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CALORIMERIC ASSESSMENT OF RATES OF DESORPTION

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ABSTRACT

This paper concerns the further testing of a new double calorimeter. We earlier reported initial development of the calorimeter and thereafter inferred rates coefficients for adsorption of moisture under a "large pressure jump". (The test materials were Silica Gel type A and water.) The current paper presents a further check on the calorimeter by demonstrating that measured desorption and adsorption rates were compatible.

A disappointing aspect was an unintended near step change in condenser pressure at the start of the experiment. The condenser design was deficient and better drainage is needed in future to maintain vapour in immediate contact with cold surfaces. Notwithstanding the lower-than-intended pressure driving force, the heat addition to the silica gel was measurable, following an exponential pattern

against time with regression coefficient better than $r^2 = 99\%$. The rate coefficients that fitted each dataset were broadly in line with coefficients reported for adsorption (within the limits of experimental error).

Keywords: Desorption, calorimetry, rate constant, large pressure jump, thermo-electric module

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NOMENCLATURE

c_{pr}	specific heat capacity of refrigerant vapour	[J kg^{-1} K^{-1}]
h_{ads}	specific heat of adsorption	[J kg^{-1}]
K	rate constant	[s^{-1}]
m_x	mass of adsorbent	kg
p	vapour pressure	Pa, mbar
p_{sat}	saturation pressure	Pa, mbar
Q_a	heat accepted/ rejected from aluminium plate	J
R	Specific gas constant	[J kg^{-1} K^{-1}]
t	time	s
T_b	temperature measured at aluminium plate (close to adsorbent)	K
T_v	temperature of refrigerant vapour	
R	specific gas constant	[J kg^{-1} K^{-1}]
X	adsorbent loading	[kg (adsorbate)/kg (adsorbent)]
X^*	adsorption capacity (loading under equilibrium)	[kg (adsorbate)/kg (adsorbent)]
A_0	Pre-exponential constant	(-)

INTRODUCTION

This paper concerns the development of a double calorimeter that tracks the processes of adsorption or desorption. The measured rates of the adsorption of moisture onto silica gel beads were published previously [1]; in the current paper we have further tested the instrument by ascertaining whether or not measured rates of desorption are identical. Results were not of the quality wished for (in terms of the control of boundary conditions). Nonetheless, they usefully confirm previous adsorption data, and point to future improvements in the experiment.

Adsorbents are employed in Adsorption Heat Pumps (AHPs); devices that amplify heat or convert waste heat to refrigeration. A number of adsorption cycles of varying complexity are described, for example Oliveria et al [2]. Ng [3] argues that the adsorption cycle has several advantages over the liquid, absorption cycle including minimal number of moving parts, cooling pumps that are easily purchased, and that the absence of corrosive materials allows the use of low-cost carbon steel. Within AHPs, the important aspects of the adsorbent are its adsorption capacity, the sensitivity of this capacity to temperature, and the rate of refrigerant uptake.

One of the most widely used methods of evaluating adsorption kinetics and equilibria is the magnetic levitation scale (mainly the Rubothermscale [4,5]) and the "large temperature jump" (LTJ)[6]. The Rubotherm device is expensive, and demands extensive fitting out for corrosive or high pressure refrigerants. The sample pan is held within a constant temperature environment, but one cannot cycle the pan temperature in a controlled manner. The "large temperature jump"(LTJ) [6] operates by resting a single grain of adsorbant on a plate, stepping the plate temperature in the same way as the isobaric processes within a chiller cycle, and monitoring the mass adsorbed (equal to the calculated mass lost from a reservoir of adsorbate vapour). The LTJ produces excellent data for single grains, but should it be required to test several dozen grams of adsorbent, quite possibly adhered to fins or mixed with a

heat transfer enhancement, then the necessary reservoir could be huge. Our calorimeter has worked with samples weighing between 5 g and 15 g [1] and also adsorbent sandwiched between 40-mm long fins [7].The method is intended ultimately for relatively complex systems, for instance when the adsorbent is coated onto large fins so that a large sample must be dealt with [8]. The temperature control is to within 0.1 K of set point, and to date the temperatures of inert, aluminium samples can be cycled in the form of triangular wave or sine wave with simultaneous measurement of heat flow [9]. The calorimeter [1] simultaneously detected heats of phase change in both evaporation and adsorption. To check the method adsorption capacities were inferred from measured heat rejection and confirmed to be within 10% of independently published gravimetric measurements [10]. Because the equipment is at an earlier stage of development, it has to date been more straightforward to run tests with the adsorbent held nominally isothermal and to impose "large pressure jumps" [11].

