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Review

DIFFERENTIAL THERMAL ANALYSIS UNDER HIGH-PRESSURE GAS ATMOSPHERES: APPLICATIONS TO MATERIALS SCIENCE AND ENGINEERING. A REVIEW *

YUTAKA SAWADA

Department of Industrial Chemistry, Faculty of Engineering, Tokyo Institute of Polytechnics, Iiyama, Atsugi-shi, Kanagawa 243-02 (Japan)

HIROSHI HENMI

Department of Industrial Chemistry, School of Engineering, Tokai University, Kitakaname, Hiratsuka-shi, Kanagawa 259-12 (Japan)

NOBUYASU MIZUTANI ** and MASANORI KATO

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 (Japan)

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ABSTRACT

Applications of differential thermal analysis under high-pressure gas atmospheres are critically reviewed. High-pressure differential scanning calorimetry and thermogravimetry are described. The influence of gas pressure (partial pressure of carbon dioxide and water vapor) on decarbonation reactions is intensively discussed with new results and interpretations.

Other applications of high-pressure DTA to materials science and engineering are also reviewed, i.e. dehydration, oxidation and other inorganic and organic reactions, and phase transitions such as boiling, melting and polymorphism. Materials which are used under normal pressure are often characterized more clearly by analysis under high-pressure gas atmospheres; e.g. separation of superimposed DTA peaks (two endothermic peaks or an endothermic peak and an exothermic peak), evaluation of oxidation stability, determination of self-ignition temperature, etc.

Prospects for high-pressure DTA are also discussed.

INTRODUCTION

Throughout the long history of differential thermal analysis, the appearance of high-pressure DTA seems natural since chemical reactions and

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

** Author to whom all correspondence should be addressed.

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phase transitions are influenced not only by temperature but also by pressure. Probably the first report on high-pressure DTA was by Smyth and Adams [1] in 1923. Various instruments for high-pressure thermal analyses (DTA, DSC, TG, measurement of electro-conductivity and magnetic susceptibility, etc.) were constructed in the 1970s as reviewed by Wendlandt [2] in 1986. Applications of high-pressure thermal analyses, especially DTA, are spreading steadily in various fields of materials science and engineering, the main reasons for which are: (i) in situ observation under high-pressure gas atmospheres is indispensable for inorganic and organic reactions and phase transitions; (ii) materials which are used under normal pressure are often characterized more clearly by analysis under high-pressure atmospheres. The present paper critically reviews the instrumentation, applications and prospects for DTA under high-pressure gas atmospheres. High-pressure DSC and TG are mentioned where applicable.

INSTRUMENTATION

Off-the-shelf high-pressure DTA or DSC (and/or TG) instruments are available, for example, from Shinku-riko Co. Ltd. [3] and Rigaku-Denki Co. Ltd. (Japan). However, laboratory-constructed instruments have often been used, incorporating conventional DTA or DSC (and/or TG) assemblies within a pressure chamber, e.g., a vessel for hydrothermal synthesis.

Pressure medium

Gases are most often used as a pressure medium: uncondensable inert gases (argon, nitrogen, helium), condensable inert gases (freon, etc.), uncondensable reactive gases (oxygen, hydrogen, carbon dioxide, carbon monoxide, etc.) and condensable reactive gases (water, ammonia, sulfur, selenium, tellurium, etc.). When used below ~ 100 atm, gas can be supplied easily by direct connection with a gas cylinder; overflowing is also available. An extra pressure generator is necessary for higher pressures. The pressure chamber is sometimes filled with liquid carbon dioxide [4]; a high-pressure gas atmosphere (up to 3000 atm, non-isobar condition) is obtained relatively easily on heating.

Liquid pressure media are also used, e.g. silicone oil [5,6] and 3-methylpentane [7]. Liquid samples, such as liquid crystals, can be pressurized directly with a piston assembly when no gaseous phase coexists.

Saito et al. [8] described high-pressure DTA using a solid pressure medium. DTA measurement using the solid pressure medium (pyrophyllite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$; talc, $3MgO \cdot 4SiO_2 \cdot H_2O$, etc.) appears to be extremely difficult [9].

