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February 21, 2012

Thermochimica Acta

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Measurement of moisture outgassing of the plastic-bonded TATB explosive LX-17

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Highlights

- A system to directly and exclusively monitor moisture outgassing was constructed
- Moisture outgassing from plastic-bonded TATB at 65°C was monitored for 2 weeks
- Moisture outgassing occurred mainly in the first 10-20 h, reaching 50-70 ppm
- The data agreed with previous studies and a recently developed kinetic model

Abstract

Moisture outgassing during isothermal heating of LX-17, a plastic-bonded explosive consisting of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), was monitored. A moisture outgassing measurement system was constructed to directly monitor the water vapor released from the heated material in real time using an aluminum oxide probe mounted in the stainless steel sample chamber. The total pressure in the sample chamber was also monitored. Solid samples were heated and monitored for 2 weeks at 65°C. Moisture outgassing occurred mainly in the first 10-20 h, reaching approximately 50-70 ppm (parts water per million parts LX-17). The total pressure exceeded the water vapor partial pressure, indicating that outgassing of other species occurred. Good agreement (within an order of magnitude) with previous moisture outgassing studies on TATB-based materials was demonstrated. In addition, the data appeared to validate use of a recently developed kinetic model for predicting moisture outgassing rates of solid TATB formulations.

Keywords: explosive, LX-17, moisture, outgassing, TATB, water

1. Introduction

Moisture in a sample can be detrimental to an experiment by inducing chemical reactions within the material, outgassing from one material and altering or damaging other materials in the experiment, or complicating analysis and detection of other species. In some cases, water is a decomposition product, making it difficult to determine whether the water present at the end of a reaction was produced via chemical reactions or was pre-existing in the material. The material 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is one such example. It reacts via several different mechanisms depending on the pressure and temperature conditions; one of the dominant mechanisms generates water as a reaction product [1-6]. Work is ongoing to clarify the conditions that favor one mechanism over another; in order to fully understand these mechanisms one must also characterize the pre-experiment moisture content and outgassing rates. In particular, researchers need guidance on the initial moisture content in TATB-based

samples, the amount of moisture that can be removed from solid high density parts, and what kinds of conditions are best for drying such samples without damaging them.

Moisture-related studies of TATB-based materials are nearly non-existent in the peer-reviewed literature. However, several previous studies (mostly internal technical reports from Pantex Plant and Lawrence Livermore National Laboratory) have attempted to quantify the initial water content and/or moisture outgassing of TATB formulations, including PBX-9502 (95% TATB, 5% Kel-F 800 binder) and LX-17 (92.5% TATB and 7.5% Kel-F 800 binder). Karl Fischer titration is the preferred method of measuring water content in TATB-based samples [7-11]. However, the accuracy of Karl Fischer analysis applied to TATB is unknown due to the low solubility of TATB in conventional solvents and the lack of a proven method of quantifying the water content in TATB [12]. Further, the method cannot distinguish between free water in the bulk material (which may be released over time), bound water in the bulk material (which would remain trapped in a solid sample), and loosely bound (physisorbed) water on the material surface (which accumulates upon exposure to ambient humidity). Nuclear magnetic resonance was attempted to quantify water content in plastic-bonded TATB with limited success at low moisture levels [13]. Other researchers attempted to indirectly monitor the outgassing of moisture from samples, during or after heating, by introducing a secondary material to react with the released water to produce hydrogen; the pressure rise associated with hydrogen production [9] or mass spectrometry for hydrogen detection [14, 15] was used to estimate moisture outgassing.

Recently, Glascoe et al. investigated the rates and mechanisms of moisture release from a TATB formulation [16]. They developed kinetic models based on experiments performed on powder samples under ultra high vacuum at temperatures above the TATB sublimation threshold. These conditions are unreasonable for a preconditioning (i.e., drying) step because, although the temperatures remain below the decomposition threshold, the sublimation of the sample renders it unusable for the actual experiment. In many cases, experimentalists require drying guidance for solid parts, not powders, under relatively mild temperatures. If used appropriately, these models could be applicable to practical conditions; however, experimental validation is necessary.

