

hole and thus move from one equilibrium position to another it certainly requires greater energy in a viscous system comprising larger molecules than in a relatively less viscous system comprising smaller molecules. Thus because of the larger size of paraffin molecules and stronger intermolecular forces the activation energy per mole for viscous flow in TP system is greater compared to that in TC and TN systems and evidently slightly greater in TC system compared to that in TN system. However, for a more quantitative understanding of the viscosity behaviour of binary mixtures in terms of their constituent parts, a study over a wide range of temperature comprising mixtures of precise molecular constituents is essential.

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## ON THE NATURE OF LOCAL STRAINS DURING SELF-DIFFUSION IN CUBIC METALS

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ATOMIC diffusion in solids involves local strains in the lattice but their nature is not clear at the moment. We suppose that the activation energy for diffusion may be related to the elastically stored energy. Since any strain can be resolved into dilational and shear components, the activation energy may be directly related to the products of shear and dilational strains with Shear and Bulk Moduli. This communication presents an empirical analysis of the data available for a wide range of metals to indicate the nature of strain involved in diffusion.

We find that activation energy for self-diffusion can be described by the following relation:

$$Q = (AK + BG)\Omega N/J$$

where,  $Q$  is activation energy for self-diffusion in Kcal/mol;  $K$  is bulk modulus in Pascals;  $G$  is shear modulus in Pascals;  $\Omega$  is atomic volume in meter<sup>3</sup>;  $N$  is Avogadro's number, ( $6.023 \times 10^{23}$  atoms/mol);  $J$  is heat equivalent in Kcal/Joule, ( $4.17 \times 10^{-3}$  Kcal/Joule).  $A$  and  $B$  are coefficients which depend upon the crystal structure.

Values of  $A$  and  $B$  for B.C.C. structure are 0.172 and 0.058 respectively while the corresponding values for F.C.C. structure are 0.002 and 0.587.

Table 1 presents the data and the calculated activation energies for B.C.C. metals. It may be seen that the fit is extremely good for some elements such as Fe, Nb,

**Table 1** Experimental data and calculated values of  $Q$  for B.C.C. metals

Metal	K (GPa) (1, 2)	G (GPa) (1, 2)	$\Omega \times 10^{30}$ , (m <sup>3</sup> ) (3)	$Q$ observed, (Kcal/mol) (l)	$Q$ calculated, (Kcal/mol)
V	158.00	46.69	13.8	73.65	59.98
Cr	160.00	115.30	12.0	73.70	59.94
Fe	169.79	81.60	11.7	61.30	57.73
Nb	170.29	37.50	17.9	96.00	81.83
Mo	261.20	125.60	15.5	92.20	117.57
Ta	196.29	69.19	18.0	98.70	98.37
W	311.00	160.60	15.8	140.30	143.87
Li	11.80	4.24	21.6	12.67	7.10
Na	8.30	2.53	39.4	10.09	8.99
K	3.30	1.30	76.3	9.75	7.09
Rb	2.30	00.91	89.2	9.40	5.78

Table 2 Experimental data and calculated values of  $Q$  for F.C.C. metals

Metal	$K$ (GPa) (1, 2)	$G$ (GPa) (1, 2)	$\Omega \times 10^{30}$ , (m <sup>3</sup> ), (3)	$Q$ observed, (Kcal/mol) (3)	$Q$ calculated, (Kcal/mol)
Al	78.89	25.00	16.5	34.50	35.51
Ca	18.26	7.38	43.4	38.50	27.39
Ni	190.00	76.00	10.9	67.86	70.97
Cu	133.50	46.40	11.8	50.40	46.84
Pd	184.39	45.00	14.7	63.30	56.89
Ag	99.69	30.30	17.0	45.20	44.26
Pb	40.40	5.59	30.3	25.65	14.74
Ce	19.80	12.00	34.3	36.60	35.09
Pt	275.70	52.82	15.1	66.47	68.80
Au	171.00	26.00	16.9	41.70	38.24
Th	54.00	30.80	32.9	71.60	86.24

W and Ta but relatively poor for metals like Li and Rb. The average difference between the calculated values and experimentally observed values is 19%. Table 2 presents the data and the calculated values of the activation energy for F.C.C. metals. The fit seems to be very good for all elements excepting Pb and Ca. The mean deviation between the calculated and experimentally observed values is 12%.

A look at the empirical equation makes it clear that  $A$  and  $B$  should be identified as dilational strain and shear strain terms. It is then interesting to note that during diffusion dilational strains are introduced locally in B.C.C. structure, while in F.C.C. structure, primarily shear strains are introduced. Apparently, the B.C.C. structure being open allows the migration of atoms by momentary local expansion and contraction of the adjacent regions. The shear strain is relatively insignificant. F.C.C. structure being closely packed does not permit contraction of adjacent regions. The atomic diffusion, then, involves local shear.

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### NITROGEN CHEMISORPTION SUPPRESSION IN THE STRONG METAL SUPPORT INTERACTION STATE OF Co/TiO<sub>2</sub> CATALYST

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THE suppression of chemisorption capacity for CO and hydrogen and the increase in CO hydrogenation activity induced in group VIII metals supported on oxides like TiO<sub>2</sub><sup>1</sup>, MgO<sup>2</sup>, Nb<sub>2</sub>O<sub>5</sub><sup>3</sup>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub><sup>4</sup>, as a result of high temperature ( $\geq 773$  K) reduction (HTR) in hydrogen has been considered to be due to strong metal-support interaction (SMSI)<sup>5</sup>. Earlier studies were confined only to the probe molecules of hydrogen and CO<sup>6,7</sup>. This has greatly limited the scope of identifying the cause of SMSI behaviour. In this communication, the possibility of using nitrogen as probe species for the SMSI behaviour of Co/TiO<sub>2</sub> system is considered. Reports are available on the characterization of SMSI state of Ni, Ru, Rh, Pd and Pt supported on oxides like TiO<sub>2</sub><sup>9</sup>. Similar studies on Fe and Ir are limited<sup>10</sup> and practically no report is available on supported cobalt systems.

Fifteen per cent cobalt on titanium dioxide was prepared by adding the required amount of aqueous solution of cobalt nitrate to freshly prepared TiO<sub>2</sub> (by the hydrolysis of TiCl<sub>4</sub>) powder and dried at 110°C (incipient wetness method) with constant stirring. About 1 g of this sample was reduced at 673 K (LTR) or at 803 K (HTR) in a flow of hydrogen for 3 hr. Adsorption was measured with an accuracy of  $\pm 0.01$  ml in a conventional volumetric unit at room temperature at a pressure of 200 torr for 12 hr. CO was hydrogenated at 583 K using a mixture of CO:H<sub>2</sub>