Pressure control and influence of self-generated atmospheres

When the specimen evolves gas, during thermal decomposition, evaporation, reduction, desorption, etc., the partial pressure of the evolved gas increases to form a so-called "self-generated atmosphere" in spaces between the specimen powders or in micro-cracks of the specimen through which the evolved gas escapes. In the case of thermal decomposition in vacuo or under relatively low pressures (for example ~ 1 atm), precise control and measurement of the partial pressure of the gas is difficult or impossible due to the self-generated atmosphere, since sufficient ventilation is not possible in many cases [10]. However, control of gas pressure is relatively easy when only a single gas is used under high-pressure gas atmospheres; e.g. decarbonation under a high-pressure carbon dioxide atmosphere. The control and measurement of partial pressure is difficult when the gas evolved by the specimen is different from the atmosphere, e.g. decarbonation under a nitrogen atmosphere. If practically no gas mixing occurs, all the carbon dioxide evolved from the specimen will remain around the surface of the specimen instead of nitrogen. Thus, the actual partial pressure of carbon dioxide will be approximately the same as that of the total pressure of the system. The partial pressure of the evolved gas is affected by various experimental factors such as the shape and size of the specimen container, the amount and packing density of the specimen powder, flow rate of the inert gas such as nitrogen, the heating rate, etc. A systematic and quantitative study on the influence of self-generated atmospheres is thus necessary.

Control and measurement of the partial pressures of condensable gases are extremely difficult. Pressure control of condensable gases is difficult or often impossible since the gas-delivery system (pipes, valves, etc.) must be heated in order to avoid condensation. Sealed capsules are often used for hydrothermal synthesis or chalcogenide synthesis where the partial pressure in the capsule is not measured directly but estimated, when possible, from thermochemical data. The influence of the self-generated water vapor atmosphere on the decomposition temperature of basic carbonates will also be discussed later.

APPLICATIONS

High-pressure reactions

Decarbonation

Examples of the application of thermal analyses (DTA/DSC and TG) to carbonates under high-pressure gas atmospheres [1,11–24] are listed in Table 1. Some results of recent studies are described below.

TABLE 1

Applications of thermal analyses to decarbonation reactions under high-pressure gas atmospheres

Authors	Analysis	Specimen	Atmosphere		T_{max} (°C)	Ref.
				(atm)		
Smyth and Adams (1923)	DTA	$CaCO_3$	CO_2	1000	1350	1
Stone (1954)	DTA	$MgCO_3$	CO	6	1000	11
Rabatin and Card (1959)	TG	$MnCO_3$	CO_2	13	700	12
Sasaki et al. (1969)	TG	$MnCO_3$	CO_2	30	850	13
		$CaC_2O_4 \cdot H_2O$	N_2	50	1050	
Williams and Wendlandt (1973)	TG	$NaHCO_3$	CO_2	27	500	14
			N_2	69	500	
Dobner et al. (1976)	TG	$CaMg(CO_3)_2$	CO_2	30	1100	15
Li and Rogan (1978)	TG	$CaMg(CO_3)_2$	CO_2	60	1100	16
Sawada et al. (1979)	DTA	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$	CO_2	50	700	17
			N_2	45	700	
			Ar	20	700	
		$MgCO_3 \cdot 3H_2O$	CO_2	50	700	
Yamaguchi et al. (1980)	DTA	$PbCO_3$	CO_2	50	700	18
Yamaguchi et al. (1980)	DTA	$2PbCO_3 \cdot Pb(OH)_2$	CO_2	50	700	19
Rogan and Li (1980)	TG	$CaMg(CO_3)_2$	CO_2	34	1000	20
Henmi et al. (1985)	DTA	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$	CO_2	50	350	21
Henmi et al. (1986)	DTA	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$	CO_2	50	500	22
			N_2	50	500	
Henmi et al. (1986)	DTA	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$	N_2	25	300	23
		$CuCO_3 \cdot Cu(OH)_2$	CO_2	50	500	
		$2CuCO_3 \cdot Cu(OH)_2$	CO_2	40	400	
		$2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$	CO_2	50	500	
			N_2	50	400	
		$2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$	CO_2	50	350	
			N_2	50	300	
Henmi et al. (1987)	DTA	$(BiO)_2 \cdot CO_3$	CO_2	50	700	24
			N_2	50	500	
Sawada et al. (1987)	DTA	$MgCO_3$	CO_2	50	800	present work
		$CdCO_3$	CO_2	50	550	
		$NiCO_3 \cdot 6H_2O$	CO_2	50	450	