The objective of the current study is two-fold: (1) to develop a technique for non-destructive monitoring of moisture release from solid materials and (2) to explore the validity of Glascoe's kinetic model for solid samples under practical conditions. The approach involves sealing an array of samples in a small chamber and heating the chamber to 65°C. Because it is common for samples, including TATB formulations, to outgas multiple species in addition to water, moisture is monitored directly using an aluminum oxide moisture sensor; pressure is monitored concomitantly with a separate pressure transducer. Without a means of gas analysis such as mass spectroscopy or infrared spectroscopy, commercially available instruments based solely on headspace pressure or sample weight loss do not differentiate between outgassed species and, hence, do not measure moisture outgassing exclusively. Herein we describe the apparatus and experiments on the TATB formulation LX-17, and compare our results with previous studies. In general, our experiments indicate that the kinetic outgassing model developed by Glascoe et al. [16] is applicable to solid samples under mild conditions and these two studies, taken together, provide researchers with key knowledge about the effectiveness of drying samples, especially solid parts, prior to experimentation.

2. Materials and methods

2.1. Experimental setup

A schematic diagram of the moisture outgassing measurement system is shown in Fig. 1. All components are stainless steel. All connections are vacuum compatible: type CF or VCR with metal gaskets are used throughout the system with the exception of the pump connection which is type KF with a Viton gasket. The system includes two stainless steel sample chambers, each containing a combination moisture/temperature probe (GE Panametrics M-Series aluminum oxide probe) and a gas-independent pressure transducer (MKS Instruments 230E Baratron). Only one of the chambers was used in this study.

Output from the moisture/temperature probe and pressure transducer was directed to a GE Panametrics MMS3 hygrometer connected to a PC running GE Panametrics PanaView data acquisition software. Data were acquired at 30-s intervals. The total volume of each sample chamber was estimated to be 190 ml.

To reduce the hazard associated with a single large quantity of pressed LX-17, a stainless steel sample holder was fabricated to hold 22 individual pressed LX-17 wafers (Fig. 2). The LX-17 molding powder (wet-aminated) was pressed in a die at 105°C for 5 minutes in air. The molding powder was not oven dried prior to pressing. The pressed wafers were stored in Ziploc bags under ambient conditions prior to use. Time between pressing and use (storage time) was 11 days for Batch 1 and 1 day for Batch 2. Each wafer weighed approximately 9-10 mg and was approximately 3.14 mm in diameter by 0.67 mm thick. The average density was approximately 1.85 g/cm³ for Batch 1 and 1.90 g/cm³ for Batch 2 (theoretical maximum density = 1.937 g/cm³ [17]). After placing the samples in the holder, the holder was placed in the sample chamber.

A turbo vacuum pump system (Alcatel Drytel 1025 with an AMD4 dry roughing pump and ATH 31+ turbo pump; pump speed 30 L/s) was used to evacuate the system overnight (~16 h) to a pressure of approximately 8×10^{-5} Pa as indicated by a vacuum gauge (MKS Instruments 972 DualMag with PDR900 controller) located near the vacuum pump inlet. The actual pressure in the sample chamber was not measured, but was somewhat higher due to the increased distance from the pump. The initial pump down was performed to remove free water molecules as well as those loosely bound to the surfaces of the LX-17, holder, and chamber wall. House nitrogen gas was then bled into the system (while actively pulling vacuum) until the pressure reached approximately 150 Pa as indicated by the vacuum gauge and the pressure transducer in the sample chamber. The moisture/temperature probe indicated a water vapor partial pressure of approximately 0.01 Pa after the nitrogen backfill. The chamber valve was then closed and the oven (Binder FP 115) was ramped to 65°C. Though the oven reached 65°C within a few minutes, the chamber temperature increased at a much slower rate, reaching 65°C in approximately 3 hours. The actual heating profile in the chamber is shown in Fig. 3; this profile was used in all experiments.

