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**Effect of Air in the Thermal Decomposition  
of 50 wt.% Hydroxylamine/water**

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**ABSTRACT**

This paper presents experimental measurements of the thermal decomposition reaction of 50 wt% hydroxylamine/water (HA) in an oxygen-free environment using an APTAC calorimeter. Overall kinetics, onset temperatures, heats of reaction, and energy release rates vs. temperature are presented. These results are compared with the corresponding data for HA decomposition reaction in air. This information is especially valuable for the design of HA storage facilities.

Presented also are the gas-phase decomposition products measured by spectrophotometry for the HA decomposition reaction in air and a discussion of the HA decomposition mechanism.

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## Abstract

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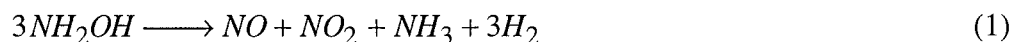
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## 1 Introduction

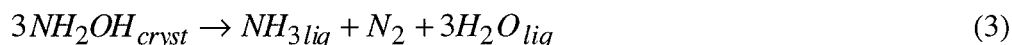
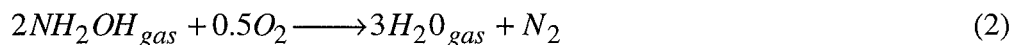
Thermal stability data of hydroxylamine solutions are urgently needed since there is limited information available for this important industrial compound [1],[2],[3]. This particular chemical has been involved in two recent accidents causing the death of nine people. The Mary Kay O'Connor Process Safety Center has studied this system [2],[3] and continues to do so. The focus of this paper is to measure the difference in thermal behavior for the decomposition of hydroxylamine 50 wt.% solution in water (HA) with and without air. The results will help elucidate possible mechanisms for the HA decomposition and will be useful for safe process control strategies involving HA.

## 2 Background

The thermal decomposition products of HA are not completely known. Some well recognized process safety handbooks such as Sax's *Dangerous Properties of Industrial Materials* report the decomposition products to be noxious NO<sub>x</sub> gases. A possible pathway for the formation of these products is the following reaction:

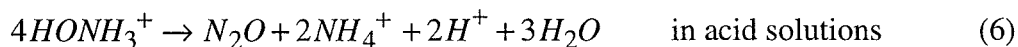


which is endothermic ( $\Delta H_{rxn} = 421.2$  KJ/mol) contrary to experimental observations for HA decomposition. Other references [4] suggest the possibility of an oxidation reaction or a decomposition reaction:



The first reaction is a combustion reaction with an approximate  $\Delta H_{rxn}$  of -247.9 KJ/mol, and the second reaction is a decomposition with an approximate  $\Delta H_{rxn}$  of -561 KJ/mol.

Some other references describe the complex nature of the decomposition reaction system by addressing the possibility of distinct pathways depending on the pH [5]:



There are some reports of HA decomposition products under various conditions. The species NO, N<sub>2</sub>, N<sub>2</sub>O, and NH<sub>3</sub> have been measured when hydroxylamine decomposes over Nuchar in refluxing isopropanol [6]. N<sub>2</sub>O and NH<sub>4</sub> were detected when HA disproportionates in acid media [7]. Lunak [8] states that the decomposition products of HA in alkaline media are NH<sub>3</sub>, N<sub>2</sub>, N<sub>2</sub>O, and hyponitrite (N<sub>2</sub>O<sub>2</sub><sup>2-</sup>). Lunak assumed that the reaction proceeds through the nitroxyl (HNO) intermediate. Lunak confirmed the presence of the intermediates N<sub>2</sub> and N<sub>2</sub>O when the decomposition reactions were carried out at various conditions and with various metal catalysts. It was assumed that HA decomposition will not occur without a metal catalyst.

The thermal decomposition products of HA under runaway conditions have not been measured. The decomposition products could be different than those mentioned above, mainly because:

- 1) The liberated self-heat increases the temperature during the experiment and this thermal energy could activate a wider spectrum of reactions.
- 2) Since the experiments are carried out in a closed cell environment, all the decomposition products can react further.

It is important to detect the decomposition products under these runaway conditions, which are similar to the conditions in the event of a process upset.

## 3 Experimental Details

### *3.1 Samples*

To determine the decomposition products under runaway conditions, we utilized a well-characterized sample available from Aldrich (Aldrich Hydroxylamine 99.999% 50-wt.% solution in water, No. 46,780-4). No industrial samples were utilized since those contain unidentified proprietary stabilizers.

### *3.2 Apparatus*

Data were collected using an Automatic Pressure Tracking Adiabatic Calorimeter (APTAC), which is discussed elsewhere [9]. During a run, the pressure outside the sample cell is controlled with nitrogen to match the pressure inside the sample cell. This equipment feature allows the use of relatively thin sample cells, which makes possible low thermal inertia experiments. This feature also facilitates the use of cell materials that can not stand a relatively high pressure differential such as glass. Several heating modes can be programmed in the APTAC (heat-wait-search, isothermal, ramp, etc.). Among the data collected are time, temperature, pressure, heat rate, and pressure rate.

For the experiments reported here, a vacuum was created in the sample cell, so the APTAC was modified to support a vacuum in the sample cell with the container vessel open.

For the analytical measurements, a spectrophotometer from the Chemistry department and a GC from the Catalysis group in the Chemical Engineering department were used.

### *3.3 Experimental method*

For the present work, all experiments were performed in a closed cell environment. Some experiments were run with ambient air above the sample and for the others the air was evacuated. The evacuation procedure consisted of two parts:

- 1) HA samples were transferred to glass sample cells using disposable plastic pipettes. The mass of the sample was obtained by weight difference. Because of the relative small amount of sample, no stirring was used during the APTAC runs.
- 2) The sample cell was mounted in the APTAC calorimeter. Liquid nitrogen was used to freeze the sample to  $-102\text{ }^{\circ}\text{C}$  before pulling the vacuum (0 - 0.5 psia). After the air above the sample was removed, the sample cell was closed.