In Fig. 1, DTA peak temperatures for two normal carbonates with the calcite structure, $MgCO_3$ and $CdCO_3$, are plotted with equilibrium conditions between the respective carbonate and oxide. Although the equilibrium

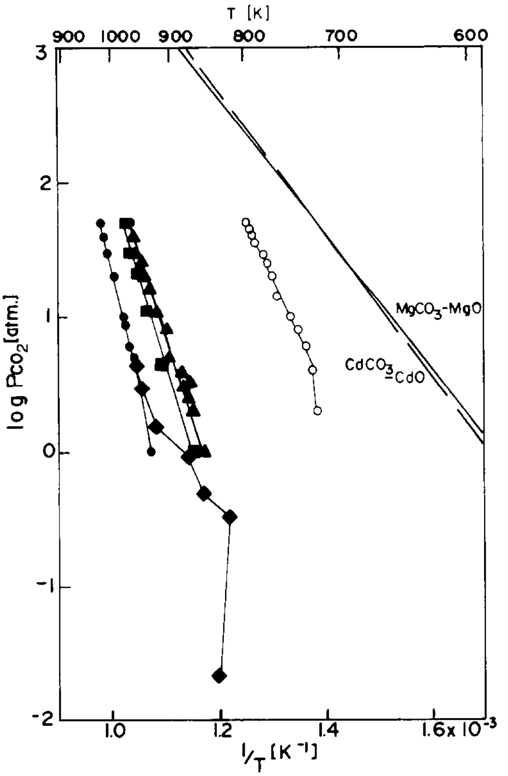

Fig. 1. Thermal decomposition of $MgCO_3$ and $CdCO_3$ under high-pressure carbon dioxide atmospheres. (●) DTA peak temperature of $MgCO_3$ (pulverized natural magnesite, present work); (▲) DTA peak temperature of $MgCO_3$ obtained via decomposition of hydromagnesite, $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$, under high-pressure carbon dioxide atmospheres [17]; (■) DTA peak temperature of $MgCO_3$ obtained via decomposition of nesquehonite, $MgCO_3 \cdot 3H_2O$, under high-pressure carbon dioxide atmospheres [17]; (◆) DTA peak temperature of $MgCO_3$ (pulverized natural magnesite) reported by Stone [11]; and (○) DTA peak temperature of $CdCO_3$ (synthesized powder, present work). (———) Equilibrium between $MgCO_3$ and MgO, and (— — —) equilibrium between $CdCO_3$ and CdO, based on thermochemical data [25,26].

conditions of both carbonates are very close, it is apparent that the high-pressure DTA peak temperatures are markedly different. This suggests that the decomposition mechanism is governed not only by the equilibrium conditions but also by other factors (kinetic factors). DTA peak temperatures by Stone [11] ($MgCO_3$) shown in Fig. 1 agree with the present data only in the high-pressure range.

The DTA results for thermal decomposition of basic carbonates [17,21–23] are summarized in Table 2. Peak temperatures of decarbonation for some basic carbonates were independent of carbon dioxide pressure in the high-pressure range. The temperatures are close to the critical temperature of water (374° C) above which no condensed water exists. The peak tempera-

TABLE 2

Results of differential thermal analysis for thermal decomposition of basic carbonates under high-pressure carbon dioxide atmospheres

Metal ion	Basic carbonate (natural or synthetic)	Peak temp. of decarbonation at 50 atm (°C)	Dehydration during decarbonation	Saturation of peak temp. of decarbonation	Decomposition process	Ref.
Mg^{2+}	$MgCO_3 \cdot 3H_2O$ (syn.)	710	not obs.	not obs.	multiple steps	17
	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ (syn.)	690	not obs.	not obs.		17
Co^{2+}	$2CoCO_3 \cdot 3Co(OH)_2 \cdot nH_2O$ (syn.)	490	obs.	not obs.		23
Ni^{2+}	$NiCO_3 \cdot 6H_2O$ (syn.)	410	obs.	obs.		present work
	$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (syn.)	400	obs.	obs.		22
Cu^{2+}	$CuCO_3 \cdot Cu(OH)_2$ (nat.)	400	obs.	obs.	single step	23
	$2CuCO_3 \cdot Cu(OH)_2$ (nat.)	350	obs.	obs.		23
	$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ (syn.)	330	obs.	obs.		21
Zn^{2+}	$2ZnCO_3 \cdot 3Zn(OH)_2 \cdot H_2O$(syn.)	310	obs.	obs.		23

