveniently to construct the modulus–temperature curves (modulus measured at constant strain after a fixed time t_1) we have designed two tables (Tables II and III) such that

$$\frac{\log E_{r,T}(t_1) - \log E_2}{\log E_1 - \log E_2} \quad (3)$$

can be obtained as a function of T for polymers of different values of T_d which obey equation 2.

To use these tables, one first determines, from Table II, the quantity $X = 100/T_d\ (\log t_1 + 1.45)$ for the appropriate values of T_d and t_1. Then, in Table III, one looks up X and the desired $T_R (= T/T_d)$ and finds the quantity desired.

In this manner, a series of modulus–temperature curves (after 10 seconds stress–relaxation) were computed for polymers having T_d's ranging from −70 to 130°. These curves are shown in Figs. 2 and 3. It is noteworthy that polymers with a low glass transition region also have a narrow transition range, so that the change in properties of a useful

Table III

Values of $\frac{\log E_{r,t}(t) - \log E_2}{\log E_1 - \log E_2} \times 100 = \frac{1 - \text{erf}[X - f(T_R)]}{2} \times 100$

$X \rightarrow$ / T_R	−2.25	−2.00	−1.75	−1.50	−1.25	−1.00	−0.75	−0.50
0.940	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.9
.945	100.0	100.0	100.0	100.0	100.0	100.0	99.9	99.8
.950	100.0	100.0	100.0	100.0	100.0	100.0	99.9	99.7
.955	100.0	100.0	100.0	100.0	100.0	100.0	99.9	99.6
.960	100.0	100.0	100.0	100.0	100.0	99.9	99.8	99.3
.965	100.0	100.0	100.0	100.0	100.0	99.9	99.6	98.9
.970	100.0	100.0	100.0	100.0	99.9	99.7	99.3	97.7
.975	100.0	100.0	100.0	100.0	99.8	99.5	98.8	97.1
.980	100.0	100.0	100.0	99.9	99.7	99.2	97.9	95.4
.985	100.0	100.0	99.9	99.8	99.4	98.4	96.4	92.5
.990	100.0	100.0	99.9	99.6	98.9	97.3	94.2	88.8
.995	100.0	99.9	99.7	99.1	97.8	95.2	90.6	83.2
1.000	99.9	99.8	99.3	98.3	96.1	92.1	85.6	76.0
1.005	99.8	99.5	98.7	96.9	93.5	87.7	79.0	67.5
1.010	99.7	99.1	97.7	95.0	90.1	82.5	71.9	59.0
1.015	99.3	98.3	96.1	92.1	85.6	76.0	63.8	50.0
1.020	98.9	97.4	94.3	89.1	81.0	70.0	56.7	42.7
1.025	98.1	95.8	91.5	84.6	74.7	62.2	48.3	34.6
1.030	97.0	93.7	88.0	79.4	68.0	54.5	40.5	27.6
1.035	95.4	90.8	83.5	73.3	60.6	46.6	33.1	21.4
1.040	93.5	87.7	79.0	67.5	53.9	40.0	27.2	16.8
1.045	90.8	83.5	73.3	60.6	46.6	33.1	21.4	13.6
1.050	87.7	79.0	67.5	53.9	40.0	27.2	16.8	9.4

$X \rightarrow$ / T_R	−0.25	0.00	0.25	0.50	0.75	1.00	1.25	1.50
0.940	99.6	98.9	97.4	94.3	89.1	81.0	70.0	56.7
.945	99.5	98.6	96.7	93.1	87.1	78.2	66.4	52.8
.950	99.2	98.1	95.6	91.3	83.9	74.2	61.7	47.7
.955	98.9	97.3	94.2	88.8	80.6	69.5	56.2	42.2
.960	98.3	96.1	92.1	85.6	76.0	63.8	50.0	36.2
.965	97.3	94.2	88.8	80.6	69.5	56.2	42.2	29.1
.970	95.9	91.7	84.9	75.1	62.8	48.9	35.1	23.1
.975	93.8	88.3	79.8	68.5	55.1	41.0	28.1	17.5
.980	90.8	83.5	73.3	60.6	46.6	33.1	21.4	13.6
.985	86.2	76.9	64.9	51.1	37.2	24.9	15.1	8.3
.990	80.6	69.5	56.2	42.2	29.1	18.3	10.4	5.3
.995	72.8	60.0	46.1	32.5	21.0	12.3	6.5	3.1
1.000	63.8	50.0	36.2	24.0	14.4	7.9	3.9	1.7
1.005	53.9	40.0	27.2	16.8	9.4	4.8	2.2	0.9
1.010	44.9	31.5	20.2	11.7	6.2	2.9	1.2	.5
1.015	36.2	24.0	14.4	7.9	3.9	1.7	0.7	.2
1.020	29.6	18.6	10.7	5.5	2.6	1.1	.4	.1
1.025	22.7	13.5	7.3	3.5	1.5	0.6	.2	.1
1.030	17.2	9.7	4.9	2.2	0.9	.3	.1	.0
1.035	13.6	6.7	3.2	1.4	.5	.2	.1	.0
1.040	9.4	4.8	2.2	0.9	.3	.1	.0	.0
1.045	6.7	3.2	1.4	0.5	.2	.1	.0	.0
1.050	4.8	2.2	0.9	0.3	.1	.0	.0	.0

