Glass Transition of Coal

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The study of mechanical or thermal properties of coal on heating is of great importance in structural investigation and industrial problems. It is well known that coals, especially caking or coking coals, have a polymeric character, and show plastic deformation at room temperature[1] and softening or flow phenomena on heating.[2] It appears, however, that very few detailed investigations on the change of mechanical or thermal properties of coals heated over the range from room temperature to the softening point have yet been made. D. H. Bangham and R. E. Franklin[3] measured the thermal expansion coefficient of three bright coals. They showed that coals have a gradual increase in the thermal expansion coefficient over the range from room temperature to about 300°C. The present authors have measured the change of hardness and volume for several vitrains of every rank over the range from room temperature to about 160°C by using two distinct hardness methods and one dilatometric method, and have found that coals have a few characteristic points over this temperature range.

Experimental Procedure

Indentation Hardness Method.—Coal specimens about 1 cm. wide and 5 cm. long, and about of 2 cm. thick parallel plane were cut perpendicular to the bedding planes, using a motor-driven diamond cutter. One plane of surface perpendicular to the bedding planes of the specimen was highly polished by using glass plates with carborundum and alumina, and woollen cloth with alumina. The specimens were air-dried at room temperature and ordinary humidity.

Fig. 1 shows the experimental apparatus which modified the Akashi micro-hardness tester having a diamond Knoop indenter.[4] The coal specimen, of which the base and two long sides are covered with three electric heating plates settled in a vise, is placed on a steel table with a copper block cooled by water. The position of the vitrain layer can be adjusted by means of screws. The temperature of the vitrain layer is measured by a thermistor surface thermometer located very closely to the indenter and controlled by a suitable variable resistor. The coal specimen is heated at the heating rate of 1°C/min. over the range from room temperature to 160°C. The load of indenter is 100 g. and

1) D. W. van Krevelen and J. Schuyer, "Coal Science, Aspects of Coal Constitution", Elsevier, Amsterdam (1957), p. 275.
2) D. W. van Krevelen and J. Schuyer, loc. cit. p. 286.
3) D. H. Bangham and R. E. Franklin, *Trans. Faraday Soc.*, 42B, 289 (1946).
4) H. Honda and Y. Sanada, *Fuel*, 36 ,403 (1957).

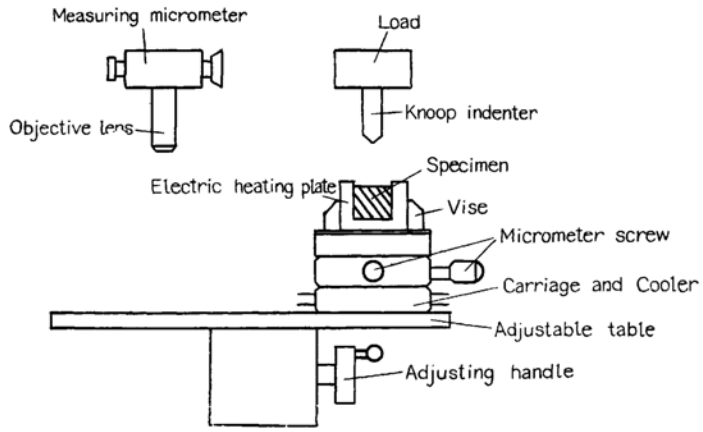

Fig. 1. Apparatus for the determination of the indentation hardness.

the time taken in the duration of the load is 30 sec. The hot impression under the elevated temperature is made every five minutes, i. e. every 5°C. After an impression has been made, the specimen is moved to a new position along the vitrain layer by means of the screw for the distance of 15/100 mm. After all impression have been completed, the furnace is cooled to room temperature and then Knoop hardness numbers are determined from the length of the long diagonal of indentation.

Pendulum Hardness Method. — The preparation of coal specimens, the heating method, the heating rate, and the measurements of temperature are the same as those in the case of indentation hardness test.