2.2. Measurements and calculations

The gas-independent pressure transducer exhibited a slight offset that varied nonlinearly with temperature. The offset was quantified by measuring the output at zero pressure (i.e., pressure below the detection limit of the transducer) as a function of temperature (Fig. 4). This offset was subtracted from the transducer output to yield the corrected total pressure at a given temperature.

Following the pump down and nitrogen backfill, some residual water molecules inevitably remain in the sample chamber; some are free (measurable) and some are loosely bound to the walls of the sample chamber and other surfaces (not immediately measurable). Upon heating, some of the surface-bound water molecules are freed from the walls and contribute to the measured water vapor partial pressure, P_w , and the total pressure, P_{tot} . To remove the contribution of these residual water molecules, P_w and P_{tot} were measured versus time for an empty sample holder (“empty run”) using the same pump down, nitrogen backfill, and temperature ramp used for the test samples (“test runs”), and the resulting pressure versus time curves were subtracted from those for the test samples. Note that time $t=0$ corresponds to the onset of heating after the pump down and nitrogen backfill (i.e., the sample chamber is at room temperature and approximately 150 Pa at $t=0$).

In theory, subtraction of the empty run curve from the test run curve yields pressure values due only to outgassing of the test sample. However, the initial water vapor partial pressure at $t=0$, P_{w0} , measured by the moisture/temperature probe after the pump down and nitrogen backfill was slightly different for the empty and test runs. Therefore, the empty run curve was first scaled to the P_{w0} of the test run before subtracting it from the test run curve by multiplying by the ratio of the test run and empty run initial water vapor partial pressures, $P_{w0}^{test} / P_{w0}^{empty}$. Since the total pressure measured by the gas-independent pressure transducer was also slightly different at $t=0$ for empty and test runs, the same method of subtraction of a scaled empty run was used to calculate the total pressure rise due to outgassing

for the test runs. As shown in Fig. 5, $P_w(t)$ and $P_{tot}(t)$ are approximately proportional to the initial pressures P_{w0} and P_{tot0} , respectively, for the empty runs. This linear relationship permits scaling the empty run data as described.

The number of outgassed water molecules in moles after a given time, $n(t)$, was calculated using the ideal gas law:

$$n(t) = [P_w^{\text{test}}(t) - P_w^{\text{empty}}(t)]V/RT \quad (1)$$

where V is the chamber volume (0.19 L), R is the gas constant (8.3144 J/mol-K = 8.3144 L-kPa/mol-K), and T is the chamber temperature in Kelvin. The moisture outgassed, O_w , after a given time in units of ppm (parts water per million parts of LX-17, or milligrams of water per kilogram of LX-17) was calculated by

$$O_w(t) = 10^6 \times n(t)M_w/m \quad (2)$$

where M_w is the molecular weight of water (18 g/mol) and m is the total mass of LX-17 in the sample chamber (~0.21 g).

3. Results and discussion

3.1. LX-17 Outgassing

Figure 6 shows the water vapor partial pressure and total pressure rise in the sample chamber at 65°C over a 2-week period for two separate batches of LX-17 wafers. The curves show the results after subtraction of the scaled empty run data. Toluene, a known outgassing product of LX-17, likely accounts for some of the total pressure rise; however, a previous study indicated that the amount of toluene outgassing is significantly lower than the amount of water outgassing [9]. In addition, air trapped in the wafers during the pressing process may have also been released during heating, contributing to the total pressure rise. Both water vapor partial pressure and total pressure rise are higher for Batch 2. Using Eqs. (1) and (2), moisture outgassing relative to the total weight of LX-17 in the sample chamber (in ppm) was calculated and is plotted in Fig. 7. Batch 1 reached approximately 50 ppm and Batch 2 reached approximately 70 ppm.