The heating mode was heat-wait-search (HWS) in which the sample was heated to an initial search temperature and the temperature was allowed to stabilize (20 minutes). Then if exothermic activity was detected, as exhibited by a threshold temperature rise of  $0.05\text{ }^{\circ}\text{C}/\text{min}$ , the apparatus followed the reaction adiabatically until the reaction ended or until one of the pre-selected safety shutdown criteria was met. If no exothermic activity was detected within 20 minutes, the sample was heated to the next search temperature and the procedure was repeated until a preset maximum search temperature was attained.

A sample thermocouple with a black Teflon-coated sheath (0.06" ID) was used to prevent the metal surface from contacting the sample and catalyzing the HA decomposition.

Experimental runs were performed in sample cells of 130-cm<sup>3</sup> nominal volume and of borosilicate glass. It was presumed that glass cells provided a neutral environment without significant catalysis for the HA decomposition.

### *3.4 Uncertainties*

A type N thermocouple was used to measure sample temperatures with an overall absolute uncertainty of  $\sim \pm 1$  °C, and was checked periodically at 0 °C using an ice bath. Sample pressures were measured with Sensotec absolute pressure transducers with an overall uncertainty of  $\sim \pm 4$  psi and were checked frequently for agreement with ambient pressures. Sample weights were measured with a precision of  $\pm 0.01$  gr.

## **4 Results and Discussion**

Table 1 presents a summary of the experimental conditions along with the physical appearance of the sample residues after the experiments were completed and the samples have returned to room temperature. It is important to note that no differences were observed in the physical aspects of the residue between samples carried out with air or in an evacuated environment. In all the experiments the liquid residues were crystal clear when attached to the calorimeter, but when the sample cell was removed from the calorimeter the liquid slowly turned blue. We put some of the liquid residue into an amber container to see if light affected the change in color but that was not the case since this residue also turned blue. In a first attempt to investigate the nature of this “blue component”, we changed the pH from basic to acid and the color disappeared, but when the pH was set basic again the color reappeared. We plan to measure the uv spectra of the liquid residues to help determine the nature of this component. One possible identity for

this component is  $\text{N}_2\text{O}_3$ , since it is blue although it is unstable at room temperature and has a melting point of  $3\text{ }^\circ\text{C}$ . Apart from the liquid residue, there is thin layer of a white solid attached to the glass sample cell yet to be identified.

Figure 1 presents a typical HWS routine for the performed experiments with and without air. A summary of the data measured is presented in Table 2. The reported uncertainties are three times the standard deviation measured within the experimental replicas. The onset temperature and the maximum adiabatic temperature are basically the same for the experiments performed with and without air ( $T_{\text{on}} = 122.3$  and  $123.8\text{ }^\circ\text{C}$ ;  $T_{\text{max}} = 277.1$  and  $274\text{ }^\circ\text{C}$ , respectively), which translates to a similar adiabatic temperature rise of  $154.8\text{ }^\circ\text{C}$  and  $150.2\text{ }^\circ\text{C}$ , respectively.

Since the samples performed in vacuum start with a lower pressure, the maximum increase in pressure ( $\Delta P_{\text{max}}$ , pressure at  $T_{\text{max}}$  - pressure at  $T_{\text{on}}$ ) is reported instead of the maximum pressure. The non condensable pressure refers to the difference in pressure after the experiment was completed and cooled to  $50\text{ }^\circ\text{C}$  and the pressure when the sample was first heated to  $50\text{ }^\circ\text{C}$ . The non-condensable pressure provides an estimated of the gas produced during the experiment, which is the real danger during a runaway, since this increase in pressure cannot be tempered by the consumption of latent heat.

The time to maximum rate,  $t_{\text{MR}}$ , estimates the time available to respond to a possible catastrophe from the moment that a process deviation is first detected ( $0.5\text{ }^\circ\text{C}/\text{min}$  of heat of reaction). For  $\Delta P_{\text{max}}$ , non-condensable pressure, and  $t_{\text{MR}}$  reported in Table 2, there is practically no difference between the measurements in the two different oxygen environments within the experimental error.

Some clues about the decomposition pathway are given by the pressure data. Note that although the  $\Delta P_{\text{max}}$  is high ( $976\text{ psia}$  in air and  $888\text{ psia}$  in vacuum), the non-condensable pressure is relatively low ( $55\text{ psia}$  in air and  $68\text{ psia}$  in vacuum), which indicates that much of the pressure is due to the vapor pressure of the solvent or some products that are liquid at ambient temperature but which vapor pressures may be significant at  $T_{\text{max}}$ . The



vapor pressure of water at  $T_{\max}$  is approximately 873 psia, which suggest that much of  $\Delta P_{\max}$  is caused by water, which is consistent with the low non condensable pressure observed. It is important to note that the heat produced in the reaction was able to vaporize a compound with a large heat of vaporization. If the reaction were carried out in another solvent with lower heat of vaporization the increase in temperature should be higher. Figure 2 presents the measured vapor pressure curves for the experiments run in the two different environments. This plot is also consistent with the fact that there is relatively small gas generation, and the system can be classified as a hybrid system according to the AIChE CCPS guidelines [10].