The apparatus of the pendulum hardness tester of Walker Steele type is given in Fig. 2. It consists of the wedge-type agate fulcrum, two brass arms with weights and a small mirror. The length between the weights at the ends of the arms of the pendulum is 20 cm. The weight of the pendulum is 78 g. The damping of the pendulum hardness tester on the vitrain layer of the specimens is determined by the lamp-and-scale method. The apparatus is held in an air-thermostat. The logarithmic decrement λ of the pendulum is given by the following equation, provided that the periodic time is a constant :[5]

$$\lambda = (2.303 \log \theta/\theta')/2n$$

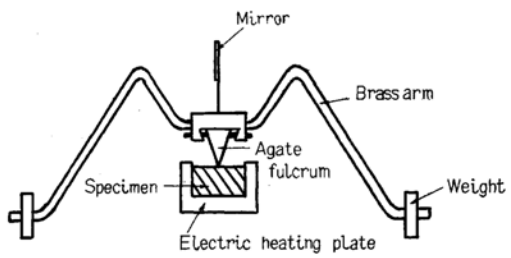

Fig. 2. Apparatus for the determination of the logarithmic decrement.

where θ and θ' are the angle from the position of rest, n is the frequency of the pendulum between θ and θ'. In this experiment, the chosen values of θ and θ' were 4° and 3°26′ respectively.

Dilatometric Method.—The coal specimen was pulverized to pass through a 30 and stand on a 60 Tyler mesh sieve. The vitrain, of specific gravity less than 1.30, was isolated by the float-or-sink method using mixtures of benzene and carbon tetrachloride. The volume change of vitrain with temperature was measured using a Pyrex glass

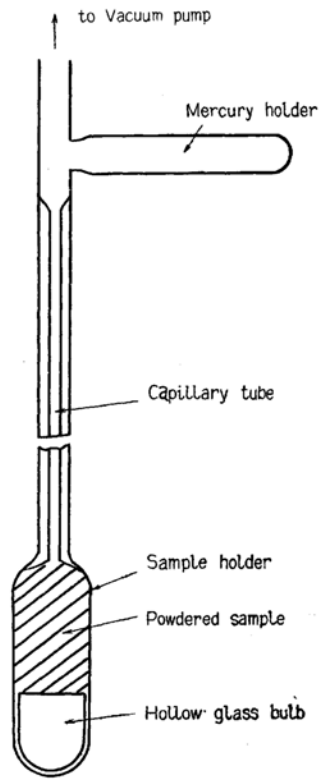

Fig. 3. Modified Bekkedahl's dilatometer.

5) Y. Inoue, K. Kanai and K. Hiroi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*) **59**, 231 (1956).

6) N. Bekkedahl, *J. Research NBS*, 42, 145 (1949).

TABLE I. ANALYSIS OF VARIOUS VITRAINS

Source		Proximate analysis, %				Ultimate analysis (d. a. f.) %		
		Moisture	Ash	V. M.	Fixed Carbon	C	H	O+N+S
Brown coal	Tempoku-Menashi	12.41	1.40	42.91	43.28	69.82	4.91	25.26
	Nakagō	13.32	3.96	38.03	44.69	74.33	5.26	20.41
Bituminous coal	Takamatsu	4.67	2.29	41.10	51.94	78.95	5.01	16.04
	Bibai	2.78	3.10	41.81	52.31	80.90	5.87	13.23
	Ashibetsu	2.98	4.05	42.93	50.04	81.11	5.49	13.40
	Akabira	3.01	3.21	42.50	51.28	82.29	5.92	11.79
	Futago	1.54	2.31	46.86	49.29	83.16	6.31	10.53
	Miike	1.21	3.36	43.95	51.48	84.53	6.11	9.36
	Ōyūbari	1.35	2.76	40.34	55.55	84.79	6.23	8.93
	Yūbari	2.28	2.70	42.08	52.94	84.85	5.96	11.16
	Hashima	1.24	2.09	35.91	60.76	86.59	5.56	7.85
	Donegan No. 1 (U.S.A)	1.75	1.16	31.29	65.80	87.16	5.26	7.22
	American (U.S.A.)	1.55	1.17	26.26	71.02	87.68	4.80	7.52
	Yatake	1.26	3.04	20.54	75.16	88.71	4.35	6.94
	Shikamachi	1.16	2.52	21.16	75.16	88.76	4.70	6.54
	Amonate and Bishop (U.S.A.)	1.06	1.40	23.53	74.01	89.16	5.19	5.20
Anthracite	Uonuki	1.68	1.80	10.80	85.72	91.16	3.97	4.87
	Hongei (Indo-China)	2.08	0.98	6.14	90.80	93.02	3.26	3.72

