Professor Hiroshi Suga

ELSEVIER

Thermochimica Acta 266 (1995) ix–xiv

thermochimica
acta

# Professor Hiroshi Suga and his scientific career

Hiroshi Suga was born on 28 February 1930 in Kyoto. He attended the Faculty of Science, Osaka University where, in 1953, he received a B.Sci. degree. Hiroshi then took up graduate studies in chemistry at the same university under supervision of Professor Isamu Nitta, a distinguished X-ray crystallographer, and under the direction of Associate Professor Syûzô Seki. The degree of Dr. Sci. was granted to him in 1960 through the thesis entitled "Orientational Order–disorder Transition in Aniline Hydrobromide". In 1959 he got married to Hiroko Hayashi. He and his wife raised four children: three sons and one daughter.

Hiroshi Suga's first academic appointment was Research Associate at the Department of Chemistry of Osaka University in 1958. He was promoted to Assistant Professor in 1962, to Associate Professor in 1966, and finally to full Professor in 1979. From 1984 to 1989 he was Director of the Chemical Thermodynamic Laboratory at Osaka University, which was founded by Professor Emeritus Seki in 1979 and Associated with the Faculty of Science. This unique laboratory was renamed the Microcalorimetry Research Center in 1989 thanks to the efforts of Hisoshi Suga and his collaborators. Until his retirement from Osaka University in 1993 as Professor Emeritus, Hiroshi Suga served as Director of this Research Center. Since 1993 he has been Professor at the Research Institute for Science and Technology of Kinki University and is also now the Deputy Director of this Institute. He spent half a year in 1969 at Kamerlingh–Onnes Laboratory, University of Leiden, to learn low-temperature physics and cryotechnologies including adiabatic demagnetization, through collaboration with Professor W.J. Huiskamp. He spent the rest of 1969 at the Clarendon Laboratory in Oxford where he learned thermal conductivity measurements of metals at low temperatures, under the direction of Professor K. Mendelssohn. In the last few years he has been active as Visiting Professor at various universities (Zhejiang, China, Umea, Sweden, and Turin, Italy). He has presented over fifty invited lectures at international conferences, institutes and universities in foreign countries.

Hiroshi Suga has authored or co-authored about 300 original scientific papers and 60 review articles. The titles of his representative papers are given below. In examining his scientific work, one is struck by the diversity of topics with which he has dealt. A common theme throughout his work has been the elucidation of phase transition mechanisms and ordering processes in disordered systems. Hiroshi Suga, together with his collaborators, have constructed various kinds of sophisticated calorimeter, with which they have opened up new scientific fields. Of particular importance in his scientific work are the works "Calorimetric study of glassy states" and "Thermodynamic investigation of ice and clathrate hydrates".

One of the most impressive achievements made by Hiroshi Suga and Professor Seki is the discovery of *glassy crystals* which contain seemingly contradicting concepts [1]. They considered various ways of making non-crystalline solids other than by supercooling of a liquid, and asked whether it is plausible to call such solids glasses. They went on to point out that the existence of a glass transition temperature and a residual entropy at 0 K are the crucial characteristics which have gradually come to be the defining criteria for glassiness. Thereupon, they were went on to undertake a systematic study of glass transitions in a number of pure compounds nudged into non-crystalline states by unconventional means. In the course of these studies with precision calorimeters, they discovered a number of anomalies not only in non-crystalline but also in crystalline states: one compound might show more than one glass transition, and thus the concept of glassiness required subdivision. They examined a number of inorganic and organic materials, and a range of compounds that form orientationally-disordered and liquid crystalline phases. They proposed to call these frozen-in states *glassy liquid*, *glassy crystal*, and *glassy liquid crystal* [2]. These findings confirmed that the glass transition was not a characteristic property of liquids but a widespread occurrence in condensed matters in relation to the freeing process of some degrees of freedom of the system, and enriched our understanding of the states of molecular aggregation. Previously, the concept of a glassy crystal was somewhat of a paradox, but now their extensive works have given it proof [3].