This paper summarises the calorimeter, gives new data for rates of desorption and compares these against previously reported adsorption rates. Problems in controlling pressures are discussed with a view to future developments in the equipment.

METHODS AND ANALYSIS

The calorimeter, its calibration and its operating procedureare described fully in [1][9]. In summary, it comprised glass adsorber and condenser sections, separated by a valve (Fig. 1). Each section was bounded by a 50-mm-diameter horizontal aluminium plate fitted with thermo-electric modules (TEMs, item5 in part b). The plate temperatures were monitored with K-type thermocouples, either lodged inside 0.5-mm-diameter holes drilled into the upper plate to give a reading T_b, or resting on the surface of the lower plate. The TEMs behaved as heaters or coolers according to the direction of electrical current. The calculated heat flows comprised three components: the Peltier effect at the TEM

faces, ohmic heating within the TEM, and thermal conduction between the TEM faces. Calibration errors of the TEM were assessed as 10% [9], comparable to the discrepancy between calorimetrically inferred adsorption capacities and Wang et al's gravimetric measurements [1, 10].

The adsorbent was a 5-gram sample of type A silica gel beads, 3-mm in diameter and adhered to an aluminium plate with silicone sealant.

In preparation for adsorption tests the adsorbent was isolated by closing the connecting valve (item 3 in Fig. 1). Heating and vacuum were applied after which the adsorbent and water were brought to their set point temperatures [1]. The connecting valve was then opened.

The adsorption capacity (Fig. 2) was estimated as follows. If changes to the sensible heat of the adsorbent are neglected, then,

$$Q(t) \approx m_x \, (X(t) - X(0))(h_{ads} - c_{p,r} \, (T_b - T_v)) \qquad [1]$$

where $c_{p,r}$ is the heat capacity of vapour at constant pressure, h_{ads} is the average isosteric enthalpy of adsorption, inferred from Antoine plots of the adsorption isotherm slope, m_x is the mass of adsorbent (silica gel), and $Q(t)$ is the net heat rejection (in joules)at time t after the start of the experiment. Also T_b is the measured, near constant temperature of the aluminium plate and T_v is the temperature of vapour approaching the sample, taken as the evaporator temperature for adsorption. For desorption one assumes $T_v = T_b$. Term $X(t)$ is instantaneous loading and for adsorption $X(0) \to 0$. At equilibrium ($t \to \infty$) Equation 1 was manipulated to give adsorption capacity X^*. Heat transfer and loading are approximately in proportion, $Q(t) \propto X(t)$.

In reference [1], the adsorption capacity was fitted to Henry's law (Fig. 2)

$$X^* = A_o (\exp [h_{ads} / RT_b] p \qquad\qquad (2)$$

where X^* is the adsorption capacity, h_{ads} = 2495 kJ kg^{-1} is the heat of adsorption, A_o = 1.92 x 10^{-12} Pa^{-1} is a pre-exponential constant. (A Toth equation [10] applies when the adsorption capacity exceeds 30%.)

Desorption tests were designed to expose each sample to a step reduction in moisture pressure. To set initial conditions, two hours were allowed for the water (lower section), water vapour and silica gel (upper section) to achieve equilibrium. The connecting valve (item 3, Fig 1a) was open, and water in the lower section was held at roughly 303 K. Then, the connecting valve was closed, the desorber temperature was maintained and the refrigerant was cooled to typically 281 K (at which the measured vapour pressure was 1100 Pa). This condition was held for 30 minutes, during which any stray heat flow to-or-from the surroundings wasestimated. The test proper was started by opening the connecting valve; pressures and heat flows were recorded against time.