dilatometer following the modified Bekkedahl's method[6]. The dilatometer employed in the test is shown in Fig. 3. The dilatometer consists of the capillary tube, the sample holder and the mercury holder. The inner diameter and the length of the capillary tube are 1.5 mm. and about 70 cm. respectively. The inner diameter and the length of the sample holder are 15 mm. and about 13 cm. respectively. One end of the sample holder is left open at first. About 15 g. of the air-dried sample is weighed into the sample holder. A hollow glass bulb, of which the outer diameter is a little smaller than 15 mm. and of which the height is about 3 cm., is settled in the sample holder, and then the end of the sample holder is sealed up. This method makes it possible to avoid any heating of the sample during the sealing operation. Mercury is put in the mercury holder. The coal sample in the dilatometer is evacuated to 10^{-3} mmHg for 6 to 8 hr. at room temperature in order to remove gas and then the desired volume of mercury is filled through the capillary. The dilatometer is settled in a stirring liquid paraffin bath, whose temperature is controlled under the heating rate of 1°C/min. The measurements of the height of mercury in the capillary tube were made visually, usually once every minute, from room temperature to 160°C.

The accuracy of determination of the Knoop hardness number itself has already been described in detail.[4] The scatter of the results in this indentation hardness method depends upon the inhomogeneity of the vitrain layer and the temperature control. Though the pendulum hardness is used as a conventional method in the measurements of the glass transition point of high polymers, the scatter of the results in this method may also depend upon the inhomogeneity of vitrain, the temperature control, and the error in the reading of n. The dilatometric method is the most conventional and its experimental accüracy is most high in the measurements of the glass transition point of high polymers. The surface temperature of vitrain is easily measured and precisely detected within 1°C by the thermistor having a very small thermo-sensitive element.[7] When the load is applied to the indenter, the surface temperature of vitrain decreases instantaneously. The maximum instantaneous decrease of temperature was about 2°C over the range of 50 to 100°C and about 5°C over the range of 100 to 160°C. In general, the glass transition temperature obtained by the pendulum method is considerably higher than that obtained by the dilatometric method. But this discrepancy becomes smaller by using a wedge instead of two balls as the fulcrum of the pendulum.[8]

The characteristics of various vitrains used are listed in Table I.

Results and Discussion

The relation between the Knoop hardness number, H_k, of air-dried coals and temperature is shown in Fig. 4. For brown coal, H_k

7) B. M. Zeffert and S. Hormas, *Anal. Chem.*, **21**, 1420 (1949).

8) K. Sato and Y. Inoue, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **15**, 421 (1958).

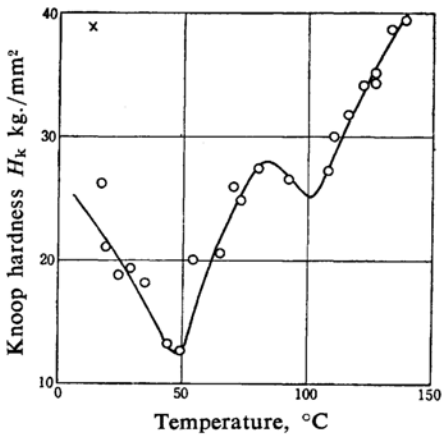

Fig. 4a. Variation of Knoop hardness with temperature for Nakagō brown coal (d. a. f. C=74.33%).