The non-condensable pressure is a clue to the moles of generated vapor, which can be compared to the theoretical moles of vapor generated by a proposed pathway. Table 3 presents the moles generated during the reaction calculated as an ideal gas. It is interesting to note that according to the decomposition of HA in alkaline solutions in Equation 4 and assuming that all the hydroxylamine reacted, the theoretical gas produced is 0.04 moles, which is approximately half of the observed value.

At this point, it is early to provide a good estimate for the heat of reaction, since the product composition is not known yet. Table 3 presents estimated heats of reaction calculated using an average  $C_p$  for the sample of 0.669 cal/(g °C), for which it was assumed that the  $C_p$  of the reacting mixture was constant over the entire temperature range.

When evaluating reaction hazards, we must know not only the amount of heat produced but also how fast this heat is liberated. Figure 3 shows the measured heat rate with respect to temperature, and Figure 4 presents the measured pressure rate with respect to temperature. The reproducibility of the experiments can be clearly observed in these graphics. It is interesting to note that from 220 °C to  $T_{\max}$  the heat and pressure rates are lower for the evacuated samples than for the samples run in air.

The equations involved in the kinetic analysis were presented in [2]. Figure 5 presents an Arrhenius plot for all the experiments assuming a reaction order of one. All experiments have practically the same Arrhenius plot despite the differences in heat rate values for the two kinds of experiments. This can be explained by the fact that in a kinetic analysis it is the shape of the heat generation rate that is significant and not the absolute values.

Figures 6 and 7 present the Arrhenius plots for different assumed reaction orders for experiments run with and without air, respectively. It can be observed by these plots that a good estimated order for the overall reaction is one.

Table 4 presents a summary of the calculated activation energies. Table 5 shows a statistical analysis from which we can conclude that there is not enough evidence to assume that the activation energies ( $E_a$ ) from the experiments with and without air are different. The calculated value for  $E_a$  is  $28 \pm 5$  Kcal/mol.

During the experiments, part of the generated heat is absorbed by the sample cell. One form to correct for the heat loss is using a  $\Phi$  factor [5]. The calculated  $\Phi$  factors for the experiments are presented in Table 3 and were used in the calculation of the  $\Delta H_{rxn}$ .

Figure 8 presents the heat rate vs. temperature measured values and a prediction of these values assuming no heat loss by the sample cell. This is an important issue for the scaling up of laboratory results to an industrial process.

#### *4.1 Analytical results*

A 200-400 nm spectrum of the gas phase samples with and without air was taken. Preliminary interpretations of these spectrums indicate that there is no difference in products for samples run with and without air. There is a region of structure at 220 nm that may be ammonia, and there are two peaks at 215 and 226 that may correspond to NO. The gas samples were analyzed also by GC, and both samples with and without air contained the same chromatographic peaks. A preliminary interpretation of these peaks shows the presence of  $H_2$ , and  $N_2$  but not ammonia. The liquid product smells strongly of ammonia.

## 5 Conclusions

In the thermal decomposition of HA solutions,  $T_0$ ,  $T_{\max}$ ,  $\Delta P_{\max}$ , non condensable pressure,  $t_{MR}$ ,  $E_a$ , and reaction order seem not to be affected by the presence of air above the sample. So if some oxidation products are produced (NO, NO<sub>2</sub>, N<sub>2</sub>O), they are formed primarily by oxygen available within the hydroxylamine molecule. The only measured differences in the reactions are from the heat rates and pressure rates, which are lower for samples that were in vacuum.

More analytical work is needed to identify the reaction products, but at present there is no evidence to conclude that those will be significantly different for samples with and without air.

## Acknowledgments

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**Table 1. Summary of HA decomposition experiments**

Run conditions	Sample identification	Sample mass ( gr)	Remaining mass after exp (gr)	Liquid residue appearance	Solid residue appearance
AIR	HA air 1	8.09 ± 0.01	3.13 ± 0.01	Bluish when air contacted	White
AIR	HA air 2	8.04 ± 0.01	3.54 ± 0.01	Bluish when air contacted	White
Vacuum	HA vacuum 1	8.01 ± 0.01	3.62 ± 0.01	Bluish when air contacted	White
Vacuum	HA vacuum 2	8.03 ± 0.01	3.08 ± 0.01	Bluish when air contacted	White

**Table 2. Measured parameters for the HA decomposition**

Sample identification	Replicas	T <sub>on</sub> °C	T <sub>max</sub> °C	ΔT <sub>adb</sub> °C	ΔP <sub>max</sub> psia	Non condensable pressure psia	t <sub>MR</sub> min
HA air	2	122.3 ± 1.3	277.1 ± 2.2	155 ± 3	976 ± 74	55 ± 5	191 ± 57
HA vacuum	2	123.8 ± 1.5	274.0 ± 0.7	150 ± 1	888 ± 115	68 ± 5	128 ± 82

**Table 3. Moles generated and calculated heat of reaction for HA decomposition**

Sample	Non condensable pressure Psia	Moles of vapor generated	Bomb mass g	Sample mass g	Bomb Cp J/g/°C	Sample Cp J/g/°C	Φ factor	ΔT <sub>adb</sub> °C	-ΔH rxn (Kcal/mol)
HA Air 1	51.5	0.017	51.50	8.09	0.462	2.80	2.049	154.0	13.94
HA Air 2	58.3	0.019	52.38	8.04	0.462	2.80	2.074	155.6	14.25
HA vac 1	70.8	0.024	51.50	8.01	0.462	2.80	2.060	150.4	13.68
HA vac 2	64.3	0.021	51.50	8.03	0.462	2.80	2.057	150.0	13.63

**Table 4.** Summary of kinetic parameters for the overall HA decomposition

Sample	$dT/dt_{\max}$	$dP/dt_{\max}$	rxn order	$E_a$ Kcal/mol
HA in air	$81 \pm 11$	$1204 \pm 180$	1	$29.5 \pm 0.5$
HA in vacuum	$66 \pm 51$	$940 \pm 170$	1	$27.0 \pm 3.9$