$X \rightarrow$ / T_R	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75
0.940	42.7	29.6	18.6	10.7	5.5	2.6	1.1	0.4	0.1
.945	38.9	26.2	16.1	9.0	4.5	2.0	0.8	.3	.1
.950	34.1	22.3	13.2	7.1	3.4	1.5	.6	.2	.1
.955	29.1	18.3	10.4	5.3	2.5	1.0	.4	.1	.0
.960	24.0	14.4	7.9	3.9	1.7	0.7	.2	.1	.0
.965	18.3	10.4	5.3	2.5	1.0	.4	.1	.0	.0
.970	13.8	7.5	3.6	1.6	0.6	.2	.1	.0	.0
.975	9.9	5.0	2.3	0.9	.3	.1	.0	.0	.0
.980	6.7	3.2	1.4	.5	.2	.1	.0	.0	.0
.985	4.1	2.3	0.7	.3	.1	.0	.0	.0	.0
.990	2.5	1.0	.4	.1	.0	.0	.0	.0	.0
.995	1.3	0.5	.2	.1	.0	.0	.0	.0	.0
1.000	0.7	.2	.1	.0	.0	.0	.0	.0	.0
1.005	.3	.1	.0	.0	.0	.0	.0	.0	.0
1.010	.2	.0	.0	.0	.0	0	.0	.0	.0
1.015	.1	.0	.0	.0	.0	.0	.0	.0	.0
1.020	.0	.0	.0	.0	.0	.0	.0	.0	.0
1.025	.0	.0	.0	.0	.0	.0	.0	.0	.0
1.030	.0	.0	.0	.0	.0	.0	.0	.0	.0
1.035	.0	.0	.0	.0	.0	.0	.0	.0	.0
1.040	.0	.0	.0	.0	.0	.0	.0	.0	.0
1.045	.0	.0	.0	.0	.0	.0	.0	.0	.0
1.050	.0	.0	.0	.0	.0	.0	.0	.0	.0

low-temperature rubber at its glass transition is even more striking than the change in properties which conventional thermoplastics undergo on heating.

Determination of T_d from Modulus–Temperature Curves.—In practice, one is likely to be faced with the problem of determining T_d for a given polymer. The modulus–temperature curve is a convenient method for this. If the modulus–temperature curve was obtained at $t_1 = K_d = 127$ seconds, T_d would be identical with T_{50}, the temperature at which $[\log E_{r,T}(t_1) - \log E_2]/(\log E_1 - \log E_2)$ is equal to 50%. T_{50} is easily determined from an enlarged plot of the modulus–temperature curve. Shorter times, *e.g.*, 5 or 10 seconds, are preferable for speedy determination of T_d. For a given T_d, T_{50} is a function of t_1. We can derive a simple expression for $\Delta = T_{50} - T_d$ for any value of t_1 by noting that when $[\log E_{r,T}(t_1) - \log E_2]/\log E_1 - \log E_2 = 0.50$

$$\frac{100}{T_d}(\log t_1 + 1.45) = f(T_{50}/T_d) = f(1 + \Delta/T_d) \quad (4)$$

In paper I,[2] we tentatively approximated $f(T/T_d)$ as a linear function of T/T_d, which decreases when T/T_d increases; also $f(T/T_d) = 0$ when $T/T_d = 1$. So we can write $f(1 + \Delta/T_d) = -(\Delta/T_d)\, g(\Delta/T_d)$, where $g(\Delta/T_d)$, which is given in Table IV, is nearly constant. Making this substitution in equation 3, one obtains

$$\Delta = -\frac{100}{g(\Delta/T_d)}(\log t_1 + 1.45) \quad (5)$$

TABLE IV

VALUES OF $g(\Delta/T_d)$

Δ/T_d	$g(\Delta/T_d)$	Δ/T_d	$g(\Delta/T_d)$
−0.060	27.0	0.000	36.0
− .055	28.2	.005	36.0
− .050	29.2	.010	34.0
− .045	30.2	.015	33.3
− .040	31.25	.020	31.5
− .035	31.7	.025	31.2
− .030	32.7	.030	30.7
− .025	33.6	.035	30.3
− .020	34.5	.040	29.5
− .015	34.7	.045	29.1
− .010	36.0	.050	28.6
− .005	36.0		

To use equation 4, it is necessary to proceed by trial-and-error. Knowing T_{50}, one assumes a likely value for $g(\Delta/T_d)$, *e.g.*, 36.0, and solves for Δ. This gives a tentative value of T_d, from which a better value of $g(\Delta/T_d)$ can be found, and so on.