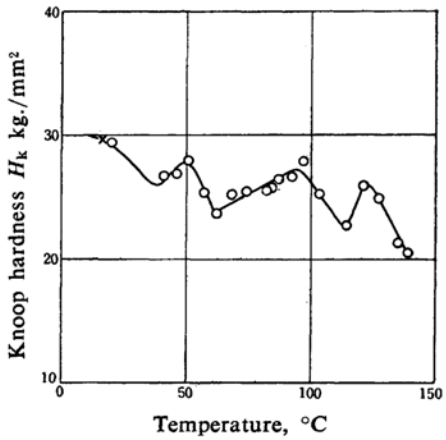

Fig. 4b. Variation of Knoop hardness with temperature for Yūbari coking coal (d. a. f. C=84.85%).

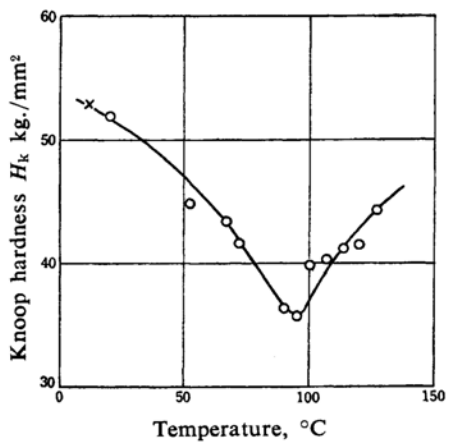

Fig. 4c. Variation of Knoop hardness with temperature for Hongei anthracite (d. a. f. C=93.02%).

decreases with temperature increase to a minimum at about 50°C, increases with temperature to a maximum, decreases again with temperature increase to a second minimum at about 100°C, and then increases with temperature. For bituminous coal H_k shows three minimum values over the range from room temperature to 160°C. For anthracite H_k decreases with temperature increase to a minimum at about 100°C, and then increases with temperature. The temperatures showing the minimum values of H_k of various air-dried vitrains are listed in the first column of Table II. Namely, over this temperature range, air-dried brown coal, bituminous coal and anthracite have two, three and one characteristic points respectively.

After the specimens heated to about 160°C were allowed to cool in an ordinary atmosphere, the Knoop hardness of the specimens was again measured at room temperature. These values of H_k at room temperature are shown by cross marks in Fig. 4. The values of H_k of the cooled bituminous coal and anthracite coincide almost exactly with those of the non-heated original coals respectively. This shows that these coals do not change their chemical constitutions if heated over the range from room temperature to about 160°C. However the value of H_k of the cooled brown coal is much higher than that of the non-heated original brown coal and the cooled brown coal has many tiny cracks on the surface. These phenomena may be attributed to the fact that some chemical reactions such as dehydration occur in the specimen of brown coal by heating over the range from room temperature to about 160°C, as if in the curing of thermosetting plastics, e. g. phenol-formaldehyde resin.

The relations between the logarithmic

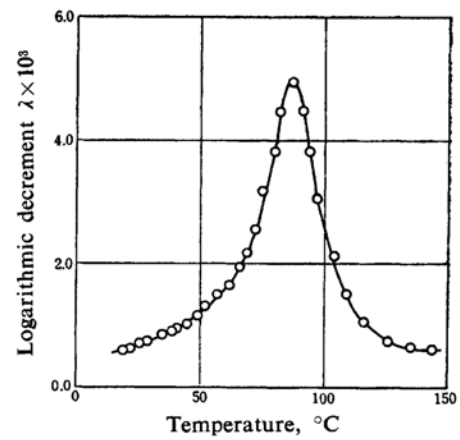

Fig. 5. Variation of logarithmic decrement with temperature for maleic acid-glycol-styrene resin.