**Table 5.**  $E_a$  hypothesis testing for HA decomposition

$$H_0 : \mu_1 = \mu_2$$

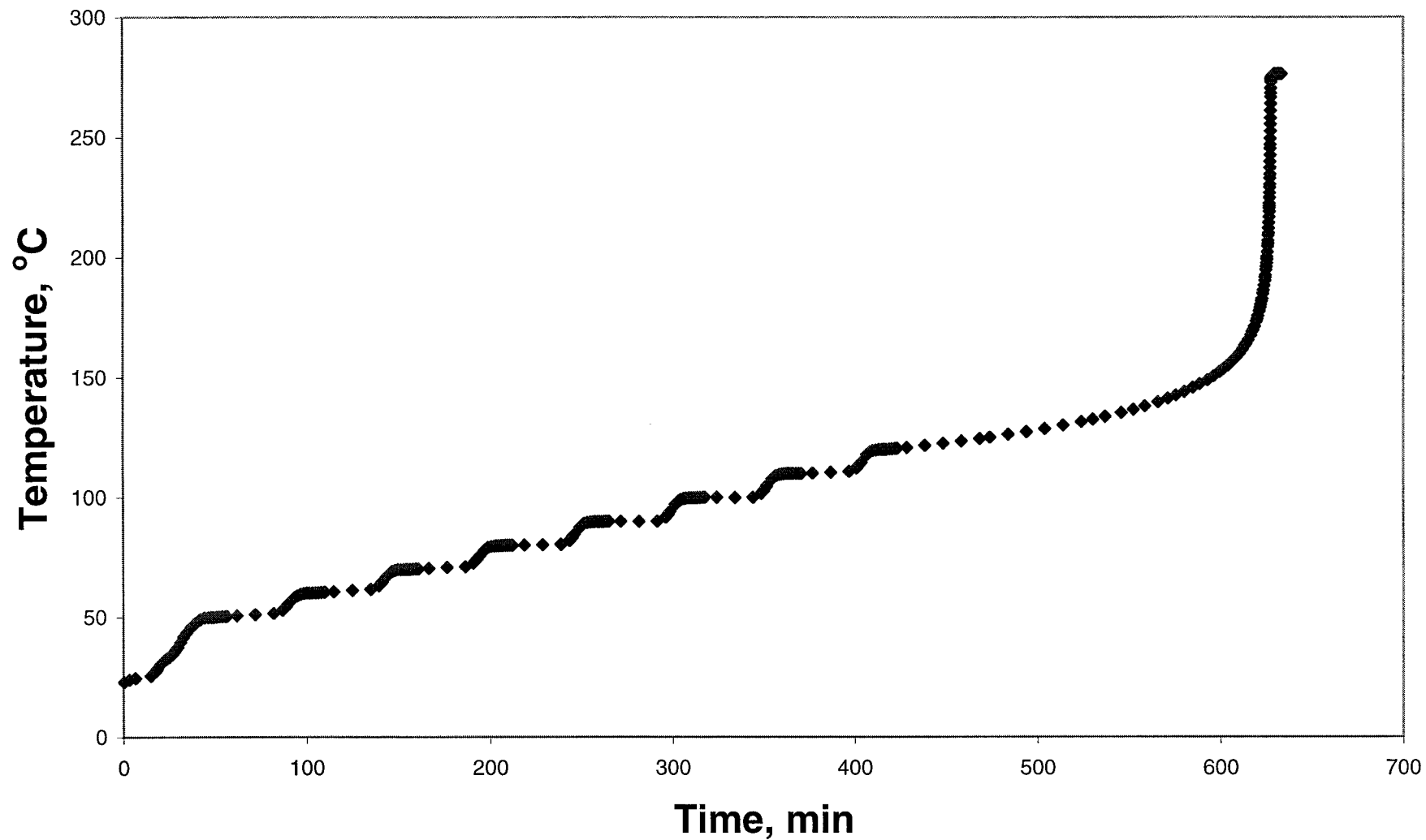
$$H_1 : \mu_1 \neq \mu_2$$

Rejection zone:

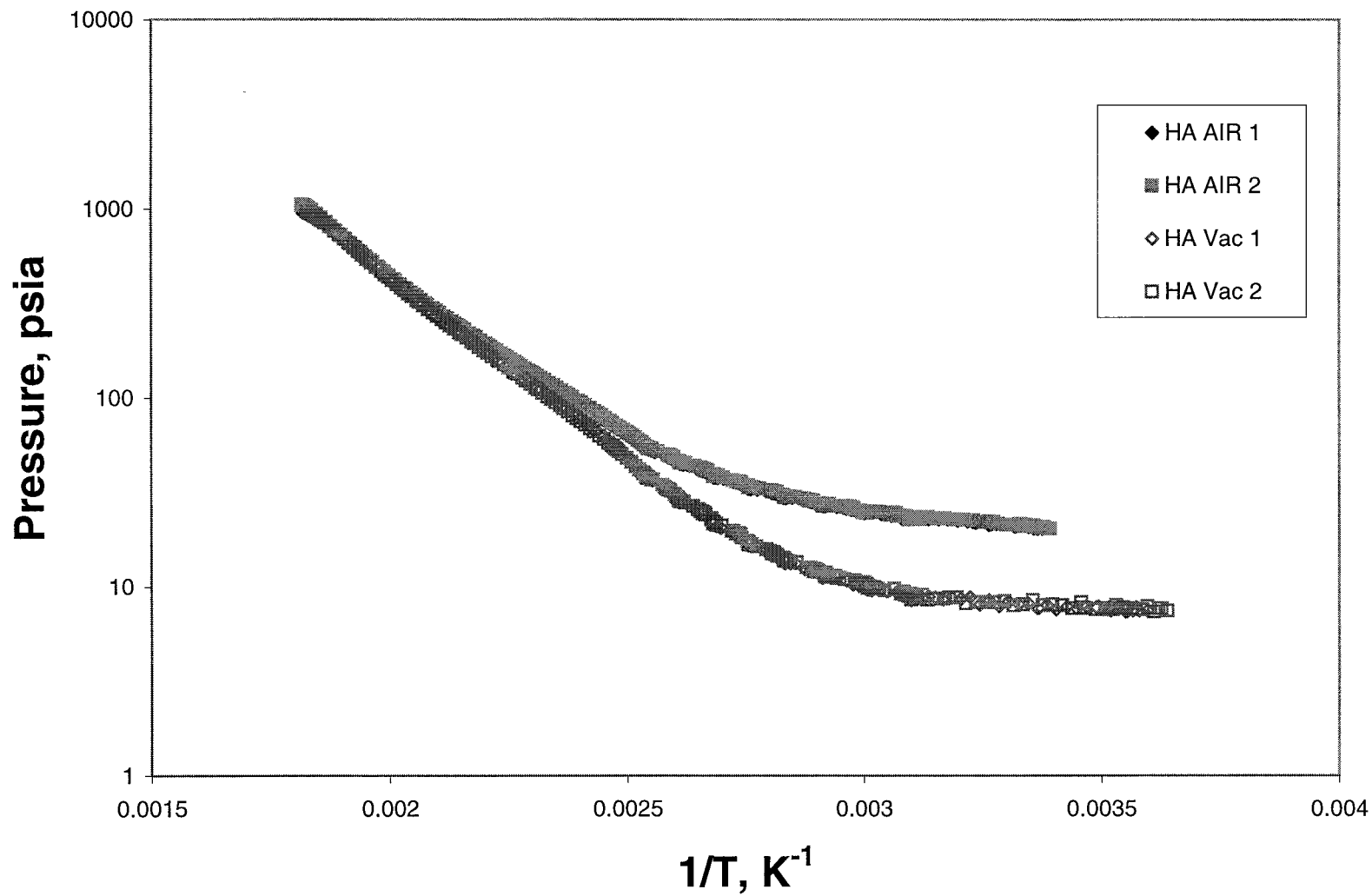
$$|t_o| > t_{\alpha/2, v}$$

Sample	$E_a$ Mean	variance	sp	$t_o$	$t_{0.25, 2}$
HA in air	29.4513	0.029408	0.916	2.6531	4.303
HA in vacuum	27.0211	1.648648			