Based on the renewal of the concept of the glass transition, Hiroshi Suga was challenged to realize an ordered state of ice. Heat capacity measurement of ice performed by Professor W.F. Giauque (the Nobel Prize Winner in 1949) showed a slight anomaly around 100 K and a finite amount of residual entropy. This fact violates the third law of thermodynamics. Professor L. Pauling (the Nobel Prize Winner in 1954) interpreted the residual entropy in terms of the half-hydrogen statistical model. But nobody could realize a hypothetical ordered state of ice. Hiroshi Suga considered the anomalous heat capacity behavior as being due to freezing out of the water molecules by prolongation of the relaxation time during the course of development of the order parameter at low temperatures. He tried to accelerate the reorientational motion of water molecules and finally succeeded in realizing the ordered ice (designated as ice XI) below 72 K by doping a trace amount of potassium hydroxide [4]. In this new crystalline state the protons of water molecules sit on the regularly arranged positions and hence no residual entropy exists. This phase has proved to belong to an orthohombic system. His discovery was achieved by a dramatic shortening effect of KOH on the relaxation time for the proton rearrangement: this idea had not occurred to anybody previously. This fascinating work was done as an extension of his studies on glassy crystals, and opened up a new realm in *Doping Chemistry*. One cannot control the time, but one can control the molecular dynamics in crystals by doping a particular kind of lattice defect. Needless to say, water (and thus ice) is a very important and fundamental material not only on earth but also in the cosmos. In that sense, the discovery of ordered ice does actually play a fundamental role in the understanding of nature. His pioneering spirit is admirable and deserves a high reputation.

Outside his laboratory, Hiroshi Suga has served as President of the Japan Society of Calorimetry and Thermal Analysis (1991–1993). He was also active as a member of the IUPAC I·2 Committee on Thermodynamics (1981–1993), and as a member of the National Committee of Chemistry established in the Science Council of Japan (1988–1994). He organized many domestic and international conferences: organizer of International Workshop on Biocalorimetry (1977, Kyoto), organizer of the 14th (1978, Kyoto), the 20th (1984, Osaka) and the 25th (1989, Osaka) Conference on Calorimetry and Thermal Analysis, organizer of the 2nd Japan–China Joint Symposium on Thermal Measurements (1989, Osaka), a member of the Organizing Committee of the 11th IUPAC Conference on Chemical Thermodynamics (1990, Como), and the International Conference on Physics and Chemistry of Ice (1990, Sapporo). He has now much to do as chairman of the Organizing Committee of the 14th IUPAC Conference on Chemical Thermodynamics to be held in Osaka in 1996. Hiroshi Suga has served as the Editor-in-Chief of *Calorimetry and Thermal Analysis* (1976–1978) and on the editorial boards of *The Journal of Chemical Thermodynamics* (1976–1979). *Thermochimica Acta* (1981–), and the *Journal of Thermal Analysis* (1991–). A well-known book “Chemical Thermodynamics” written by J.G. Kirkwood and I. Oppenheim (McGraw–Hill Book Co.), was translated into Japanese by him and Professor Seki.

He is (or was) a Fellow of the Chemical Society of Japan, the Physical Society of Japan, the Crystallographic Society of Japan, the Polymer Society of Japan, the Japan Society of Calorimetry and Thermal Analysis, the Chinese Chemical Society, the New York Academy of Sciences, and the American Association for the Advancement of Science.

Hiroshi Suga's scientific activities, covering a wide range of chemical thermodynamics, in particular the study on ordering processes in disordered systems, have gained a high reputation. His realization of ordered ice drew thunderous applause. For those breakthrough scientific achievements he received the Physico-Chemical Division Award from the Chemical Society of Japan, the Huffman Memorial Award from the US Calorimetry Conference, and the Kurnakov Memorial Medal from the Russian Academy of Sciences. In 1995 he was awarded the Japan Academy Prize, the most honourable prize in Japan with a long history.

He enjoys listening to Clasical music from Bach to modern composers like Prokofiev, his favorite being Gustav Mahler. He also likes his collection of natural stones and minerals which he considers as one of the most beautiful gifts from God. It should be of interest to remark here that Professor H. Suga considers himself to be born as a chemical thermodynamicist because his name contains fundamental thermodynamic quantities, i.e., $H$ (enthalpy), $S$ (entropy), $U$ (internal energy), $G$ (Gibbs energy), and $A$ (Helmholtz energy).

