Thermogravimetric Method for Accurate Determination of Thermodynamic Quantities at High Temperatures

K . H . Harbbi

Department of physics, College of Education Ibn- AL - Haithem, University of Baghdad .

Abstract

This researd exhibit's a method to determine the change in Gibbs function,(enthalpy,entropy, and specific heat capacity) for monovariant heterogeneous equilibria .The thermodynamical quantities were obtained indirectly with in the measurment of temperature dependent on equilibrium system.

Introduction

The chemical reactivity of solids is strongly dependent on thermodynamic parameters. These parameters can be modified previousely by thermal treatments to the material. This fact explain's the importance of determination the thermodynamic parameters in order to enhance the reactivity of solids .

Experimental measuring techniques of thermodynamic constants yield, especially at high temperatures ,results which are often not accurate

enough for partical purposes and not sufficiently precise for theoretical calculations .The proposed method can be used to measure a certain chemical reactions i.e. the changes of Gibbs function(ΔG) ,enthalpy (ΔH)
,entropy (ΔS) , and heat capacity (Δ Cp) , which have the inter – relations
(1—3) :

$\Delta G = -RT \ln \rho$ --------------------------[1]

Where ρ is the equilibrium constant depend on temperature, and the enthalpy is defind by the equation

$\Delta H = \Delta H^o + \int \Delta Cp\, dT$ -------------------[2]

The integral can be determined by substitutiny for the Cp's the empirical equations expressing their temperature dependence .If ΔH^o calculate from(3):

$$\Delta H^o = \frac{R\, d \ln(1/\rho)}{d(1/T)} \quad \text{--------[3]}$$

Then equation [2] can be used to proied ΔH at any temperature . The entropy can be determined at constant temperature from Nernst's equation which is define as (3):

$\Delta S = (\Delta H^o + RT \ln \rho) / T$ ------------[4]

Hence,heat capacity may be found from

$\Delta Cp = \Delta S / \ln T$ ------------------------[5]

The aim of this investigation is used the above method to determine of thermodynamic quantities exactly which is an important application in many studies such as phases transition , behaviour of pure material , superheating of substances and chemical reaction.

Calculations

At high temperature ranges the equilibrium constant could be obtained from thermo gravimetry diagram of the system (4)

$$\text{Calcite(s)} \rightarrow \text{CaO (s)} + CO_2\text{ (g)}$$

The Gibbs function can be calculated from equation [1] for any temperature (993^0 K, 1013^0 K ,1033 ^{0}K, 1053 ^{0}K and 1063 ^{0}K) .The value of ΔH° determined from relation [3] its result can be used to evaluated the entropy from equation [4] . The heat capacity calculated from equation [5] ,then simply could be find the value of enthalpy from relation [2] for any one of the above temprature .

Results and Discussion

The results of the thermodynamic quantities for the reaction: Calcite (S) $\rightarrow$ CaO(S) + CO_2(g) are listed in table (1) . These results show decrease in the value of Gibbs function with increasing the decomposition temperature because the Gibbs function dependence on the logarithm of this equilibrium constant which has increase with temperature , and the values of heat reaction or enthalpy are increase slowly , as the activation energy dependence on calcinations temperature . the values of entropy increase then decreases.

When the thermal degradation of calcite is decrease . Also the method used in this investigation combines advantages over the other measurement methods (5) , control on accuracy and precision of the relevant parameters , their representatively for equilibrium conditions , and the possibility of measurement and control of the gas composition for reliable information about pressure and temperature in the sample is possible only at low reproducible ration rates . Otherwise the response of reactant on thermal stress gives information which is not characteristic. For the reaction , but only artifact of the experimental procedure (6,7) . The stress in this work that approach to equilibrium for both sides is necessary for indirect methods to give character , the influence of repetitive measurements (8) .In principle this method can be applied to obtain thermodynamic as well as over all kinetic information about heterogeneous equilibrium with one, or more than one , participating gaseous component . Sublimation , evaporation , gas adsorption , and surface energy studies seem possible though extension to systems with several components in the condensed phase is less probable due to possible nonequilibrium conditions . This work also combines advantages of some other thermal analysis methods (9 , 10) . The present method naturally has some limiting factors for all equations which can give adequate thermodynamic information only if

_ equilibrium conditions are assumed ;

_ If on synchronously occurring parasitic processes are involved ;

_ If no phase transitions occur in the temperature range of interes ;

_ Their mutual solubility has to be negligible .

conclusion

1- This method permits the determination of the reaction Gibbs function , enthalpy , entropy , and specific heat capacity for monovariant heterogeneous condensed phase / gas equilibrium.

2- The differentil thermal analysis represent's the base for thermodynamic quantities evaluation.

3- The stability in values of the thermodynamic quantities above, give's an insight for phases to be hetrogenous .

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Table(1) : Thermodynamic quantities at different temperature

T (K°)	ρ X 10^{-3}	Δ G KJ / mol.	Δ H KJ / mol.	Δ S J / mol.K°	Δ Cp J/ mol.K°
993	9.083	38.813	273.733	206.633	29.943
1013	20.020	32.938	274.469	208.353	30.105
1033	34.104	29.014	274.976	208.118	29.987
1053	58.780	24.810	275.495	208.157	29.910
1063	63.468	24.367	275.515	206.616	29.648

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طريقة القياس الوزني الحراري لتعيين كميات ثرموداينميكيه بدقه عند درجات حرارة عالية

خالد هلال حربي

قسم الفيزياء ، كلية ألتربية ابن الهيثم ، جامعة بغداد

الخلاصة

في هذا البحث تم عرض طريقه لتعيين التغير في داله جبس ، المحتوى الحراري ، الانتروبي والسعة الحرارية النوعية للتوازن المتجانس ألاحادى التغاير . وتم الحصول على الكميات الثرموداينميكيه بطرقه غير مباشره بوساطة قياس درجات الحرارة المعتمده على النظام المتوازن .