Not obs., not observed; obs., observed.

ture saturation suggests that the water caused by dehydration plays an important role in decarbonation; the water will remain on the surface of the specimen by capillary condensation or adsorption under high-pressure atmospheres at temperatures below the critical point of water so as to accelerate the decomposition.

Dolomite, $CaMg(CO_3)_2$, decomposes in two steps under carbon dioxide atmospheres; the DTA peak temperature of the first step is surprisingly shifted to a lower temperature at higher P_{CO_2} (< 1 atm) [27–30]. There are only a few reports on decarbonation under high-pressure atmospheres. Sulfur removal from fuel gases using half-calcined dolomite as a cyclic H_2S/CO_2 acceptor was investigated by high-pressure TG by Dobner et al. [15] and Li and Rogan [16]. Rogan and Li [20] reported that the rate of calcination (decarbonation) was independent of P_{CO_2} and the pellet diameter but dependent on the temperature.

Dehydration or hydration, etc.

Other applications of high-pressure thermal analyses to inorganic reactions [3,31–49] are shown in Table 3.

The dehydration process has been studied by various workers [31–40] who controlled the partial pressure of water vapor (self-generated atmo-

TABLE 3

Applications of high-pressure thermal analyses to other inorganic reactions

Reaction	Authors	Analysis	Specimen	Atmosphere	Ref.
Dehydration	Stone (1952)	DTA	Na-montmorillonite	hydrothermal	31
	Lodding and Hammell (1960)	DTA	$Al(OH)_3$	N_2	32
			α-FeOOH	N_2	
	Stone (1960)	DTA	Ca-montmorillonite	N_2	33
			$CuSO_4 \cdot 5H_2O$	O_2	
	Brown, Jr. et al. (1972)	TG	$CuSO_4 \cdot 5H_2O$	N_2	34
	Williams and Wendlandt (1973)	TG	$CuSO_4 \cdot 5H_2O$	N_2	35
			$BaBr_2 \cdot 2H_2O$	N_2	
	Williams and Wendlandt (1973)	DTA	$CuCl_2 \cdot 2H_2O$	N_2	36
			$CoSO_4 \cdot 7H_2O$	N_2	
	Veprek et al. (1974)	DTA	$CaSO_4 \cdot 2H_2O$	hydrothermal	37
	Amita et al. (1983)	DTA/TG	$CaSO_4 \cdot 2H_2O$	N_2	38
	Amita et al. (1984)	DTA	$CaSO_4 \cdot 0.5H_2O$	N_2	39
	Burdett (1985)	TG	molecular sieve	CO_2	40
Hydride formation or decomposition	Tobola (1975)	DTA and DPA	NaH, etc.	H_2	41
	Nomura et al. (1979)	DTA/TG	Mg–Ni alloys	H_2	42
Oxidation or reduction	McKewan (1962)	TG	Fe_3O_4	H_2	43
	Biermann and Heinrichs (1962)	TG	CrO_6	O_2	44
	Kato et al. (1977)	DTA/TG	$Na_2S \cdot 9H_2O$	O_2	3
	Ueda et al. (1979)	DTA	FeO	H_2	45
Chalcogenide synthesis	Bollin and Kerr (1961)	DTA	Bi_2Se_3, Cu–S system, etc.	S or Se (sealed)	46
	Bollin (1970)	DTA	Ag–S system, etc.	S (sealed)	47
Solar cooling	Diawara et al. (1986)	DTA	$CaCl_2$	NH_3	48
			zeolite	freon	
Decomposition	Gusev et al. (1985)	DTA	NH_4COONH_2	(sealed)	49
			$Cu(HCOO)_2$	(sealed)	

sphere) "indirectly" by controlling the pressure of the surrounding atmosphere (an inert gas such as nitrogen). The partial pressure of water vapor remained unknown when using a gas flow system or a closed system with a relatively large pressure vessel. Estimation of the partial pressure of water vapor in a closed capsule is possible only when equilibrium is accomplished and thermochemical data are obtainable.