This special issue of *Thermochimica Acta* is dedicated to Professor Hiroshi Suga on the occasion of his 65th birthday. It consists of 32 papers on “Transition Phenomena in Condensed Matter”, contributed by former students, collaborators and friends to show their appreciation for him. The theme title is closely related to his lifework and the phrase “Transition Phenomena” involves both phase transitions occurring in thermodynamical equilibrium states and glass transitions or relaxation phenomena encountered in nonequilibrium states.

*Michio Sorai*
*Jaroslav Šesták*

## References

[1] H. Suga and S. Seki, J. Non-Cryst. Solids, 16 (1974) 171.
[2] H.Suga, S. Seki, Faraday Discuss. Royal Soc. Chem., 69 (1980) 221.
[3] R.W. Cahn, Nature, 253 (1975) 310.
[4] Y. Tajima, T. Matsuo and H. Suga, Nature, 299 (1982) 810.

## A list of selected papers

[1] Nuclear magnetic resonance experiment on solid hexamethyldisilane.
T. Yukitoshi, H. Suga, S. Seki and J. Itoh, J. Phys. Soc. Jpn., 12 (1957) 506.
[2] On the orientational order–disorder transition in crystalline aniline hydrobromide.
H. Suga, Bull. Chem. Soc. Jpn., 34 (1961) 426.
[3] Thermodynamic properties and order–disorder phase transitions of potassium cyanide.
H. Suga, T. Matsuo and S. Seki, Bull. Chem. Soc. Jpn., 38 (1965) 1115.
[4] Self-diffusion in some plastic crystals.
H. Suga, M. Sugisaki and S. Seki, Mol. Cryst., 1 (1966) 377.
[5] Phase changes in crystalline and glassy-crystalline cyclohexanol.
K. Adachi, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., 41 (1968) 1073.
[6] Calorimetric study of the glassy state IV. Heat capacities of glassy water and cubic ice.
M. Sugisaki, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., 41 (1968) 2591.
[7] A phase transition in the quinol hydrogen cyanide clathrate compound.
T. Matsuo, H. Suga and S. Seki, J. Phys. Soc. Jpn., 25 (1968) 641.
[8] The so-called polymerization of vinyl acetate in the glassy state.
K. Nakatsuka, K. Adachi, H. Suga and S. Seki, J. Polym. Sci., B6 (1968) 779.
[9] Glassy crystalline state in the two-dimensional hydrogen-bonded network in stannous chloride dihydrate and dideuterate crystals.
T. Matsuo, M. Oguni, H. Suga and S. Seki, Proc. Jpn. Acad., 48 (1972) 237.
[10] A kinetic study of the energy storing enzyme-product complex in the hydrolysis of ATP by heavy meromyosin.
T. Yamada, H. Shimizu and H. Suga, Biochem. Biophys. Acta, 305 (1973) 642.
[11] Calorimetric study of the glassy state. X. Enthalpy relaxation at the glass-transition temperature of hexagonal ice.
O. Haida, T. Matsuo, H. Suga and S. Seki, J. Chem. Thermodyn., 6 (1974) 815.
[12] Thermodynamic investigation of glassy states of pure simple compounds.
H. Suga and S. Seki, J. Non-cryst. Solids, 16 (1974) 171.
[13] Calorimetric study of the glassy state. XII. Plural glass transition phenomena of ethanol.
O. Haida, H. Suga and S. Seki, J. Chem. Thermodyn., 9 (1977) 1133.
[14] High-resolutional calorimetric study on solid solutions $SnCl_2(H_2O)_x(D_2O)_{2-x}$.
M. Tatsumi, T. Matsuo, H. Suga and S. Seki, Bull. Chem. Soc. Jpn., 52 (1979) 716.
[15] Heat capacity of *p*-*n*-hexyloxybenzylideneamino-*p'*-benzonitrile.
K. Tsuji, M. Sorai, H. Suga and S. Seki, Mol. Cryst. Liq. Cryst., 55 (1979) 71.
[16] Frozen-in states of orientational and positional disorder in molecular solids.
H. Suga and S. Seki, Faraday Discus., No. 69, p. 221, R. Soc. Chem., 1980.