Table 1 summarises the expected errors of measurement in temperature, pressure and heat transfer.

3. RESULTS

This section reports the thermal behaviour of the calorimeter and compares rate coefficients for adsorption with rate coefficients for desorption.

The pressure inside the condenser section was not controlled as well as intended; the adsorption tests had been more promising(Fig. 3). Typically, the vapour pressure inside the condenser section increased from 1100 Pa to 1500 Pa after the connecting valve was opened (at time, $t > 0$ s), before gradually falling to 1400 Pa. This suggests that the water layer exerted its thermal resistance so that water surface temperature exceeded that measured at the aluminium plate.

Figure 4 serves to illustrate the correction of unwanted heat losses. On part a, attention is drawn to the portion of the graph at $t < 0$, before the start of the test proper and where ideally the indicated flow of heat would be zero. Under these conditions directly measured heat rejection corresponded to unwanted losses and instrument offset, and, on extrapolation beyond $t>0$, was subtracted from raw data. The condenser section (part (a) in Figure 1) required a relatively large adjustment, this is included to illustrate the method of correction but the corrected data were omitted from further detailed analysis. (Condenser side-walls had to be hotter than the dew point temperature, introducing the stray heat gains).Less correction was needed for the desorber section, wherein side-wall and sample temperatures were better matched.

It has been found that plots of corrected heat rejection can be fitted statistically to exponential recovery or decay [1,7],

$$Q(t)=Q(\infty)\,[1-\exp\,(-K(T_b)t)] \qquad (3)$$

Where Q is the net heat addition (in joules) and the rate constant K is approximately proportional to that used in the linear driving force model of heat transfer (see discussion section).

Exponential functions were fitted to experimental data (Fig 6) with $r^2>99\%$ (Table 2). The rate coefficient, K, for desorption increased as the nominal sample temperature T_b increased (Fig.6), and lay within the range previously found for adsorption.

To check the hypothesis that the layer of condensate formed an appreciable thermal resistance the temperature of the adsorbent was maintained at 303 K while the temperature of the refrigerant(water) was varied sinusoidally. The indicated temperature T_b followed its set point to within 0.2 K. Figure 7 shows the measured and saturation pressures ($p_{sat}(T_b)$). The saturation pressure and

measured pressure tended to good agreement in the boiling phase (increasing pressure) but diverged by as much as 600 Pa in the condensing phase. This confirms the ineffectiveness of the condenser, as observed in the desorption tests.

DISCUSSION

A previous kinetic test was reversed to study desorption rather, than adsorption. The results appear promising –the sets of rate coefficients were within 10% of each other.

One problematic aspect was the evident pressure difference between desorber and condenser (initially about 1650-1500 = 150 Pa, Fig. 3). This far exceeded any calculated frictional loss; some months after these experiments the valve was inspected and damage to the diaphragm was evident. This may have been caused solely by the use of methanol at that time, or earlier degradation may have contributed to the observed pressure loss.

More worrying is the step change in condenser pressure above its expected, initial value (Fig. 3). From tabulated saturation pressures, the surge corresponded to the water surface being 3.5 K hotter than the measured aluminium plate, at T_b, and hence a temperature gradient through the water. Even were the water to form a quiescent layer, by Fourier's law such a gradient would conduct ~0.8 watts (through a 5-mm-deep layer), of the same order as heat rejected by the condenser. We have been unable to control evaporator temperature by putting thermocouples in the bulk liquid, owing to rapid temperature fluctuations. A further measurement nearer to the water surface should be considered in future, but also an experiment is needed in which the condenser can drain freely. An increased condenser surface area would also be helpful. No pressure surges were evident when adsorption was tested, and the lower section of the rig acted as an evaporator. The limitation of the "condenser" was confirmed following the sinusoidal variation in set-point temperature T_b (Fig 7).Measured pressures

repeatedly tended to match the calculated saturation during evaporation, but lagged during condensation.