Veprek et al. [37] emphasized the importance of hydrothermal DTA (in situ observation of chemical reaction under a high-pressure water vapor atmosphere) for industrial processes involving the reaction of water with solids, e.g. production of plaster, hardening of cement paste at normal temperature or in an autoclave, synthesis of molecular sieves. They reported results on the dehydration of gypsum ($CaSO_4 \cdot 2H_2O$) via hemihydrates ($CaSO_4 \cdot 0.5H_2O$) to anhydride II, hydration of an anhydrous cement compound accelerated in an autoclave, and hydrothermal reactions for the paste $Ca(OH)_2$ and SiO_2 (silica gel or quartz).

Silica gel had been used for the removal of water vapor from the coolant gas (CO_2) in a gas-cooled nuclear reactor. Burdett [40] studied a potential replacement for a molecular seive using high-pressure TG under a carbon dioxide and nitrogen atmosphere. Complicated results were obtained due to co-adsorption of carrier gas and water.

Oxidation and reduction

Oxidation and reduction of metals and/or metal oxides are industrially important. Kinetic studies of the reactions under high-pressure atmospheres of oxygen (CrO_6 [44] and $NaS_2 \cdot 9H_2O$ [3]) or hydrogen (Fe_3O_4 [43] and FeO [45]) have been reported.

Explosives

Applications of high-pressure thermal analyses to organic reactions [50–65] are shown in Table 4.

Thermal decomposition and exothermic reactions are pressure dependent for most materials of interest in the rocket industry. Bohon [61] reported high-pressure DTA under argon atmospheres. For this purpose, versatility, ruggedness, chemical inertness to fluorine-containing samples and easy replacement of thermocouples damaged by detonations were particularly considered.

Nitro compounds and their thermal stability are of particular interest to the urethane industry. David [62] studied dinitrotoluene and tolylenediamine using high-pressure DTA under a nitrogen atmosphere.

Energy

The liquification or gasification of coal under a high-pressure atmosphere of hydrogen (or sometimes water vapor and carbon monoxide) with and without catalyzer have been investigated by DTA and TG; examples are listed in Table 4 [50–57].

Metal hydrides for energy storage have been widely investigated under high-pressure hydrogen atmospheres, e.g. Tobola (NaH) [41] and Nomura et al. (Mg–Ni alloys by DTA and TG) [42]. TG is rather ineffective since the weight change during the formation or decomposition of hydrides is relatively small. Tobola [41] reported high-pressure "differential pressure analysis (DPA)" which detects the pressure difference between a closed pressure vessel containing the specimen and high-pressure hydrogen and another

TABLE 4

Application of high-pressure thermal analysis to organic reactions

Reactions	Authors	Analysis	Atmosphere	Specimen	Ref.
Liquification or gasification of coal	Takeya et al. (1964)	DTA	H_2	coal	50
	Ishi et al. (1968)	DTA	H_2O	coal	51
	Oouchi et al. (1978)	DTA	H_2	coal	52
	Tanabe et al. (1979)	DTA	H_2	coal	53
	Arendt and van Hook (1981)	TG	H_2	coal	54
	Ghodsi and Neumann-Tilte (1983)	TG	H_2	coal	55
	Cypres et al. (1985)	DTA	H_2	coal	56
	Muhlen and Sulimma (1986)	TG	H_2O H_2 CO_2 CO	coal	57
Oxidation or combustion of oil, fat, etc.	Levy et al. (1970)	DSC	O_2 N_2 air	orange oil brake fluids motor oil	58
	Bae (1972)	TG	air N_2	crude oil	59
	Wakakura and Sato (1981)	DTA	O_2	lubricating oil	60
Explosion	Bohon (1961)	DTA	Ar	explosives propellants	61
	David (1965)	DTA	N_2	dinitrotoluene toluenediamine	62
	Raemy (1981)	DTA	N_2	coffee beans cocoa chicory	63
	Raemy and Loeliger (1985)	DTA	O_2	cellulose maltodextrin guar gum cocoa butter palm oil casein, etc.	64
Miscellaneous	Wisnewski et al. (1965)	DTA	N_2	hide and leather	65
	Levy et al. (1970)	DSC	N_2	phenoric resin	58

closed pressure vessel containing only high-pressure hydrogen for reference; the absolute pressure increases with increasing temperature in this system.