**Figure 1. HWS mode for HA decomposition**

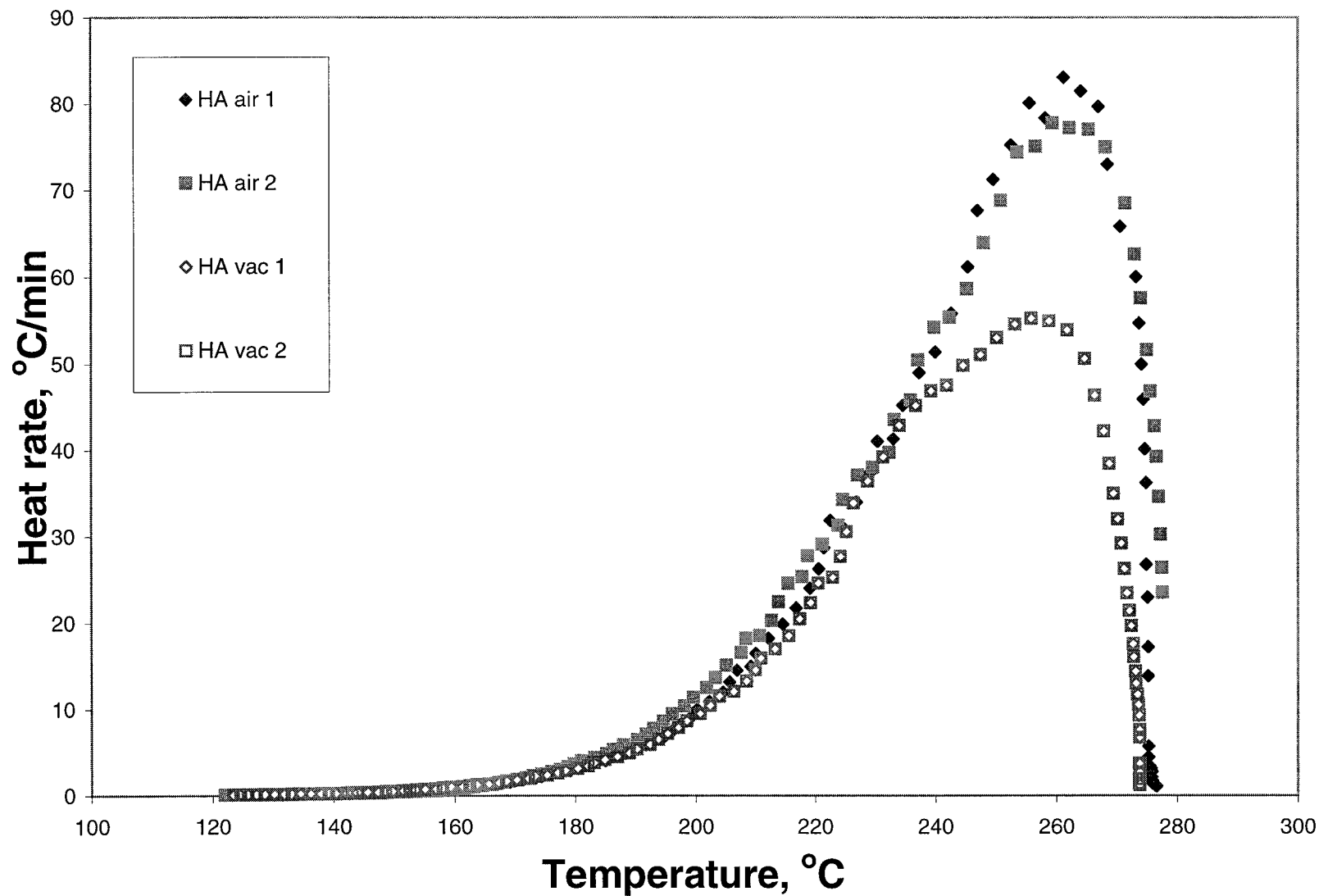


**Figure 2. HA decomposition vapor pressure**





**Figure 3. HA decomposition heat generation**