After reaching 65°C at $t \sim 3$ h, outgassing continued and then gradually abated, approaching a steady state (equilibrium). This behavior is expected based on the kinetics of diffusion and surface evaporation, which have been used to model moisture release of LX-17 [18]. The Hertz-Knudsen evaporation equation states that, for a liquid in a closed system at a given temperature that evaporates into a back pressure of its own vapor, the rate of evaporation is proportional to the difference between the equilibrium (saturation) vapor pressure and the actual partial pressure of the vapor [19]. In the case of a perfect vacuum, the partial pressure is zero and, theoretically, evaporation continues at a maximum rate indefinitely. If a perfect vacuum is not maintained, the partial pressure gradually increases due to evaporation and, hence, the evaporation rate gradually decreases. Although the rate decreases, evaporation continues until either (1) all the liquid evaporates or (2) the partial pressure reaches the equilibrium vapor pressure (evaporation and condensation occur at the same rate). Moisture outgassing of plastic-bonded TATB is a complex process involving diffusion of water through the bulk, evaporation from the surface, condensation back on the surface, and re-absorption into the bulk. In a closed system without active removal of released water, some level of moisture will remain in the material when equilibrium is reached (i.e., desorption and sorption occur at the same rate resulting in no net release of water).

If the water vapor partial pressure builds up sufficiently over the LX-17, it is possible that outgassing will stop prematurely (i.e., before all the available water in the bulk material is released). In

terms of the Hertz-Knudsen theory, if the partial pressure reaches the equilibrium vapor pressure of water over LX-17, the outgassing rate will drop to zero. To determine if this scenario occurred in our system, additional testing was performed in which the Batch 2 wafers were subjected to a second aging cycle (data not shown in figures). At the end of the first cycle, the sample chamber was evacuated and backfilled with nitrogen to remove most of the moisture released during the first cycle before starting the second cycle. If the equilibrium water vapor pressure was reached in the first cycle before all the available moisture was released, then we would expect to observe additional moisture outgassing during the second cycle. However, appreciable moisture outgassing was not evident during the second cycle (water vapor partial pressure rise was ~ 1 Pa), indicating that outgassing did not stop prematurely in the first cycle. A previous study on a solid pressed material consisting of 90% TATB and 10% Kel-F binder reported an equilibrium water vapor pressure of approximately 400 Pa at 62°C [20]. The original water vapor partial pressure (before subtraction of the scaled empty run) for Batch 1 and Batch 2 reached approximately 20 and 27 Pa, respectively (data not shown in figures), further supporting the conclusion that the equilibrium water vapor pressure was not reached in our system. Hence, the outgassing of the LX-17 samples abated as a result of thermodynamic and kinetic limits on transport and desorption of moisture from the sample.

It is unclear why the water vapor partial pressure appears to decrease slightly after ~ 20 h in Batch 2. This behavior was also evident in the original Batch 2 test run (before subtraction of the scaled empty run) and in the empty run (not shown in figures), but not in Batch 1. One possible explanation is that there may have been a very slow leak at the angle valve (V3 in Fig. 1) which only became evident after the moisture outgassing rate slowed significantly. Such a leak would cause the environment in the sample chamber to slowly equilibrate with the environment between the angle valve and the neighboring closed valves in the system (initially at $P_{total} \sim 150$ Pa and $P_{w0} \sim 0.01$ Pa). While this unexpected behavior may indicate a potential flaw in the system, the deviation from the expected behavior appears to be relatively minor with respect to the total amount of moisture released.

3.2. Comparison to historical data

Our results are summarized together with those of previous moisture outgassing studies on TATB-based materials in Table 1. Each study is unique, so only “ballpark” comparisons can be made. Although the thermal dwell time varies from a few days up to a year, the majority of moisture is released during the first several hours in most cases, so the dwell time can be neglected for purposes of “ballpark” comparison. Based on the results of Stull et al. [7] and Glascoe et al. [16], the amount of moisture outgassing from plastic-bonded TATB increases with temperature (data not shown in the table). Therefore, studies conducted at higher temperatures are expected to report higher moisture outgassing. In addition, materials with higher initial water content are expected to exhibit higher outgassing. Given these observations, the following comparisons are made:

- Our measurement system yields a slightly lower estimate of moisture outgassing than the Karl Fischer data reported by Rigdon et al. [9] which tested similar materials at similar aging temperatures.
- Our measurement system yields a much lower estimate of moisture outgassing than the Karl Fischer data reported by Stull [8] which tested a slightly different material at a similar aging temperature. The relatively high initial water content of the solid PBX-9502 may have contributed to the relatively high moisture outgassing.
- Our measurement system yields a higher estimate of moisture outgassing than the H_2 pressure data reported by Rigdon et al. [9]; however, this difference may be due, at least in part, to the fact that the molding powder was oven dried in the previous study.
- Our measurement system yields a lower estimate of moisture outgassing than the kinetic model data reported by Glascoe et al. [16] which was based on testing of a different material. It is possible that the PBX-9502 powder had a higher initial water content than our solid LX-17, resulting in more outgassing, or that the high surface area of the powder facilitated transportation of the moisture out of

the sample. It is also possible that the mass spectrometry method of water detection was more sensitive than the aluminum oxide sensor.

Each of the methods used in the studies shown in [Table 1](#) will measure pre-existing loosely bound (physisorbed) water molecules that are released from the surface of the material when heated in addition to water that diffuses out from the bulk. The amount of physisorbed water on the material surface depends on the ambient humidity and duration of exposure to ambient humidity prior to testing. In this study, the amount of physisorbed water was minimized by the initial pump down prior to testing. A similar technique was used in the pressure method by Rigdon et al. [\[9\]](#) and in the mass spectrometry method by Glascoe et al. [\[16\]](#). It is unclear if the other studies attempted to minimize the amount of physisorbed water prior to testing. Given the relatively low water content in the material, the contribution of physisorbed water can be significant. In [Table 1](#), it appears that even under prolonged heating at mild temperature, only a small fraction of the moisture can be driven out of a solid sample.

As stated previously, one of the goals of this study was to explore whether the kinetic model presented by Glascoe et al. [\[16\]](#) was applicable to solid samples under realistic conditions (i.e., mild temperatures) for a drying study. [Figure 8](#) shows the results of this study overlaid with kinetic predictions based on the isoconversional kinetic model reported in Glascoe et al. [\[16\]](#). The kinetic model provides a rate only and no guidance to actual moisture content, thus the initial concentration of water in an experiment is key to effectively predicting how much water can be removed during mild heating. Because the initial water content in our experiment was unknown, the kinetic model was scaled with an “initial water content” in order to match the outgassing amplitudes of the experimental data and better facilitate a comparison of outgassing rates between experiments and the kinetic model. It is clear from [Figure 8](#) that the rate of outgassing predicted by Glascoe’s kinetic model matches quite well with the rate of moisture outgassing measured by our experiments.

4. Conclusions

Moisture outgassing during isothermal heating of solid LX-17 was estimated using a commercial off-the-shelf aluminum oxide moisture sensor in a stainless steel vacuum system. Moisture outgassing occurred mainly in the first 10-20 h of heating at 65°C, reaching approximately 50-70 ppm (parts water per million parts LX-17). Previous studies using different methods of analysis reported moisture outgassing from approximately 10-400 ppm on similar materials at similar temperatures. Given the variations in analysis method and material composition and processing among this and previous studies, our results appear to be in good agreement with those reported previously. All reported data are considered to be estimates since the accuracy of the methods is unknown, and there is no gold standard for TATB moisture measurement. The simple system used in this study appears to provide useful estimates of moisture outgassing of TATB-based materials; however, the results must be considered in light of the fact that released moisture was not actively removed from the system, allowing absorption/adsorption to occur simultaneously with outgassing. As a result, the moisture outgassing rate is expected to be slower, and the total amount of outgassing lower, than that measured in a system with active moisture removal (e.g., active vacuum or other moisture sink). In practice, the environment surrounding the plastic-bonded TATB, including the ambient water vapor partial pressure and the presence of water-absorbing/reactive materials and water-adsorbing surfaces, will impact its outgassing kinetics. Given these considerations, the outgassing data support the applicability of Glascoe’s kinetic moisture outgassing model to solid parts under practical (e.g., oven drying) conditions.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. The authors thank S. Weber for pressing the wafers, L. Dinh for helpful technical discussions, and R. Maxwell and W. McLean for guiding and supporting this work.