Notwithstanding issues with pressure control, the desorption trends matched the exponential form of the adsorption trends. Equation 1 indicates $Q \propto X*$ and then differentiating Equation 3 gives Gluekauf's linear driving force model [12]

$$\frac{dX}{dt} = K(T_b)(X^*(p,T_b) - X)$$ [4]

Note, however, that the temperature gradients within the bead, and thermal resistance from bead to plate, render the coupled conduction and diffusion complex. Thus, here Gluekauf's straightforward model does not yield a reliable intra-bead diffusivity from the rate coefficient, $K(T_b)$. With regard to LTJ in particular, Aristov [13] remarks on the tendency of uptake (X) to follow the linear kinetics, notwithstanding sophisticated coupled phenomena.

The difference in rate coefficients – adsorption versus desorption – is 10% at most if lines of best fit are considered, versus scatter of ± 20% in the adsorption study. Greater accuracy and repeatability could come through using larger sample masses and hence larger equipment (larger TEMs have since become commercially available). Also, the binder may well have progressively blocked mesopores to the detriment of both the magnitude and the consistency of rate coefficient $K(T_b)$. Tests without binder are in progress.

The rate coefficient might be less for desorption than for adsorption, owing to temperature gradients inside the beads. The interior bead temperature would exceed T_b during adsorption and be less than T_b during desorption. The local, centre-of-bead driving force would thus be reduced for both processes. (For desorption intra-bead cooling reduces local X - $X^*(T)$, for adsorption intra-bead heating reduces $X^*(T)$ - X). On the other hand one would expect temperature peaks to increase rate coefficients for adsorption but decrease them for desorption.

Our ultimate intention is to use this method to simulate complete cycles of an adsorption heat pump. One difficulty is the finite heat capacity of the aluminium plate separating sample from TEM, which if too large prevents sufficiently rapid temperature change. Some experiments [7] have now been completed with the TEM inside the adsorption/ desorption vessel, and in direct contact with the sample.

CONCLUSIONS

A calorimeter was previously employed to study rates of moisture adsorption. The function has been reversed, to study desorption. It is encouraging that for both types of experiment the sorbent heat rejection or addition follows an exponential function, and that within current experimental error the measured rates of mass transfer are similar. However, the moisture pressure requires more effective and precise control. This could be achieved by building a condenser that drains freely.

ACKNOWLEDGEMENTS

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Figure 7 Response to a sinusoidal change in set point temperature T_b (a) over several cycles (b) detailed view of one cycle. T_b varied sinusoidally between 281 K and 298 K. Term p_{sat} is the saturation temperature calculated from T_b

