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Virtual Instrument Based for Automation Measuring the Decomposition Equilibrium Constant of Matter and Enthalpy Change

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The automation measuring systems based on virtual instrument was developed, which was applied to measure the decomposition equilibrium constant of matter and enthalpy change. which can acquire real-time automatic experimental data, dynamic display, automatic drawing p~T curve and showing the equation of p~T curve, automatic data processing and generating K^{Θ}_{p} and $\Delta_r H^{\Theta}_{m}$ important parameters of physical chemistry. Experiment results show that it developed on LabVIEW 8.0 was simple and effortless in designing program, the interfaces of beautiful and friendly, easy-extending, It was applied to measure the decomposition reaction of ammonium carbamate, the relative error of $\Delta_r H^{\Theta}_{m}$ is -0.30 per cent compare with the references and avoids resulting mistaking by human error from operation by human date recording and date-processing by handwork. The accuracy and recurrence of experimental results are greatly improved.

Key Words: Ammonium carbamate, LabVIEW, Virtual instrument, Constant balance.

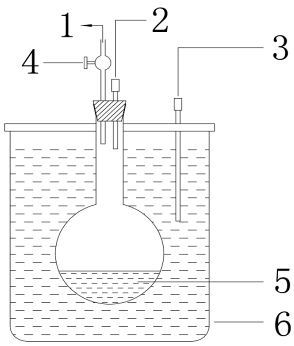
INTRODUCTION

Virtual instrument[1] is a modern automatic monitoring and control apparatus which colligated the technology of device, sensor, computer, *etc.,* and take full advantage of modern digital information technology. It simulated the control panel of traditional instruments by the computer's display function and used hardware equipments such as I/O *etc.* to complete the acquisition and condition of signal and made use of software programming to achieve real-time automated data collection, dynamic display, data processing and also it displayed measurement results in many forms, *etc.*, therefore it can complete a number of testing function with high intelligence. Virtual instrument based on the design of ‘software is the instrument’ that indicate the central role of the software in virtual instrument. At present, the most representative software is graphical programming software — LabVIEW[2] offered by NI Company to develop the virtual instrument, which has been widely applied in many areas of the world.

Equilibrium constant is a very important physical and chemical measure, in the scientific research and production practice, to accurately measure the chemical reaction equilibrium constant has important theoretical significance and application value. When pure liquid or pure solid break down to generate the gas, The equilibrium constant is an important physical and chemical parameters to determine their nature. It's accuracy depends on the accurate determination of decomposition pressure and temperature when solid-gas or liquid-gas two-phase reached equilibrium state, as well as the follow-up data processing. The author improved the method of the conventional determination of physical decomposition constants by using modern instrument and sensor technology. The automation measuring systems based on virtual instrument has been developed for measuring the decomposition equilibrium constant of matter and enthalpy change, which has realized automatic real-time data collection, data processing and the results display *etc.*, simplified the experimental operation, avoided human error and greatly improved the accuracy of measurements.

Measuring method and principle: Generally, during the experiment of pure solid and pure liquid substances generated gas, we can measure the equilibrium constant of different temperatures by measuring a series of decomposition pressure at different temperatures, according to the principles of thermodynamics.