Diawara et al. [48] studied the zeolite–freon and $CaCl_2$–ammonia systems for solar cooling by high-pressure TG.

Chalcogenide syntheses

Bollin and Kerr [46] and Bollin [47] systematically investigated chalcogenides by high-pressure DTA under a closed system (in a glass vial);

TABLE 5

Applications of high-pressure differential thermal analysis to phase transitions of inorganic compounds

Transition	Authors	Specimen	Pressure (atm)	Ref.
Melting	Goranson and Kracek (1932)	$K_2Si_4O_9$	3000	66
	Kracek (1946)	Ag–S system	(sealed)	67
	Yoder, Jr. (1952)	$CaMgSi_2O_6$	5000	68
	Clark (1959)	alkali haloids	25000	69
	Harker (1964)	Ca–Si–O–(OH)	1000	70
	Cohen and Klement, Jr. (1974)	$NaNO_3$	6000	71
	Koster van Groos (1979)	$NaF–Na_2CO_3$	10000	72
Boiling	Wisnewski et al. (1965)	H_2O	2	65
	Levy et al. (1970)	H_2O	70	58
Polymorphysm	Gibson (1928)	SiO_2 (quartz)	3000	4
	Goranson and Kracek (1932)	$K_2Si_4O_9$	3000	66
	Kracek (1946)	Ag–S system	(sealed)	67
	Yoder, Jr. (1950)	SiO_2 (quartz)	10000	73
	Koster van Groos and Ter Heege (1973)	SiO_2 (quartz)	10000	74
	Cohen and Klement, Jr. (1973)	$CaCO_3$	5000	75
	Klement, Jr. and Cohen (1974)	Ca_2SiO_4	7000	76
	Cohen et al. (1974)	SiO_2 (quartz)	7000	77
	Cohen and Klement, Jr. (1974)	$NaNO_3$	6000	78
	Cohen and Klement, Jr. (1975)	SiO_2 (cristobalite)	6000	79
	Cohen and Klement, Jr. (1979)	SiO_2 (cristobalite)	6000	80
		$AlPO_4$	6000	
		$GaPO_4$	6000	

Cu–S, Fe–S and Ag–S systems, $CuFeS_2$, Bi_2Se_3 and some minerals (MoS_2, ZnS, etc.) were reported. This kind of investigation must be effective as a preliminary survey before synthesis although the pressure of the volatile component is not measured directly.

High-pressure phase transitions

Applications of high-pressure DTA (and DSC) to phase transitions of inorganic compounds [4,58,65–80] and organic compounds [5–7,58,81–95] are shown in Tables 5 and 6, respectively.

Boiling

Wisnewski et al. [65] studied the boiling point of water using high-pressure DTA up to ~ 2 atm nitrogen. They reported a good agreement between the DTA peak temperature and the boiling point predicted from equilibrium

TABLE 6

Applications of high-pressure differential thermal analysis to phase transitions of organic compounds