Table 1 Measurement uncertainties and error analysis

Table 2 Conditions for the desorption test presented in Figure 5b (Condenser temperature = 285 K)
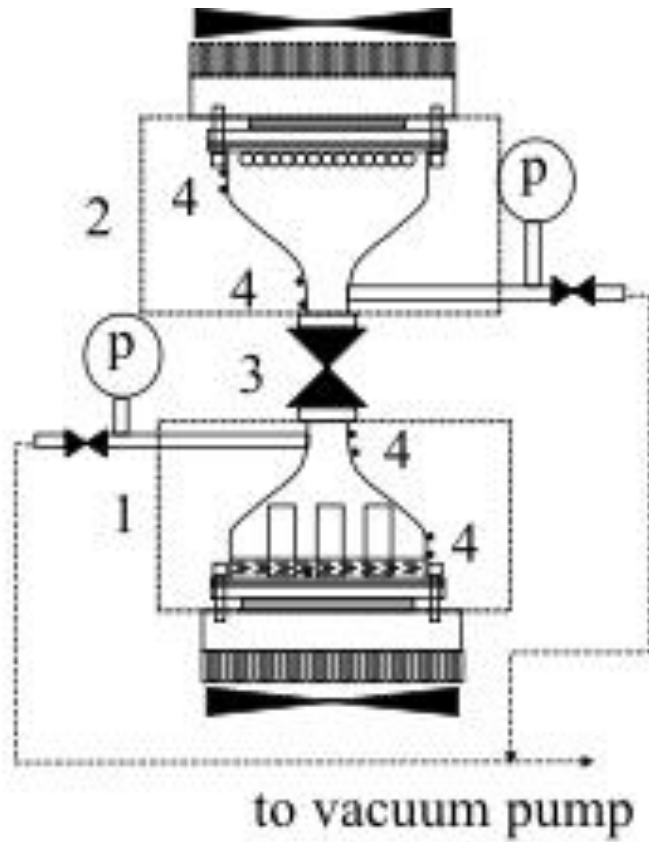
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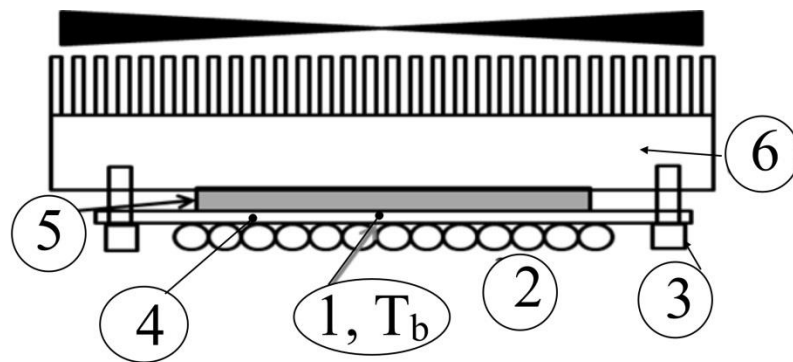