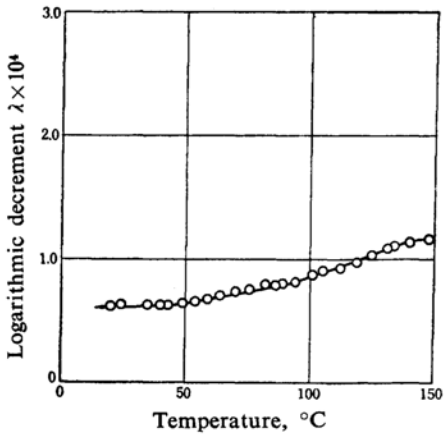

Fig. 6. Variation of logarithmic decrement with temperature for phenol-formaldehyde resin.

decrement, λ, of the pendulum on maleic acid-glycol-styrene resin, loosely cross-linked linear polymer, and phenol-formaldehyde resin (moulded C state), three-dimensional network polymer, and temperature are shown in Fig. 5 and Fig. 6 respectively. The value of λ of maleic acid-glycol-styrene resin increases suddenly with temperature to a maximum at 87°C. Thereafter the value of λ decreases suddenly with temperature increase and becomes almost the same at about 150°C as that of room temperature. This change of λ with temperature shows a typical glass transition phenomenon of loosely cross-linked linear polymer. Further, the glass transition point of maleic acid-glycol-styrene resin is 87°C. On the other hand, the value of λ of phenol-formaldehyde resin increases slowly with the temperature over the range from room temperature to 150°C and does not show a maximum. This change of λ with temperature shows a character of three-dimensional network polymer.

The relation between the logarithmic decrement, λ, of the pendulum on air-dried coals and temperature is shown in Fig. 7. For brown coal λ increases with temperature to a maximum at about 50°C, decreases with temperature increase to a minimum, increases again with temperature to a second maximum at about

Table II. Glass transition points of various vitrains

Source		Carbon (d. a. f.) %	Glass transition temperature, °C: by indentation hardness method, Air-dried coal			by pendulum hardness method, Air-dried coal			by dilatometric method, Air-dried coal			by dilatometric method, Strongly dried coal		
			T_{g_1}	T_{g_2}	T_{g_3}	T_{g_1}	T_{g_2}	T_{g_3}	T_{g_1}	T_{g_2}	T_{g_3}	T_{g_1}	T_{g_2}	T_{g_3}
Brown coal	Tempoku-Menashi	69.82		50	100		50	100		50	106		52	—
	Nakagō	74.33		50	100		65	110		50	117			
Bituminous coal	Takamatsu	78.95	43	70	120	30	57	120	—	51	129			
	Bibai	80.90	45	80	160									
	Ashibetsu	81.11	60	80	120	60	80	145						
	Akabira	82.29	30	80	140	35	90	116						
	Futago	83.16	48	70	105									
	Miike	84.53	40	65	95		92	125						
	Ōyūbari	84.79	50	72	96	40	70	140						
	Yūbari	84.85	38	62	113	40	67	135	29	75	145	38	61	133
	Hashima	86.59	25	50	85									
	Donegan No. 1 (U.S.A.)	87.16	35	80	93	30		105						
	American (U.S.A.)	87.68	33	70	120		80	110						
	Yatake	88.71							34	68	149	20	65	100
	Shikamachi	88.76	35	60	105	40	77	120						
	Amonate and Bishop (U.S.A.)	89.16	35	75	105		70	120						
Anthracite	Uonuki	91.16	25		90	25		105						
	Hongei (Indo-China)	93.02			95			130			122			—