Usually according to the Clausius-Clapeyron equation predicts a linear plot of ln p* *vs.* 1/T and the enthalpy change $\Delta_r H^{\ominus}_m$ of decomposition reaction obtained by straight line slope. In the conventional experiments, balance pipe was used to determine whether the system to reach equilibrium state. The relevant control operations of balance pipe was a measurement problem because improper operation of balance pipe led to the experiments failure and artificial observation of two liquid levels whether is equal height or not, which are very tedious and inevitably bring human error. We improved the conventional method to measure physical decomposition equilibrium constant by using the equipment chart of measuring physical decomposition pressure as shown in Fig. 1. The system temperature and pressure signals from temperature sensors and pressure sensors was entered into the computer experiment through the temperature measurer and pressure gauge instrument. At beginning of the experiment, we use a vacuum pump to system pump the air in the system and maintain a certain degree of vacuum and then close off the piston and disconnect vacuum pump system. The measure can be the static method as well as can be dynamic. Static method is fixing a series of temperature, when the pressure kept constant then collected temperature and pressure data. But the more simple and easy method is dynamic method which used the process controlling temperature measurer or voltage regulator to control temperature rising rate, so that the system under test can increased temperature slowly as required. When experiments begins, make temperature constant at first and after the system is stable, open controlling temperature measurer for controlling the water bath temperature slow to heat up. Obviously because the system keep slow heating rate, the system has been in near equilibrium state and decomposition occurs. During the slow warming process, the system pressure and temperature data collected automatically real time to virtual instrument system and the system automatically store, display temperature-pressure curve and automatically display measurement results. Compared with the traditional method of static measuring balance pressure equipment, the measuring device of Fig. 1 is much simpler, the occupied space is small, soft-junction is less and is difficult to leak and cleaning equipment, loading sample and exchanging sample is more simple and convenient, especially, omitted balance pipe equipment, avoided manual operation which brought inevitably a lot of man-made error. By the collected temperature and the corresponding pressure, the equilibrium constant K^{Θ}_{p} at some temperature can be gained conveniently and as well according to the test data will achieve the average standard reaction enthalpy change $\Delta_r H^{\Theta}_{m}$, the standard gibbs free energy change $\Delta_r G^{\Theta}_{m}$ and the standard entropy change $\Delta_r S^{\Theta}_{m}$ and so on. It is clear that the virtual instrument system can be applied to the sample whether is solid or liquid.



1 = Vacuum system, 2 = Pressure sensor, 3 = Temperature sensor, 4 = Piston, 5 = Sample, 6 = Constant temperature water bath

Fig. 1. Experimental device

Configuration for virtual instrument's system: The configuration of virtual instrument's system was shown in Fig. 2, which contained the equipment of self-designed and self-installed measuring physical decomposition equilibrium constant, DP-AF precision digital pressure gauge, SWC-II_D precision digital temperature measurer and computer components. The pressure and temperature of system under test were sent by sensors to the pressure gauge and temperature measurer, then the data of pressure and temperature were sent through the serial port to the computer, the computer based on LabVIEW 8.0 virtual instrument testing platform can carry out real-time data display, storage, automatic data processing and generating the results and so on.

Design of program for virtual instrument: The design of the program for virtual instrument mainly includes virtual instrument panel operating program, data acquisition program and data processing program.

Design for virtual instrument's operating panel: The operating panel of virtual instrument's was shown in Fig. 3. Three side-by-side buttons at the bottom connected three sub-virtual instrument which can realize different functions, when click