[17] Thermodynamic properties of ferrocene crystal.
K. Ogasahara, M. Sorai and H. Suga, Mol. Cryst. Liq. Cryst., 71 (1981) 189.
[18] Phase transitions in some two-dimensional hydrogen-bonded hydrate crystals.
T. Matsuo and H. Suga, Rev. Inorg. Chem., 3 (1981) 371.
[19] Phase transition in KOH-doped hexagonal ice.
Y. Tajima, T. Matsuo and H. Suga, Nature, 299 (1982) 810.
[20] Orientational and positional disorder of ions and its freezing in the $CsNO_2 \cdot TlNO_2$ system.
K. Moriya, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 44 (1983) 1121.
[21] Ordering processes in some disordered systems.
H. Suga, Pure Appl. Chem., 55 (1983) 427.
[22] Calorimetric study of phase transition in hexagonal ice doped with alkali hydroxides.
Y. Tajima, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 45 (1984) 1135.
[23] Unusual glass transition of liquid crystal in *p*-*n*-hexyloxybenzylidene-*p*′-butylaniline.
M. Sorai, H. Yoshioka and H. Suga, Liquid Crystals and Ordered Fluids, vol. 4, Plenum Publ. Corp. NY, 1984, p. 233.
[24] Molecular motion and phase transition in hydroquinone clathrate compound.
T. Matsuo and H. Suga, J. Incl. Phenom., 2 (1984) 49.
[25] The equilibrium low-temperature structure of ice.
A. J. Leadbetter, R.C. Ward, J.Q.W. Clark, P.A. Tucker, T. Matsuo and H. Suga, J. Chem. Phys., 82, (1985) 424.
[26] Calorimetric study on thiophene from 13 to 300 K. Emergence of two glassy crystalline states.
P. Figuiere, H. Szwarc. M. Oguni and H. Suga, J. Chem. Thermodyn., 17 (1985) 949.
[27] Phase transition and glass transition in rubidium cyanide.
T. Shimada, T. Matsuo, H. Suga and F. Luty, J. Chem. Phys., 85 (1986) 3530.
[28] Thermodynamic aspects of glassy crystals: approaching the equilibrium glass.
H. Suga, Ann. N.Y. Acad. Sci., 484 (1986) 248
[29] High-pressure calorimetric study on the ice XI-Ih transition.
O. Yamamuro, M. Oruni, T. Matsuo and H. Suga, J. Chem. Phys., 86 (1987) 5137.
[30] Heat capacity and glass transition of pure and doped cubic ices.
O. Yamamuro, M. Oguni, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 48 (1987) 935.
[31] Calorimetric study of pure and KOH-doped tetrahydrofuran clathrate hydrate.
O. Yamamuro, M. Oguni, T. Matsuo and H. Suga, J. Phys. Chem. Solids, 49 (1988) 425.
[32] Heat capacity calorimetry at cryogenic temperatures.
H. Suga, M. Sorai and T. Matsuo, Proc. INCONCRYO'85, 159 Indian Cryogenics Council, 1987.
[33] Static and dynamic properties of hydrogen sulphide in hydroquinone clathrates.
H. Ukegawa, T. Matsuo, H. Suga, A.J. Leadbetter, R.C. Ward and J.W. Clark, Can. J. Chem., 66 (1988) 944.
[34] Doping effect of benzene on phase transitions on thiophene.
N. Okamoto, M. Oguni and H. Suga, Solid State Commun., 70 (1989) 219.
[35] Adiabatic calorimeter as an ultra-low frequency spectrometer.
H. Suga and T. Matsuo, Pure Appl. Chem., 61 (1989) 1123.
[36] Thermodynamic studies of clathrate hydrate.
O. Yamamuro and H. Suga, J. Therm. Anal., 35 (1989) 2025.
[37] Enthalpy relaxation in vapor-deposited butyronitrile.
M. Oguni, H. Hikawa and H. Suga, Thermochim. Acta, 158 (1990) 143.
[38] Dielectric study on pure and KOH-doped tetrahydrofuran clathrate hydrates.
O.Yamamuro, T. Matsuo and H. Suga, J. Incl. Phenom., 8 (1990) 33.
[39] Phase transition and glass transition in isocyanocyclohexane studied by a polaro-calorimeter.
I. Kishimoto, J.-J. Pinvidic, T. Matsuo and H. Suga, Proc. Jpn. Acad., 67B (1991) 66.
[40] Solid state amorphization and glass transition of tri-*O*-methyl-$\beta$-cyclodextrin.
I. Tsukushi, O. Yamamuro and H. Suga, J. Therm. Anal., 37 (1991) 1359.
[41] Thermodynamic study of ice and clathrate hydrates.
H. Suga, T. Matsuo and O. Yamamuro, Pure Appl. Chem., 64 (1992) 17.