**Figure 4. HA decomposition pressure generation**

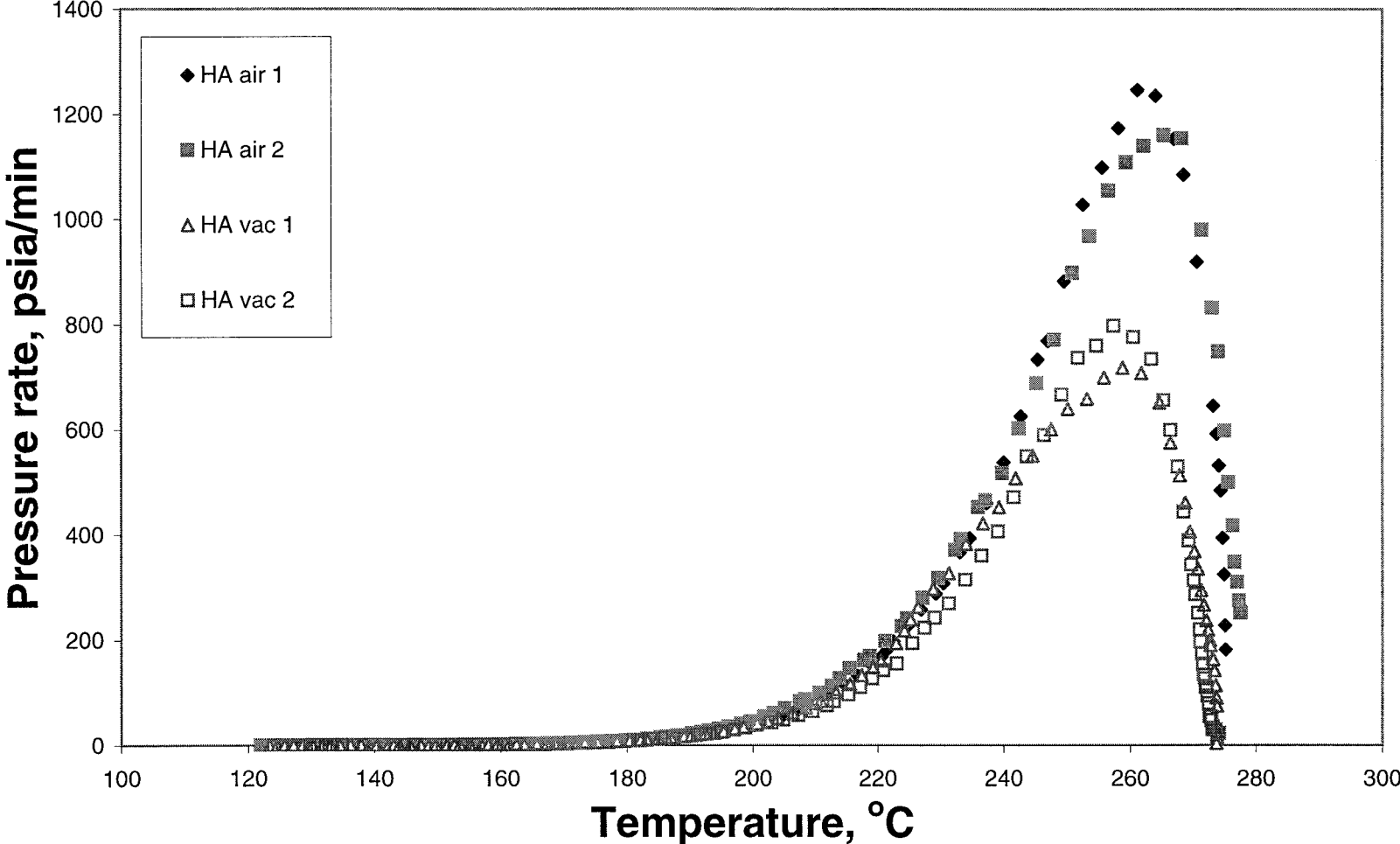
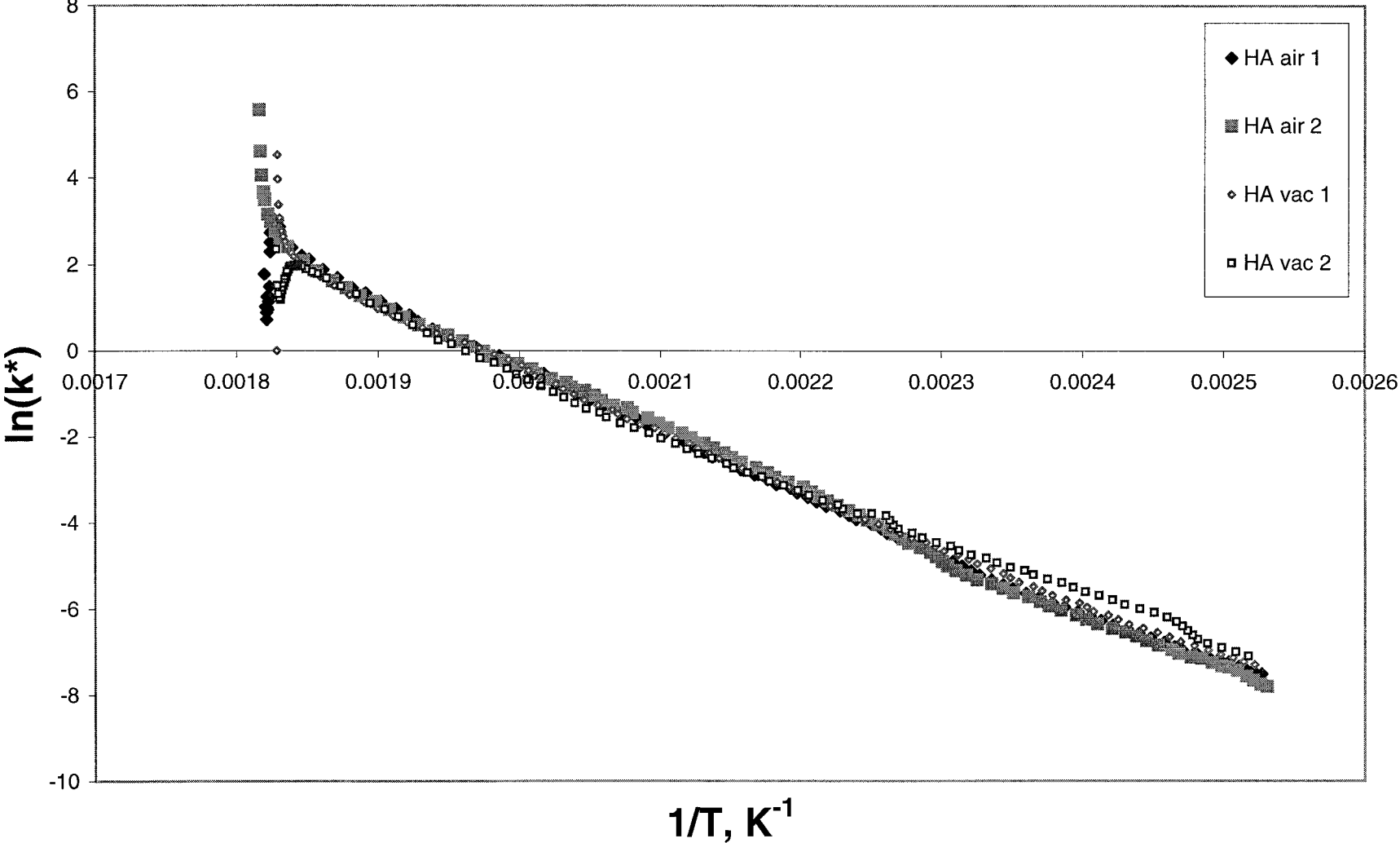
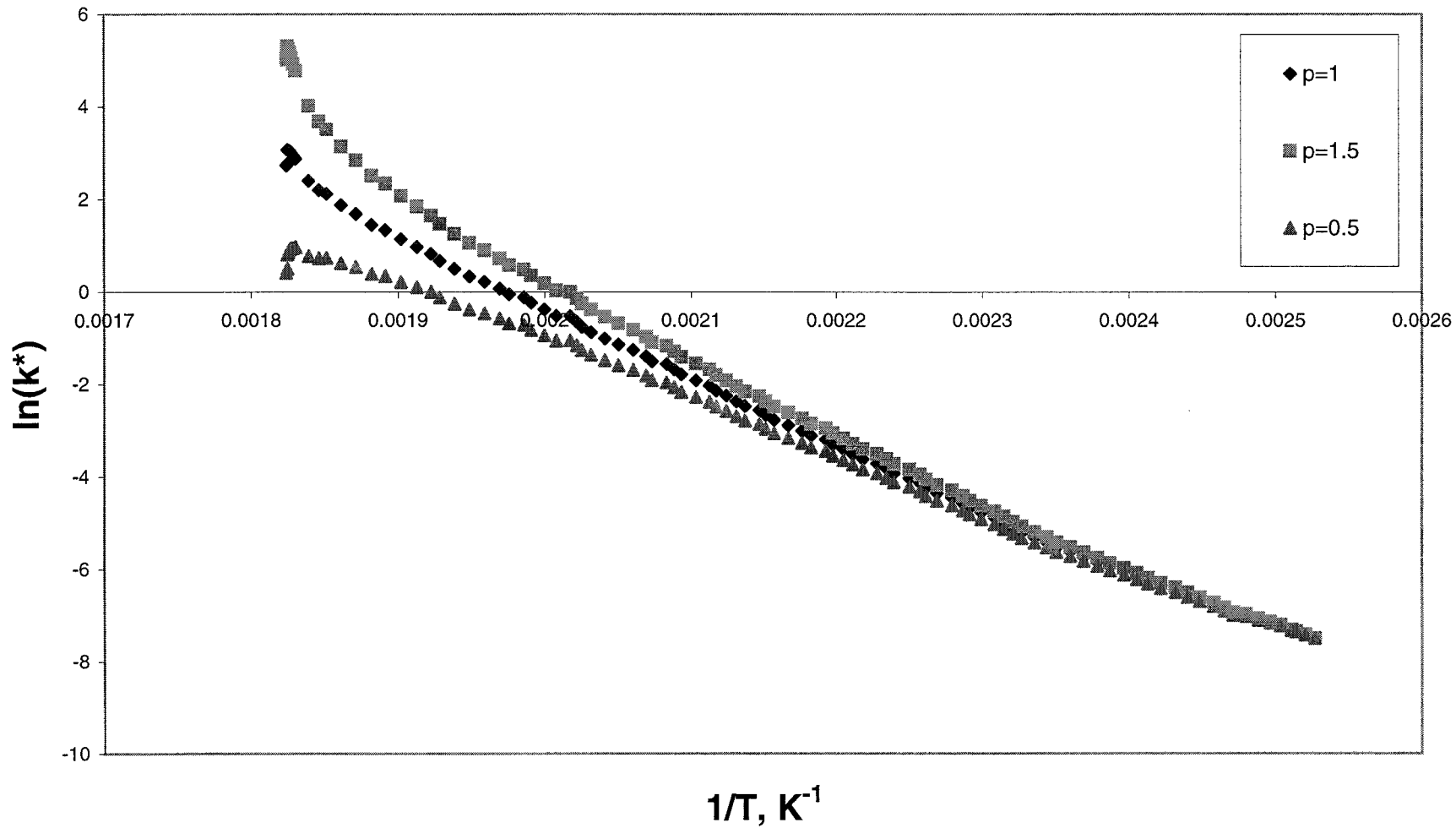