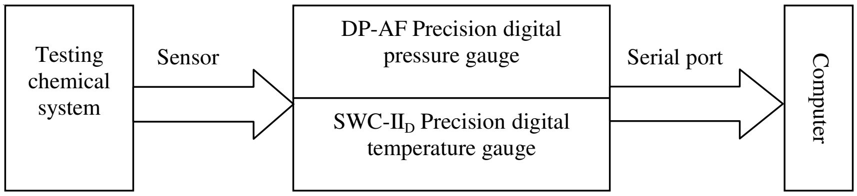


Fig. 2. Configuration for virtual instrument system

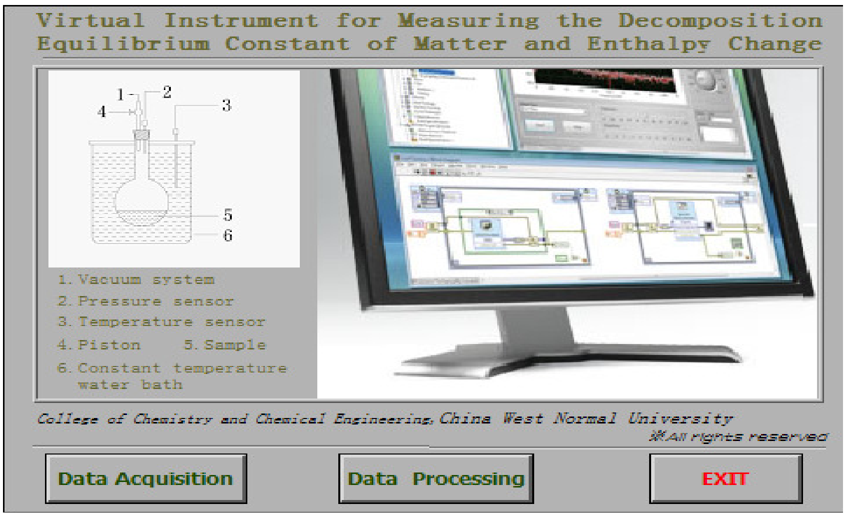


Fig. 3. Operation panel of virtual instrument

the button it will start the process of sub-virtual instrument, then go into the corresponding operation panel and complete the testing functions. Main panel operation using While Loop structure nested event structures, they include data acquisition, data processing and exiting from the program. Each event structure correspond a sub-VI, when start VI, click the controlling button, the program will drive the corresponding events trigger, implement the corresponding sub-VI program after it completed it will return to event and at the state of wait[3,4].

Design of program for data acquisition: The chart of data acquisition program shown in Fig. 4. According to communicating protocol for serial port of pressure gauge and temperature difference instrument that data is sent, called VISA Configure Serial Port note in Functions→Instrument I/O→Serial and set up nodes in all port parameters[5]. In the While Loop structure, called VISA Clear and VISA Read nodes to realize temporary clear memory and read from the serial data string length specified, using String to Byte Array converted to digital signals, which in accordance with RS-232 serial port to send data protocol to use Search 1D Array, Split 1D Array and Index Array, to adjust combination can obtain pressure and temperature data of the testing system, that is showed in the front panel display by two displaying pieces. At the same time, the pressure and temperature data also showed that wave into XY Graph real-time showed with the pressure on the temperature variation trend. After reading the data by calling the VISA Close note to close the instrument device, so as to release resources to the serial port on the LabVIEW occupied, to avoid unpredictable errors. Write To Spreadsheet File.vi and shift register and so on were called to realize data collecting automatically saving, preserved the path from the File I/O Build Path node in the decision.