If equation 2 describes satisfactorily the viscoelastic behavior of an amorphous polymer, this fact can be conveniently ascertained from an experimental modulus–temperature curve. The procedure would be to determine T_d as described in the preceding paragraph, construct the hypothetical modulus–temperature curve corresponding to this T_d (using Tables II and III), and compare the computed and the experimental values.

Equation 4 shows that the choice of a different time scale causes a shift of the modulus–temperature curve along the temperature axis approximately proportional to log time. This is another

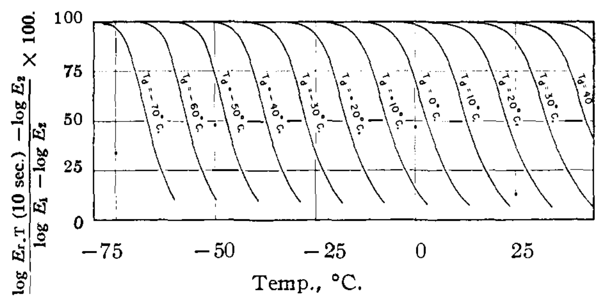

Fig. 2.—Modulus–temperature curves at 10 seconds for amorphous polymers having T_d below room temperature.

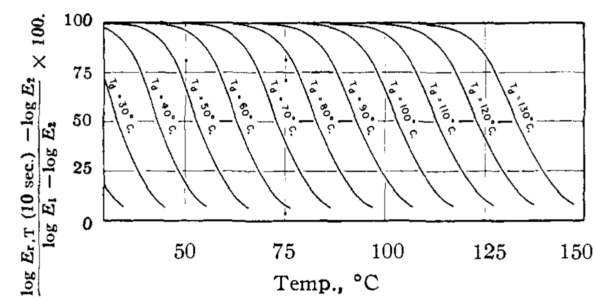

Fig. 3.—Modulus–temperature curves at 10 seconds for amorphous polymers having T_d above room temperature.

manifestation of the time–temperature superposition principle which has proved so fruitful in constructing composite stress–relaxation and dynamic modulus curves. Modulus–temperature curves on the same polymer taken at different times are very nearly parallel.

One difficulty that remains is that of making short-time stress–relaxation determinations to obtain the necessary modulus–temperature information. Many commercially available modulimeters depend on a short-time creep test, *e.g.*, in bending or torsion. Presumably, there exists a simple approximate relation between creep modulus and stress–relaxation modulus.[5] No adequate experimental proof of this relation in the transition region has been published, however.

Maximum Apparent Heat of Activation for Viscoelastic Behavior.—Another consequence of equation 2 is the existence of a simple relationship between T_d and $(\Delta H_{Act})_{max}$, the maximum apparent activation energy for stress–relaxation. The apparent activation energy is calculated from the Arrhenius equation

$$\Delta H_{Act} = 2.303R\,\frac{d \log K}{d(1/T)} \quad (5)$$

Making the appropriate substitutions gives (since K_d is constant)

$$\Delta H_{Act} = 2.303RT_d\,\frac{d \log K_R}{d(1/T_R)} = \frac{2.303RT_d^2}{100} \times \frac{d\, f(T_R)}{d\,(1/T_R)} \quad (6)$$

By definition the maximum value of ΔH_{Act} is found when $T_R = 1$, at which point

$$\frac{d\, f(T_R)}{d(1/T_R)} = -\,g(\Delta/T_d)_{max} \times \frac{d(T_R - 1)}{d\,(1/T_R)} = g(\Delta/T_d)_{max} = 36.0 \quad (7)$$

(5) T. Alfrey, Jr., "Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York, N. Y., 1948, p. 553.

Hence

$$(\Delta H_{\text{Act}})_{\max} = \frac{2.303RT_d^2}{100}(36.0) = 1.65T_d^2 \quad (8)$$

The validity of equation 8 is assessed in Table V, where experimental values of $(\Delta H_{\text{Act}})_{\max}/T_d^2$ have been collected. The data are taken from papers I[2] and II.[3] The average value of $(\Delta H_{\text{Act}})_{\max}/T_d^2$ is 1.74 (±0.06). This suggests that the maximum value of $g(\Delta/T_d)$ may be slightly greater than 36.0, which is not unreasonable.