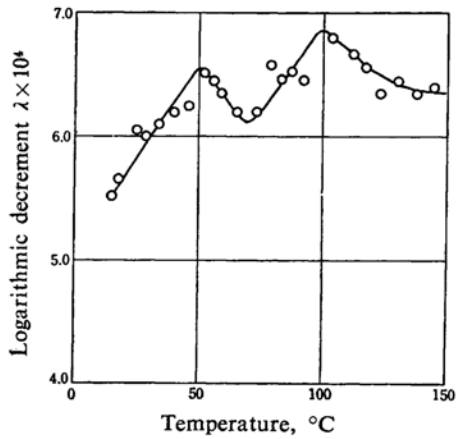

Fig. 7a. Variation of logarithmic decrement with temperature for Tempoku-Menashi brown coal (d. a. f. C=69.82%).

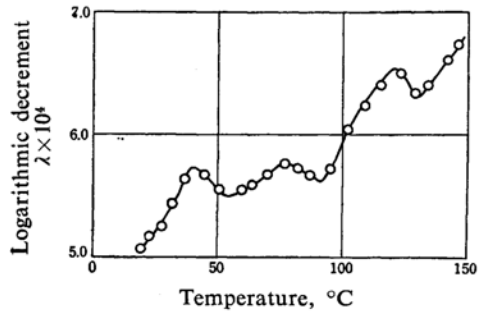

Fig. 7b. Variation of logarithmic decrement with temperature for Shikamachi coking coal (d. a. f. C=88.76%).

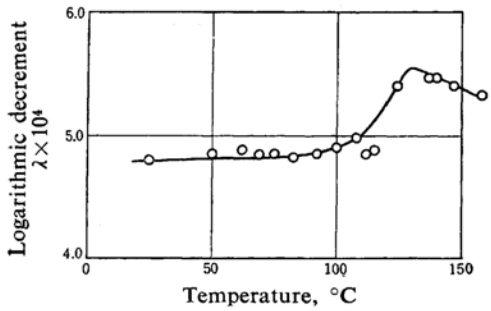

Fig. 7c. Variation of logarithmic decrement with temperature for Hongei anthracite (d. a. f. C=93.02%).

100°C, and then decreases with temperature increase. For bituminous coal λ shows three maximum values over the range from room temperature to 160°C. For anthracite λ increases with temperature to a maximum at about 130°C and then decreases with temperature increase. The temperature showing the maximum values of λ of various air-dried vitrains are listed in the second column of Table II. Over this temperature range, air-dried brown coal, bituminous coal and anthracite have two, three and one characteristic points respectively.

The relation between the reading of mercury height, V, in the glass capillary tube of dilatometer containing powdered maleic acid-glycol-styrene resin and temperature is shown in Fig. 8. The value of V increases with temperature and shows a break at 77°C. This change of V with temperature shows a typical glass transition phenomena of loosely cross-linked linear polymer. That is to say, the glass transition point of maleic acid-glycol-styrene resin obtained by the dilatometric method is 77°C and this value is slightly lower than that obtained by the pendulum method.

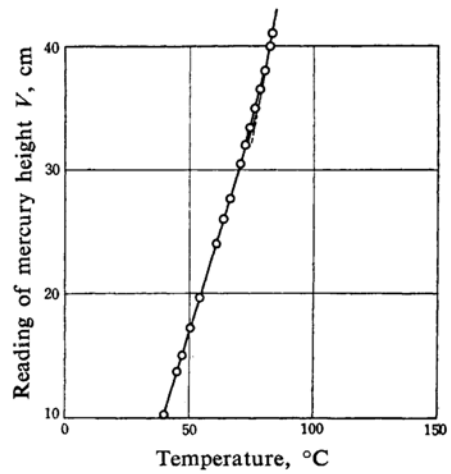

Fig. 8. Variation of reading of mercury height with temperature for maleic acid-glycol-styrene resin.