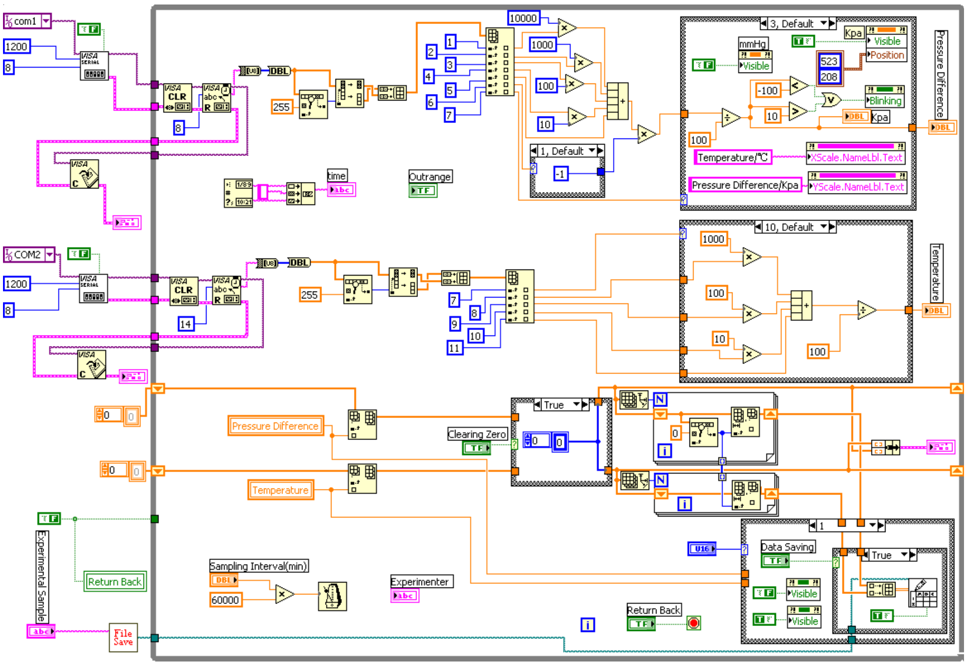


Fig. 4. The program of DAQ

Design of program for data processing: The chart of data processing program was shown in Fig. 5. Upper left in the Fig. 5, call Read To Spreadsheet File.vi function, then Feedback Node and Index Array in the Functions from the database read out the collection data, through 'eliminating the abnormal values' sub-VI. The interference of certain random errors from power grids, environmental factors and so on were eliminated. In the Case Structure, call Index Array to index the equilibrium constant K^{Θ}_{p} corresponding to the measured temperature. Upper right in the Fig. 5, call successively Exponential Fit.vi, General Polynomial Fit.vi function, Build Array and Array Max & Min, to realize the computer automatically identify and index the best fitting way of the least mean square error (MSE) and further obtain the best curve fitting of p~T in the Case Structure, fitting the coefficient into 'equation' sub-VI can automatically obtain the corresponding fitting equation expression. The raw data points and fitted curve were real-time displayed by XY Graph waveform controls. Lower right in the Fig. 5, the fitted pressure data converted to natural logarithm by the Natural Logarithm function and then it was linearly fitted by using Linear Fit.vi function with reciprocal value of temperature. The intercept and the slope of a straight line[6] were obtained that can be converted into the average heat effect $\Delta_rH^{\Theta}_m$ of material decomposition reaction. Using such Number To Engineering string function also obtained fitting linear equation. The pressure data and the reciprocal value of temperature through 'correlation coefficient' sub-VI can also obtain fitting linear correlation coefficient. Using equilibrium constant K^{Θ}_p and the average standard reaction enthalpy change $\Delta_rH^{\Theta}_m$ through solving equation can automatically obtain the standard gibbs free energy change $\Delta_rG^{\Theta}_m$ and the standard entropy change $\Delta_rS^{\Theta}_m$ at the corresponding measuring temperature and so on. Lower left in the Fig. 5, program also increased the print function which can printout the results and other related information.