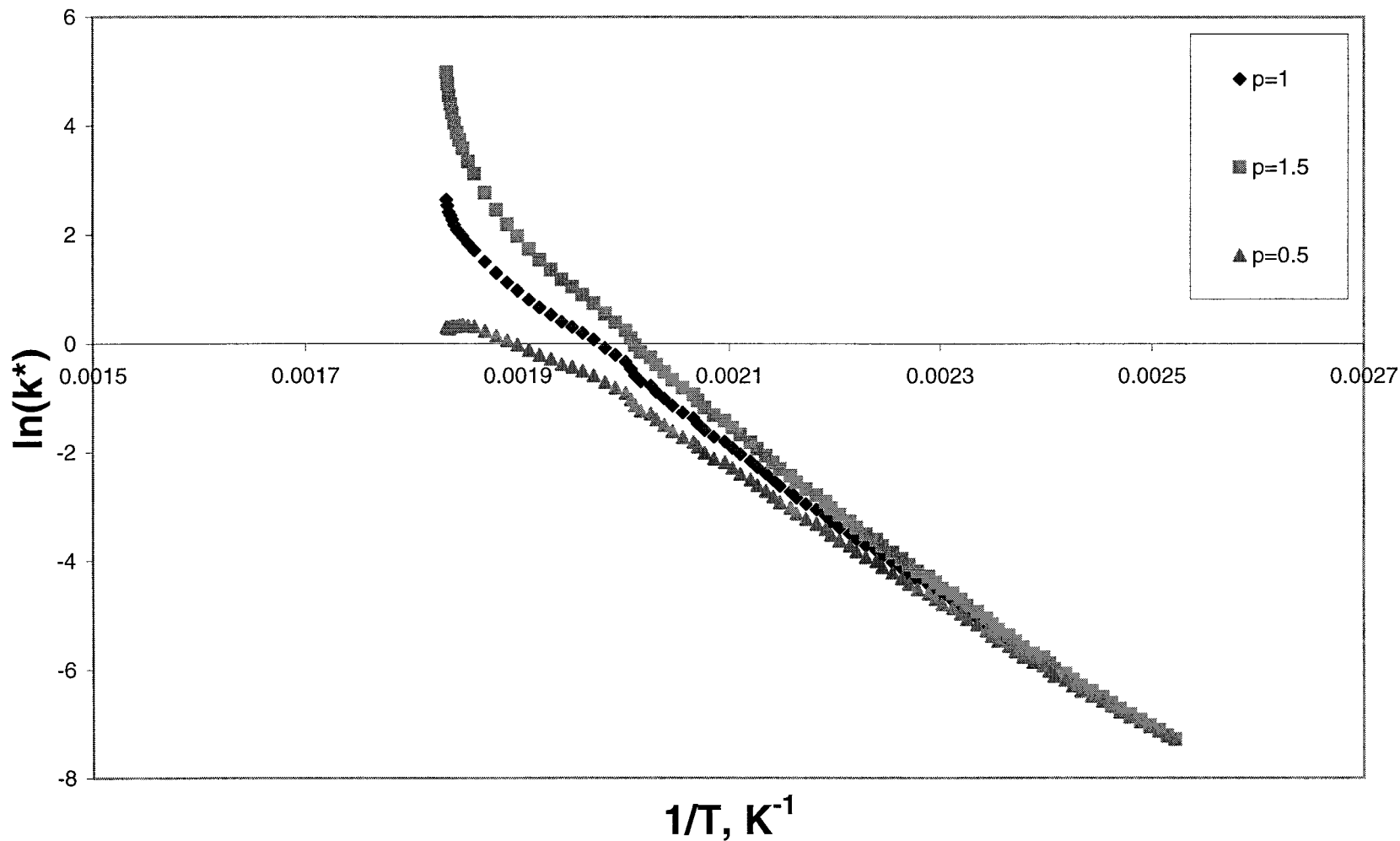
Figure 5. HA decomposition with and without air



**Figure 6. Reaction order of HA decomposition with air  
(99% reaction)**



**Figure 7. Reaction order of HA decomposition in vacuum  
(99% reaction)**



**Figure 8. Correcting data for heat losses**