The relation between the reading of the mercury height, V, in the glass capillary tube of dilatometer containing air-dried powdered coals and heating temperature is shown in Fig. 9. As to brown coal V increases suddenly at about 50°C and again at about 100°C. For bituminous coal the sudden increase of V appears three times over the range from room temperature to 160°C, As for anthracite V increases suddenly at about 120°C. The temperatures showing the breaks of V-temperature curve of various air-dried vitrains are listed in the third column in Table II. In this case too, the characteristic points of air-dried brown coal, bituminous coal and anthracite are two, three and one respectively.

In order to ensure whether the characteristic points, especially the one at about 100°C, are affected by moisture or combined water of coals or not, the V-temperature relations of the samples dried strongly at 130 to 140°C

in vacuo of 10^{-3} mmHg for 6 to 8 hr. have been measured using the dilatometer over the range from room temperature to 160°C. The characteristic points in this case are shown in the last column of Table II. For brown coal the break of V-temperature curve at about 50°C does not vanish but the one at about 100°C disappears. For bituminous coal the three breaks coincide almost exactly with those of the air-dried sample, though the third break of the strongly dried sample somewhat diminishes. For anthracite the break at about 100°C disappears. Therefore, the V-temperature curve of bituminous coal dried at room temperature in vacuo does not show the thermal hysterisis, though those of brown coal and anthracite dried at room temperature in vacuo have the thermal hysteresis as shown in Fig. 9, if heated coals are cooled under the cooling rate of 1°C/min.

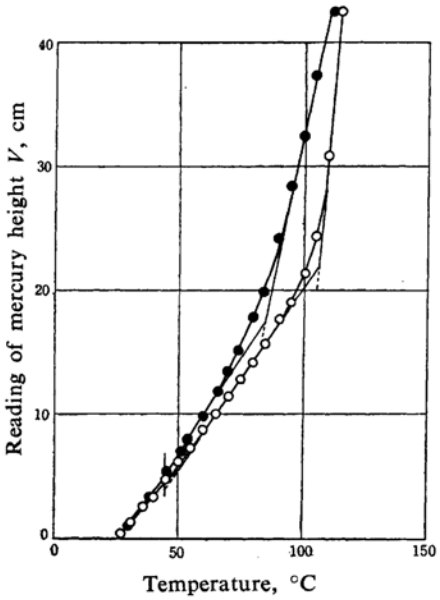

Fig. 9a. Variation of reading of mercury height with temperature for Tempoku-Menashi brown coal (d. a. f. C=69.82%).
○ heating, ● cooling

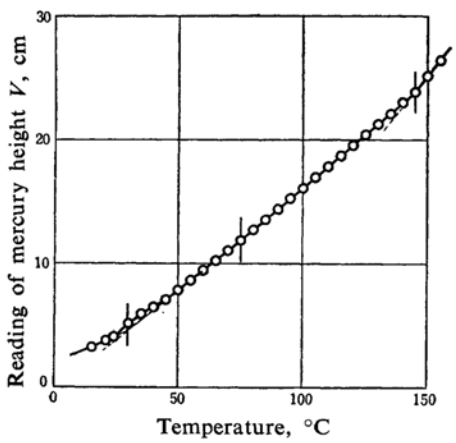

Fig. 9b. Variation of reading of mercury height with temperature for Yūbari coking coal (d. a. f. C=84.85%).

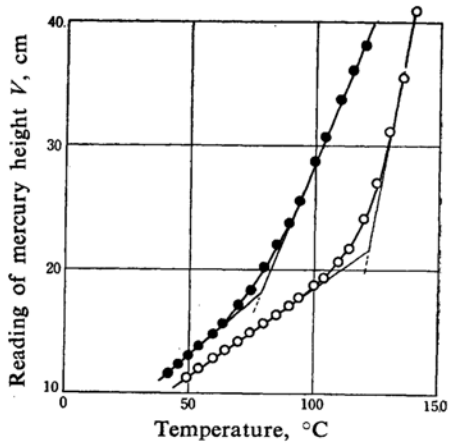

Fig. 9c. Variation of reading of mercury height with temperature for Hongei anthracite (d. a. f. C=93.02%).
○ heating, ● cooling