Authors	Specimen	Pressure (atm)	Ref.
Savill and Wall (1967)	benzene and benzonitrile	10000	81
Davidson and Wunderlich (1969)	polyethylene and poly(ethylene-butene-1) copolymer	4200	82
Levy et al. (1970)	benzoic acid	14	58
Wurflinger and Schneider (1977)	13 n-alkanes	300	83
Takamizawa (1978)	n-octadecane and n-tetracoasane	5000	84
Kamphausen and Schneider (1978)	heneicosane and hexacosane	2300	85
Sandrock et al. (1978)	*p*-ethoxy-benzylidene-*p*-n-butylaniline (EBBA)	2500	86
Spratte and Schneider (1979)	bis(4, 4′-n-alkoxybenzylidene)-1,4-phenylenediamines	3000	87
Shimizu et al. (1979)	$\{N(CH_3)_4\}_2MnCl_4$	1000	6
Scheinbein et al. (1979)	poly(vinylidene fluoride) (PVF2)	10000	88
Herrmann et al. (1980)	TBBA	1000	89
Arntz and Schneider (1980)	cyclohexane, 1,3-dimethyladamantane and 1,3,5-trimethyladamantane	4000	90
Arntz (1980)	cyclohexane	4000	91
Sandrock et al. (1981)	2-chloro-2-methylpropane	4000	92
Sandrock (1982)	diamantane	6000	93
Kleinhans et al. (1983)	4′-n-nonyloxy-4-n-cyanobiphenyl (90CB)	2000	94
Kleinhaus and Schneider (1983)	4-octyloxy-4′-cyanobiphenyl (80CB)	2000	95
Schneider (1985)	cyclohexane, 2-chloro-2-methylpropane, polyethylene and diamantane	6000	5
Yamamuro et al. (1986)	$CH_3NH_3BF_4$	2000	7

data; the partial pressure of water vapor was estimated to be equal to the total pressure.

Levy et al. [58] studied the boiling point of water using high-pressure DSC up to ~ 70 atm; the atmosphere was not mentioned, but was assumed to be nitrogen. In order to avoid evaporation and to insure equilibrium conditions, they used a small hermetically sealed aluminum sample pan which had a small (~ 0.002 in.) hole punched in the top to equalize pressure. The results (boiling point as a function of pressure) were in an excellent agreement with the available thermochemical data (steam tables). They also reported the boiling point of benzoic acid under a high-pressure atmosphere (~ 15 atm) of nitrogen.

Melting and polymorphism

Melting and polymorphism (shown in Tables 5 and 6) were studied at pressures of ~ 1000–10 000 atm which are higher than those of the reactions between gas and solid or gas and liquid, since the transition temperature changes only slightly when pressure is changed.

Phase transitions of inorganic compounds under high-pressure atmospheres were studied mainly for geology and materials science; some examples are shown in Table 5. Of these, the early application of high-pressure DTA by Gibson [4] in 1928 and Goranson and Kracek [66] in 1932 under relatively severe environments (3000 atm, 700–800 °C) should be particularly noted.

Examples of the phase transitions of organic compounds (solid, liquid, liquid crystal and plastic crystal phases) investigated by high-pressure DTA or DSC are shown in Table 6, which includes reports with non-gaseous pressure medium. The systematic reports by Schneider et al. on liquid crystals and plastic crystals are of particular interest; Schneider [5] reviewed recent results in 1985.

High-pressure analyses of the material used under normal pressure

Separation of superimposed endothermic peaks

Amita et al. [38] studied the dehydration of $CaSO_4 \cdot 2H_2O$ using high-pressure DTA under nitrogen atmospheres. They successfully separated superimposed endothermic peaks: evaporation of liquid water evolved from the crystal and evolution of water vapor from the crystal. They also determined the α/β ratio of $CaSO_4 \cdot 1/2H_2O$ by the area of the separated peaks of high-pressure DTA under nitrogen atmospheres [39].

Separation of an endothermic peak and an exothermic peak

Levy et al. [58] studied the thermal changes of a phenolic resin using high-pressure DSC under nitrogen atmospheres. They reported the separation of two competitive reactions: vaporization of water (pressure-sensitive endothermic reaction) and cure reaction (pressure-insensitive exothermic reaction). They also investigated California orange oil in air (ambient pressure and ~ 2 atm) and nitrogen (ambient pressure and ~ 3 atm). The boiling (endothermic) and the oxidation (exothermic) peaks were successfully separated.

Raemy [63] studied the thermal behavior of coffee and chicory products using DTA and heat-flow calorimetry under high-pressure nitrogen and argon atmospheres. Exothermic reactions (due to pyrolysis reactions, etc., according to his interpretation) were evidently observed since vaporization of the water contained in the food products was prevented under high-pressure atmospheres in the temperature domain of interest. The thermal behavior of food products is important for their characterization and the establishment of safe industrial processing conditions (for example, roasting) by determining the temperatures and enthalpies of the reaction.

Oxidation or combustion of oil, fat, etc.