[42] Neutron diffraction and calorimetric studies on methylammonium iodide.
O. Yamamuro, T. Matsuo, H. Suga, W.I.F. David, R.M. Ibberson and A.J. Leadbetter, Acta Cryst., B48 (1992) 329.
[43] A strong isotope effect in phase transition behaviour of ammonium hexachlorotellurate.
Y. Kume, Y. Miyazaki, T. Matsuo, H. Suga, W.I.F. David and R.M. Ibberson, Physica, B180 and 181 (1992) 594.
[44] The heat capacity of solid $C_{60}$.
T. Matsuo, H. Suga, W.I.F. David, R.M. Ibberson, P. Bernier, A. Zahab, C. Fabe and A.R.A. Dworkin, Solid State Commun., 83 (1992) 711.
[45] Thermodynamic study of ice and clathrate hydrates.
H. Suga, T. Matsuo and O. Yamamuro, Pure Appl. Chem., 64 (1992) 17
[46] Slow relaxation processes in glassy crystals.
H. Suga, in: K. Kawasaki (Ed.), Slow dynamics in condensed matter, AIP Conference Proceedings, vol. 256, New York, 1992.
[47] Molecular motion and phase transitions of clathrate hydrates.
H. Suga, T. Matsuo and O. Yamamuro, Supramolecular Chem., 1 (1993) 221.
[48] Frozen-in disorder and slow relaxation in crystals.
H. Suga, J. Chem. Thermodyn., 25 (1993) 463.
[49] A calorimetric study of deuteration effect on the phase behavior in $Rb_3H(SeO_4)_2$.
M. Fukai, T. Matssuo, H. Suga and M. Ichikawa, Solid State Commun., 87 (1993) 939.
[50] Glass transition of Myoglobin crystal.
Y. Miyazaki, T. Matsuo and H. Suga, Chem. Phys. Lett., 213 (1993) 303.
[51] Neutron diffraction and calorimetric studies of methylammonium chloride.
O. Yamamuro, N. Onoda-Yamamuro, H. Suga, T. Kamiyama, T. Ishigaki and H. Asano, J. Phys. Chem. Solids, 55, p. 20 (1994) 383.
[52] Closer relation between thermal analysis and calorimetry.
H. Suga, J. Therm. Anal., 42 (1994) 331.
[53] Thermal conductivity of low-density amorphous ice.
O. Andersson and H. Suga, Solid State Commun., 91 (1994) 985.
[54] Heat capacities and glass transitions of 1-propanol and 3-methylpentane under pressure. New evidence for the entropy theory.
S. Takahara, O. Yamamuro and H. Suga, J. Non-Cryst. Solids, 171 (1994) 259.
[55] Thermal conductivity of the Ih and XI phases of ice.
O. Andersson and H. Suga, Phys. Rev., B50 (1994) 6583.
[56] Calorimetric study on structural relaxation of 1-pentene in vapor-deposited and liquid-quenched glassy states.
K. Takeda, O. Yamamuro and H. Suga, J. Phys. Chem., 99 (1995) 1602.