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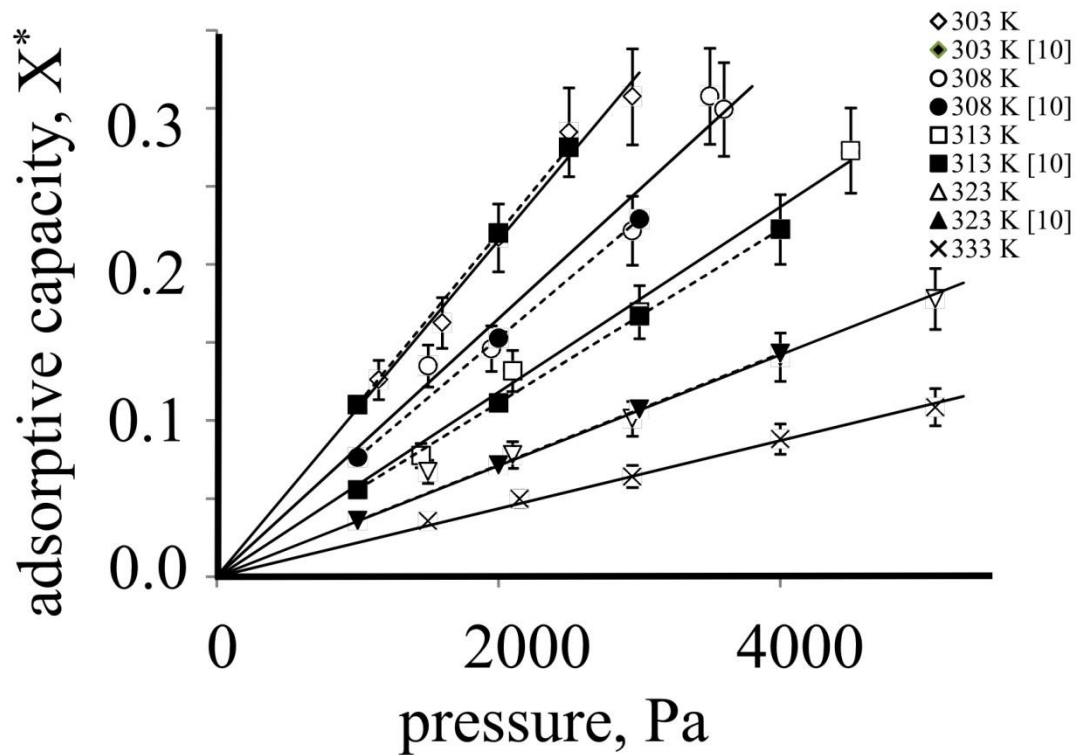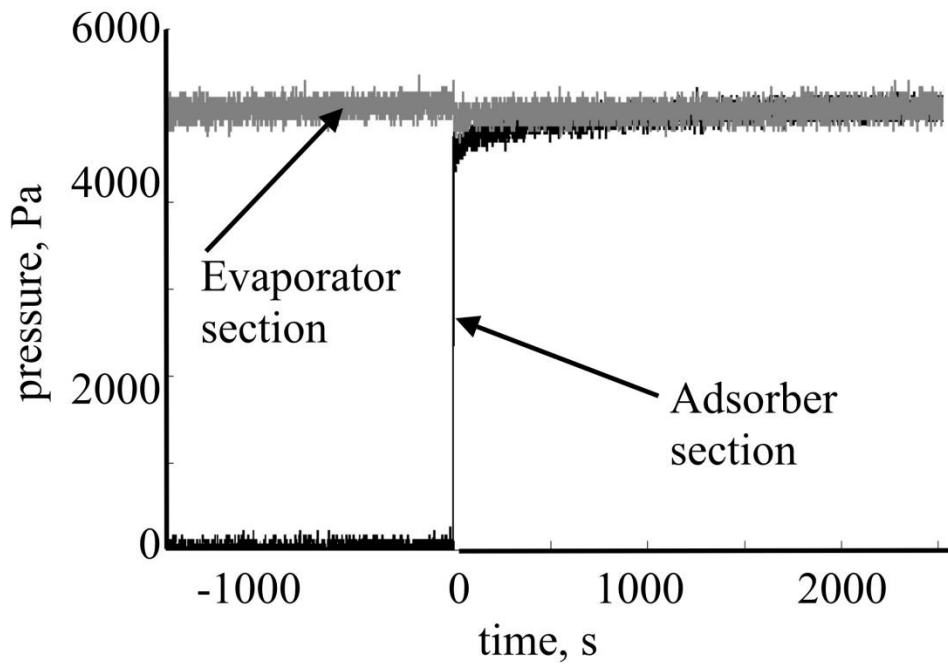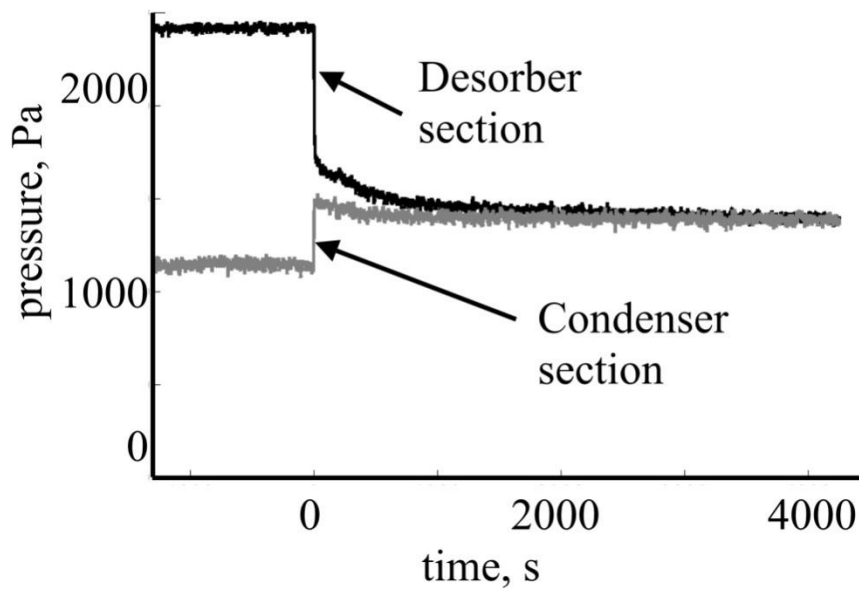
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(a)