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Table 1

Summary of moisture outgassing studies on TATB-based materials. Solid samples were obtained by pressing molding powder, which may or may not be pre-dried in an oven.

Material	Final Form	Powder pre-dried?	Initial water content (ppm)	Aging Conditions	Moisture Outgassed (ppm)	Method	Ref.
LX-17	solid	no	unknown	65°C for 2 weeks	50-70	Aluminum oxide moisture sensor	this study
LX-17	solid	no	640-1170	50°C for 12 months	91-358	Karl Fischer	Rigdon et al. [9]
LX-17	solid	no	640-1170	~70°C for 6-12 months	169-264	Karl Fischer	Rigdon et al. [9]
LX-17	solid	yes	240-400 (by Karl Fischer)	75°C for 7-8 months	5-13	Pressure increase due to H ₂ (by-product of H ₂ O plus reactive material)	Rigdon et al. [9]
LX-17	powder	no	660-770	90°C for 4 days	540-690	Karl Fischer	Stull et al. [7]
LX-17	powder	unknown	unknown	100°C for 8 days	75-199	Mass spectrometry for detection of H ₂ (by-product of H ₂ O plus reactive material)	Crawford et al. [14, 15]
PBX-9502	solid	unknown	3200	70°C for 3 weeks	3100	Karl Fischer	Stull [8]
PBX-9502	powder	unknown	1500-2800	70°C for 2 months	200-400	Kinetic predictions based on mass spectrometry for H ₂ O detection	Glascoc et al. [16]

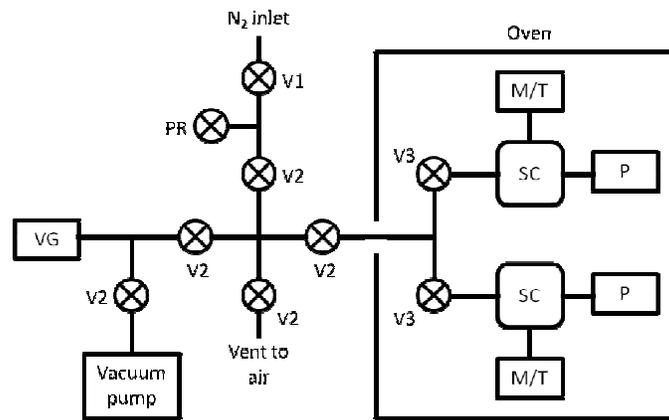


Fig. 1. Schematic diagram of the moisture outgassing measurement system. VG: vacuum gauge, PR: pressure relief valve, V1: bleed valve, V2: in-line valve, V3: angle valve, SC: sample chamber, M/T: moisture/temperature probe, P: gas-independent pressure transducer.

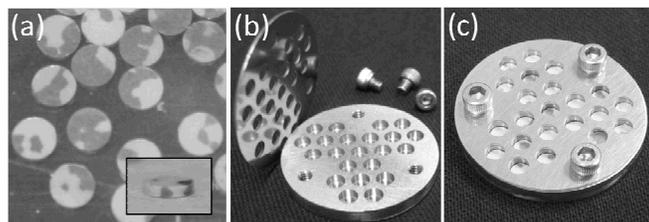


Fig. 2. (a) Pressed LX-17 wafers (~ 3.14 mm diameter, ~ 0.67 mm thickness, ~ 10 mg) and (b) stainless steel holder. (c) After placing one wafer in each well of the holder, the perforated lid was fastened with screws, trapping the wafers but allowing the outgassed species to escape.