Levy et al. [58] investigated the oxidative stability of different brands of automotive hydraulic brake fluids; no clear differences were detected by DTA under an air atmosphere at ambient pressure. The materials were successfully ranked by high-pressure DSC under oxygen atmospheres.

Other examples of oxidation or combustion [59,60] are listed in Table 4.

Determination of self-ignition temperatures

Raemy and Loeliger [64] performed high-pressure DTA under oxygen atmospheres for the investigation of spontaneous ignition and combustion of various food powders to obtain better measuring conditions compared with the previous method involving sample deposition on a heating plate or into a furnace heated to a known temperature. The advantages of high-pressure DTA under oxygen atmospheres are complete combustion of the sample by providing a large excess of oxygen and reduction of endothermic phenomena such as vaporization of the water often contained in food products.

HIGH-PRESSURE DTA IN THE FUTURE

The following technical improvements and applications are expected for high-pressure DTA (and DSC).

Sensitivity

Improvement of sensitivity of DTA or DSC requires reduction of electrical noise, better baseline stability (symmetrical heating of the specimen and the reference), constant heating rate, better heat transfer from the specimen to the thermocouple (reduction of heat capacity of the cell, direct contact between the specimen and the thermocouple), etc.

Improvement of sensitivity enables the analysis of a small amount of specimen and a small transition enthalpy change. Size effects of analysis, e.g. inhomogeneous heating, influence of self-generated atmosphere, then tend to be negligible. Analyses of thin films are of much importance today for industrial applications; these are examined for reactivity, crystallization from the amorphous phase, phase transition, thermal conductivity, etc. Analyses of very small single crystals or single grains of ultra-fine powder are also desirable.

Atmospheres

Evaluation of the partial pressure of condensable gases, such as water vapor, ammonia and freon, is extremely difficult. The influence of water vapor on reactions is important and should be investigated in detail.

The influence of self-generated atmospheres should be studied systematically using a sealed or semi-sealed capsule or forced gas flow through the powder specimen.

Non-contact temperature measurement of powders suspended in a gas stream is a useful goal.

Temperature

Rapid heating and maintaining constant temperature enable high-pressure thermal analysis under isothermal conditions. Rapid cooling enables quenching of the specimen for further analyses (for example in air or in vacuum) and an increase in the number of experimental cycles. Rapid heating and cooling require a compact DTA assembly with a small heat capacity and a high-power heater. Thermal analysis at higher temperatures enables the analysis of non-oxide ceramic materials, e.g. nitride and carbide, whose industrial importance is increasing.

In situ observation

More than one thermal analysis method should be applied simultaneously. So, DTA (and DSC), TG, differential thermal gas analysis (DTGA [96]) and other thermal analyses can be coupled with various kinds of known analytical techniques, e.g. X-ray diffraction analysis, optical microscopy.

Equilibrium data collection via oscillation methods

Equilibrium conditions are difficult to determine accurately using static equilibration techniques, particularly at low temperatures where the time required to reach equilibrium may be excessively long. Gleixner and Chang [97] tested two different cyclic thermogravimetric methods to determine the equilibrium pressure of carbon dioxide for the $CaCO_3$–CaO system as a function of temperature. The measurements involved repeated cycling of either temperature or partial pressure of carbon dioxide (< 1 atm) while holding the other parameter constant. Equilibrium was established when a symmetric mass signal was observed with no net mass change. Reliable measurements of the CO_2 partial pressure were obtained in a relatively short period of time compared to other methods. The results agreed with currently accepted values. This method can be applied under high-pressure gas atmospheres where higher reaction rates are expected.

Accessibility

Many systematic analyses are necessary to obtain a definite conclusion from the results of thermal analysis. Therefore, easier operation of the instrument will increase the efficiency of the high-pressure thermal analysis. Easier sample setting and automatic sample changing for overnight operation are anticipated developments.

Instrumentation for high-pressure thermal analysis is extremely expensive compared with that used at normal pressures; therefore, reduction of instrumental cost is desirable. A compact DTA assembly will largely reduce the wall thickness of the housing and the instrumental cost. Gas pressures below 10 atm are not subject to legal restrictions in Japan. Gas pressures below ~ 100 atm do not need a pressure generator, direct connection with a gas cylinder being convenient.

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