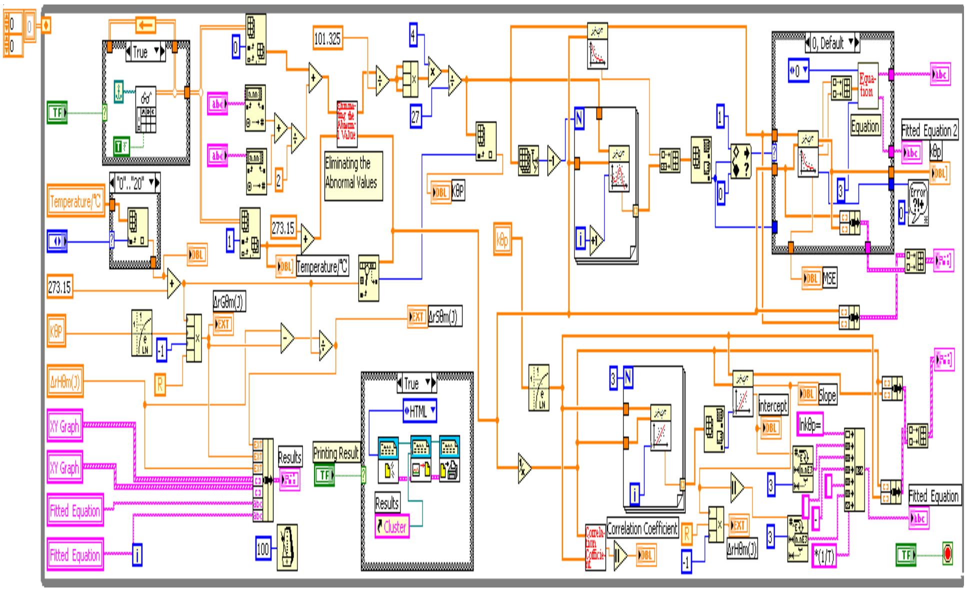


Fig. 5. The program of data processing

Applied examples and discussion: Virtual instrument system was applied to measure the decomposition reaction of ammonium carbamate according to Yang *et al.*[7]. During the experiment, the samples put into the system after which eliminated air. The baseline system automatically collect and display real-time p~T curve when clicked the data acquisition. When the system heating to the temperature setting, click the data processing in the Fig. 3, the operations panel switch to the data-processing operation panel as shown in Fig. 6. In the left side of the Fig. 6 there are the collected experimental data and the fitted curve of p~T and in the right side there is the straight line of lnp~1/T. The experimental results and the related data were shown in Table-1. We can see from Table-1, the average standard reaction enthalpy change measured for three times of the decomposition reaction of ammonium carbamate was 158.847 kJ mol^{-1}, the value of reference[8] was 159.32 kJ mol^{-1}, that is, the relative error was -0.30 %. When the temperature is equal to 25 ºC, the decomposition equilibrium constant k^{Θ}_{p} was 2.50 × 10^{-4}, the standard free energy change $\Delta_rG^{\Theta}_{m}$ was 20.560 kJ mol^{-1} and the standard entropy change $\Delta_rS^{\Theta}_{m}$ was 464.17 J mol^{-1}. The standard entropy change of the value of reference was 464.84 J mol^{-1}, so the relative error for measurement result was -0.14 %.

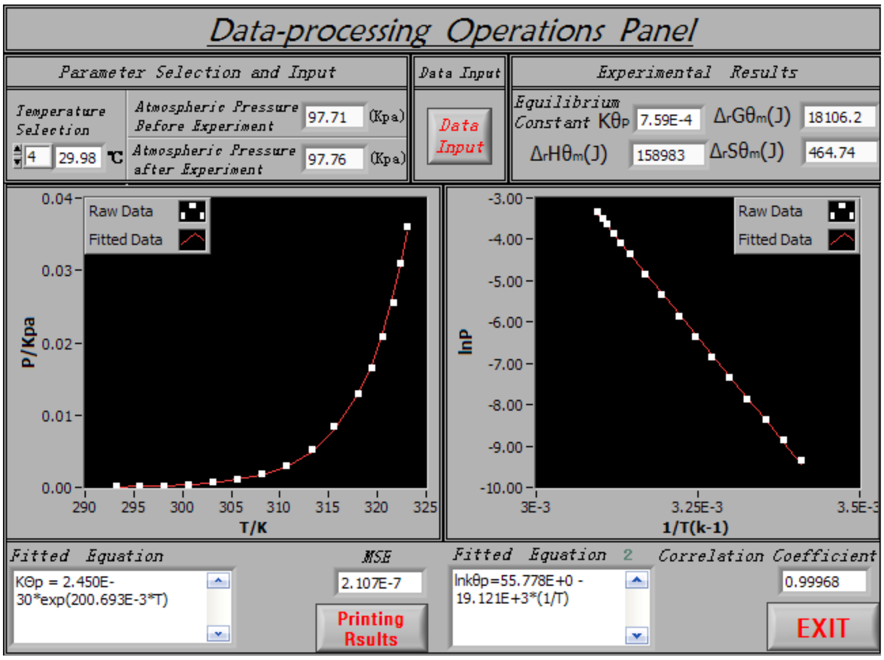


Fig. 6. The panel of data processing

TABLE-1
MEASURING RESULT AND RELATED DATA OF EXPERIMENT

$\Delta_rH^{\Theta}_{m}$ (kJ mol^{-1})		Temperature (ºC)	20.00	25.00	30.00	35.00	40.00	45.00
158.857	Average	k^{Θ}_{p} × 10^{-4}	1.42	2.50	7.59	19.70	52.50	131.00
158.919	value	$\Delta_rG^{\Theta}_{m}$ (kJ mol^{-1})	21.596	20.560	18.106	15.962	13.673	11.474
158.766	158.847	$\Delta_rS^{\Theta}_{m}$ (J mol^{-1})	468.31	464.17	464.53	463.98	463.70	463.58

The application results showed that the automation measuring systems based on virtual instrument is constructed for measuring the decomposition equilibrium constant and enthalpy change of matters, its advantage is that the human-computer interaction interfaces are friendly, manipulation is simple, auto-complete data acquisition and processing, avoid human error and improve the measurement accuracy.

Using the LabVIEW itself Build Executable Wizard tool, the LabVIEW program can be converted into ordinary common Windows applications. In addition, as the virtual instrument have the characteristics that the function is easy expanded, the embedded LabVIEW program with some slight modifications can be applied to other tracking determination occasion of temperature and pressure change for the system caused by chemical reactions.

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