TABLE V

RELATIONSHIP OF MAXIMUM APPARENT HEAT OF ACTIVATION AND DISTINCTIVE TEMPERATURE

Polymer	$(\Delta H_{\text{Act}})_{\max}$, kcal.	T_d, °K.	$(\Delta H_{\text{Act}})_{\max}/T_d^2$
Polymethyl methacrylate	300	384	2.03
Paracril 26	95.6	241.0	1.64
GR-S	85.0	220	1.75
60/40 Butadiene-styrene	101.9	237.1	1.81
50/50 Butadiene-styrene	99.0	250.8	1.57
30/70 Butadiene-styrene	140.4	285.1	1.73

Discussion

If the viscoelastic properties of a wide variety of amorphous polymers in the transition region obey equation 2, it is clear that we have developed a kind of law of corresponding states for viscoelastic properties. In particular, the function Y should be identical for all polymers having the same T_d independent of the structure of the polymer. We believe that this will indeed be found valid for many normal amorphous polymers, but will not be true for incompatible copolymers or polyblends.

Acknowledgment.—We wish to thank the Office of Naval Research for support of this work under Contract No. N6 onr-27021, Project NR 330-023.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Polarography and Standard Potential of the Oxygen–Hydrogen Peroxide Couple

BY DAVID M. H. KERN

RECEIVED APRIL 20, 1954

The generally accepted equation $O_2 + 2H^+ + 2e^- = H_2O_2$ for the first step in the polarographic reduction of oxygen has been confirmed in the *p*H range 6–14 by potentiometric null-point measurements with the dropping mercury electrode in buffered hydrogen peroxide–oxygen mixtures. The couple is completely reversible for *p*H >11. The standard potential was determined both by the above technique, and by measurements of the oxygen half-wave potential in sodium hydroxide solutions in a cell without liquid junction. The result was $E^0 = +0.695 \pm 0.005$ v. The mechanism of the reduction is briefly discussed.

The recent work of Hacobian[1] on the a.c. polarography of oxygen has produced conclusive evidence of the reversibility of the first reduction step in unbuffered neutral and basic solutions. His observations were further confirmed by his discovery of an oxidation wave of hydrogen peroxide in dilute base. Heretofore, although reversible electron exchange between the oxygen molecule and the electrode has at times been postulated,[2] the over-all process has consistently been stated to be highly irreversible in all media.[3] This assumption was supported, at least in the *p*H range 1–10, by the observation[4] that the half-wave potential ($E_{1/2}$) of oxygen throughout this range is essentially independent of *p*H, while according to the accepted equation

$$2H^+ + O_2 + 2e^- \rightleftharpoons H_2O_2 \quad (1)$$

for the over-all electrode reaction, reversibility would have led to a shift of 60 mv. per unit change in *p*H. On the other hand, the standard potential of this couple has been given by Latimer[5] as +0.682 v. on the basis of data on reaction heats and entropies, and a simple calculation shows that the overvoltage of the observed oxygen wave (generally placed at −0.05 v. *vs.* S.C.E.) rapidly diminishes as the solution becomes less acid until it disappears altogether in slightly basic solutions. Furthermore, Berl[6] has shown that the electrode reaction is reversible at activated carbon electrodes in strongly basic solutions. Practically, the reversibility of the oxygen wave in basic solutions has been exploited because of its steep shape and well developed diffusion plateau, but the appropriate thermodynamic conclusions had never been drawn.

Hacobian found that analysis of the oxygen wave in neutral unbuffered solution gave a linear log plot with a 62 mv. slope, indicating a one-electron process. The log plot analysis derives its validity from the thermodynamic current–voltage equation for the rising part of the wave, and this in turn is based on the assumption that the over-all electrode reaction is given by the expression

$$A + ne^- \rightleftharpoons B$$

where n is determined by the slope of the log plot and A and B are the diffusing species. In one mechanism proposed by Hacobian, B has a coefficient of 3/2, and in the other the reaction involving the one electron is not the over-all process between the diffusing species. Consequently the slope of his plot cannot be used to support either mechanism. An attempt was made to reproduce the log plot of Hacobian in neutral 0.05 M Na_2SO_4

(1) S. Hacobian, *Australian J. Chem.*, **6**, 211 (1953). The same conclusion was very briefly reported by Kalousek, *Collection Czechoslov. Chem. Communs.*, **13**, 105 (1948), on the basis of observations made by a simpler technique.

(2) J. Heyrovsky, "Polarographie," Springer Verlag, Vienna, p. 78.

(3) *E.g.*, I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. II, Interscience Pubishers, Inc., New York, N. Y., p. 555; M. v. Stackelberg, "Polarographische Arbeitsmethoden," Walter de Gruyter and Co., Berlin, p. 320.

(4) I. Kolthoff and C. Miller, THIS JOURNAL, **63**, 1013 (1941).

(5) W. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 2nd ed., 1950, p. 43.

(6) W. Berl, *J. Electrochem. Soc.*, **83**, 253 (1943).