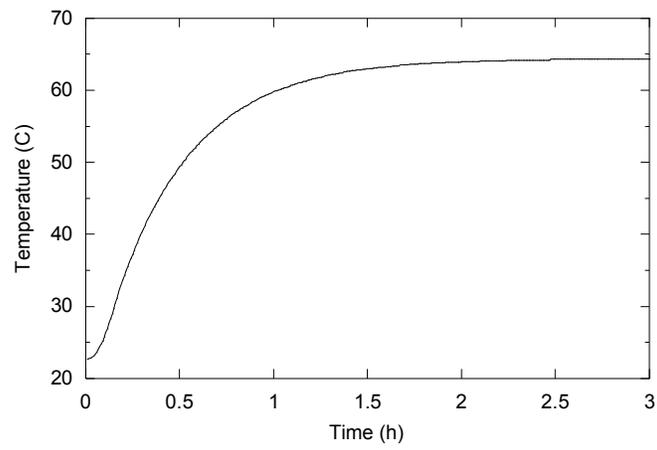


Fig. 3. Heating profile in the sample chamber. The 65°C setpoint was reached within 3 hours.

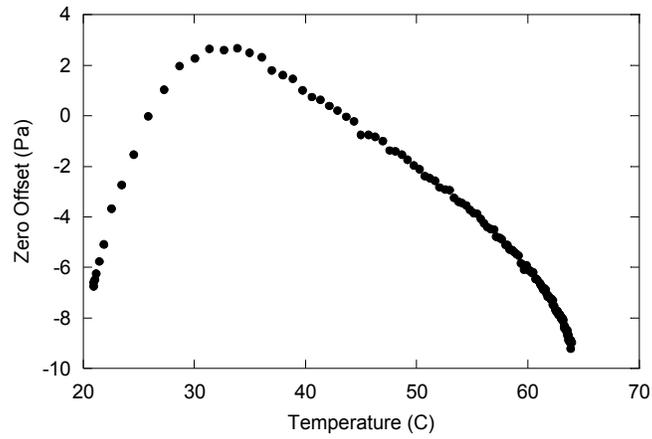
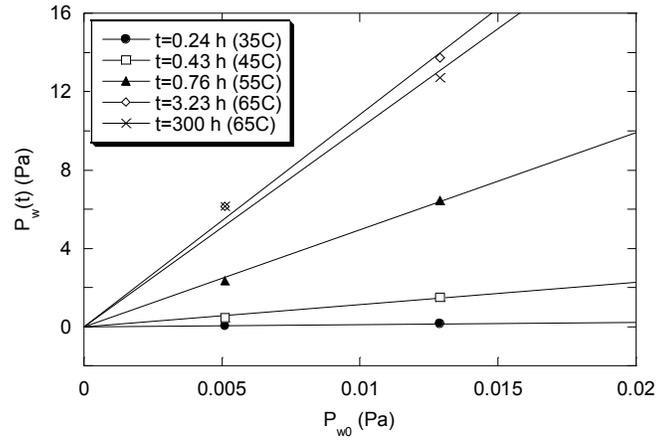


Fig. 4. Output of the gas-independent pressure transducer at zero pressure (i.e., pressure below the lower detection limit of the pressure transducer) versus temperature. This “zero offset” was subtracted from the transducer output to yield the corrected pressure at a given temperature.

(a)



(b)

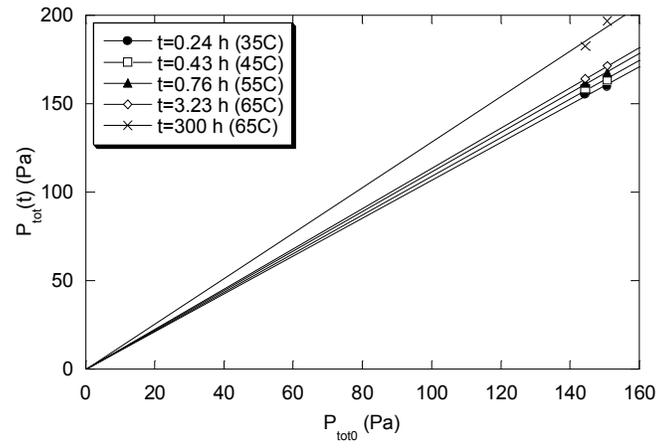


Fig. 5. (a) Water vapor partial pressure, $P_w(t)$, and (b) total pressure, $P_{tot}(t)$, as a function of the initial pressure at time $t=0$ for two empty runs. P_{w0} for the two runs are 0.0051 and 0.0129 Pa, respectively. P_{tot0} for the two runs are 144 and 151 Pa, respectively. Values at representative times $t=0.24$, 0.43, 0.76, 3.23, and 300 h are included. Linear regression fits through zero are shown.