The influence of moisture on the characteristic points is great in brown coal and anthracite, though it is almost negligible in bituminous coal. This may be attributed to the relation between internal surface area and the rank of coal.[9] On the other hand, the glass transition point of completely dried poly(vinylalcohol), one of the hydrophilic polymers, is 73°C. When the moisture content of the sample increases, this glass transition point shifts to a lower temperature and another transition point appears at a higher temperature.[10] Consequently it may be supposed that the effects of moisture on the characteristic points of brown coal are similar to those on the transition points of poly(vinylalcohol). The disappearance of the characteristic point at about 100°C in strongly dried anthracite may be attributed to the cross-linkages among the base units which anthracite has by nature.[11]

When amorphous polymers are heated, in general, they show a minimum of indentation hardness,[12] a maximum of logarithmic decrement of the pendulum[5], and a change of slope of volume-temperature curve[13] at the glass transition point or zone. Table II shows that

9) Y. Kawana, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1275 (1958).
10) Y. Sone and I. Sakurada, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **14**, 574 (1957).
11) H. Honda and Y. Hirose, *Fuel*, **37**, 323 (1958).
12) K. Ito, *J. Japanese Soc. Mech. Eng.*, **58**, 263 (1955).
13) T. Alfrey, Jr., "Mechanical Behavior of High Polymer," Interscience, New York (1948), p. 121.

the temperatures showing minimum values of Knoop hardness, the temperatures showing maximum values of logarithmic decrement and the temperatures showing breaks of V-temperature curve of the air-dried vitrain roughly coincide with one another, though the hardness methods and the dilatometric method are independent respectively. Moreover, in the dilatometric method, the temperatures showing breaks of V-temperature curve of the strongly dried bituminous coal coincide almost exactly with those of the same air-dried sample and the temperature showing a break of V-temperature curve of the strongly dried brown coal also coincides with that of lower temperature of the same air-dried sample. Therefore it seems that these characteristic points, which are not constant but change with experimental time scale etc., are the glass transition points of coals (although D. H. Bangham and R. E. Franklin[3] did not detect them) over the range from room temperature to 160°C, though the influence of adsorbed water films can not be neglected at all.

In an investigation of microplasticity, D. H. Bangham and N. Berkowitz[14] measured the critical deformation force, F_c, at which the coal particles flowed to form a translucent film. They found that F_c does not vary uniformly with temperature, but F_c shows its maxima at 120, 200 and 300°C. Also they concluded that the undulating character of the curves representing the variation of F_c with increasing temperature is associated with monolayer films adsorbed on the internal surface of the coal which are evaporated at specific temperatures; the maximum at 120°C, they relate to the loss of water vapor from the coal structure. Results similar to those of D. H. Bangham et al. were reported by C. Ellis[15] following an investigation by a similar method.

On the other hand, J. C. Macrae and A. R. Mitchell[16] studied the shapes of the curves relating failure stress to temperature for two bituminous coals and found that the maxima at 120 and 200°C are closely similar to those reported by both D. H. Bangham et al. and C. Ellis for the F_c, at which microplasticity is observable in particles of less than 30 μ in size. They, however, emphasized that it seems probable that heating to 120°C results in an increase of the failure stress by a mechanism in the nature of a strain relief in which an increased thermal vibration modifies the effect of weakness in the coal structure upon the failure stress and influence of adsorbed water films can not be considered to be wholly acceptable.

The authors' experimental results of bituminous coals may rather give support to the opinion of J. C. Macrae et al. than those of D. H. Bangham et al. and C. Ellis.

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14) D. H. Bangham and N. Berkowitz, *Coal Res.*, Dec., 139 (1945).

15) C. Ellis, *Publ. Instn. Gas Engrs.*, **No. 436**, 7 (1953).

16) J. C. Macrae and A. R. Mitchell, *Fuel*, **36**, 423 (1957).