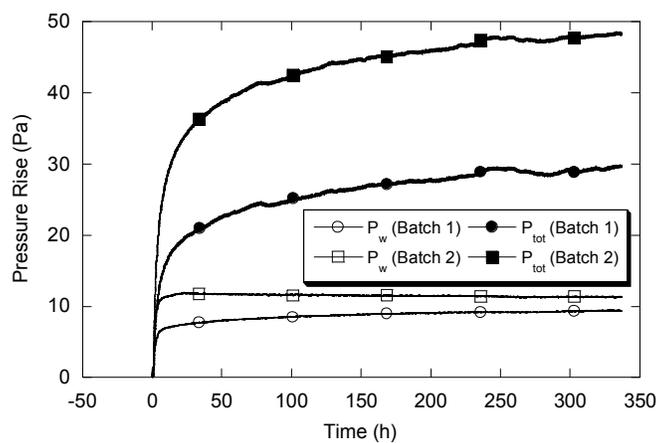


Fig. 6. Water vapor partial pressure (P_w) and total pressure rise (P_{tot}) as a function of time due to outgassing of LX-17 wafers at 65°C. Curves for two different batches of LX-17 wafers are shown.

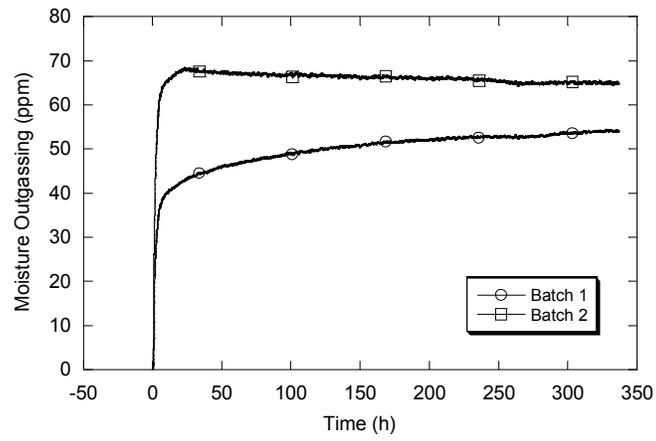


Fig. 7. Cumulative moisture outgassing (ppm) as a function of time due to outgassing of LX-17 wafers at 65°C. Curves for two different batches of LX-17 wafers are shown.

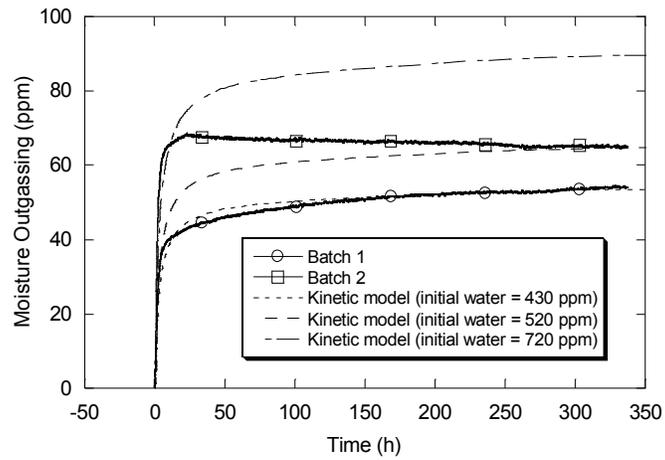


Fig. 8. Cumulative moisture outgassing (ppm) from this study overlaid with kinetic predictions based on the isoconversional kinetic model reported in Glascoe et al. [16]. Kinetic model data was scaled with an “initial water content” in order to match the outgassing amplitudes of the experimental data and better facilitate a comparison of outgassing rates between experiments and the kinetic model.