(b)

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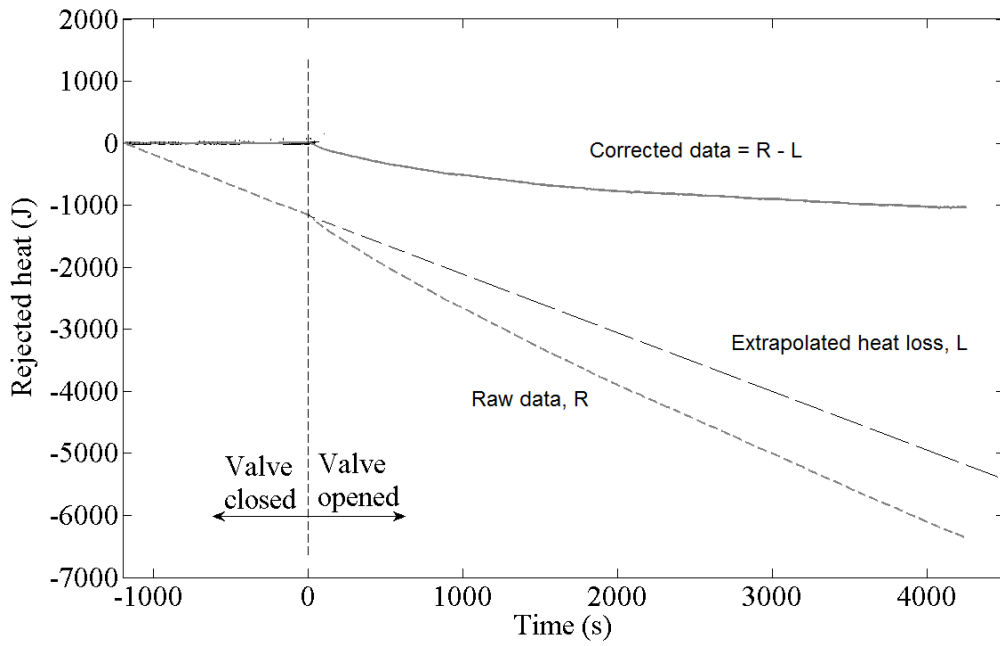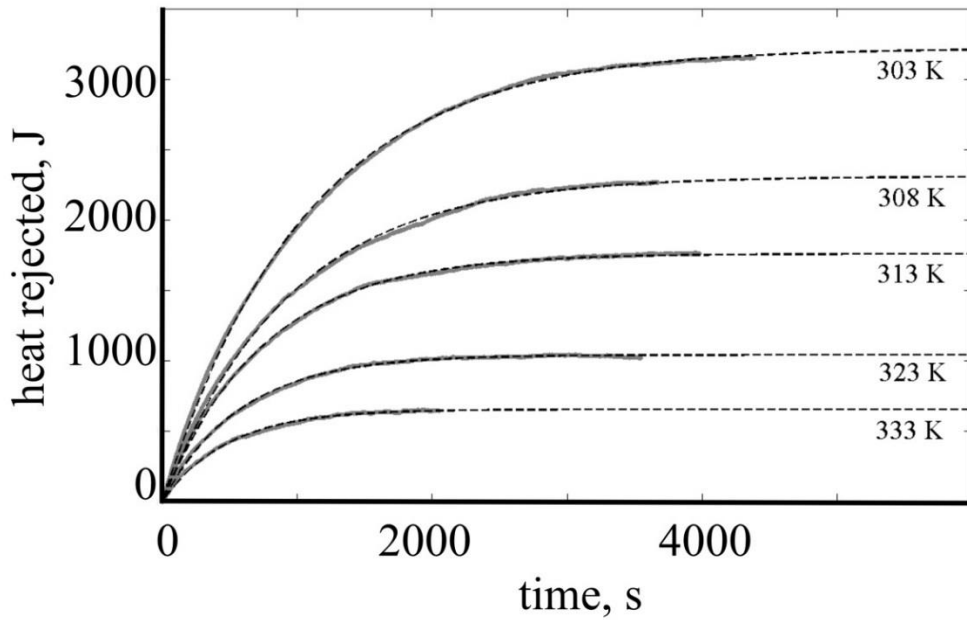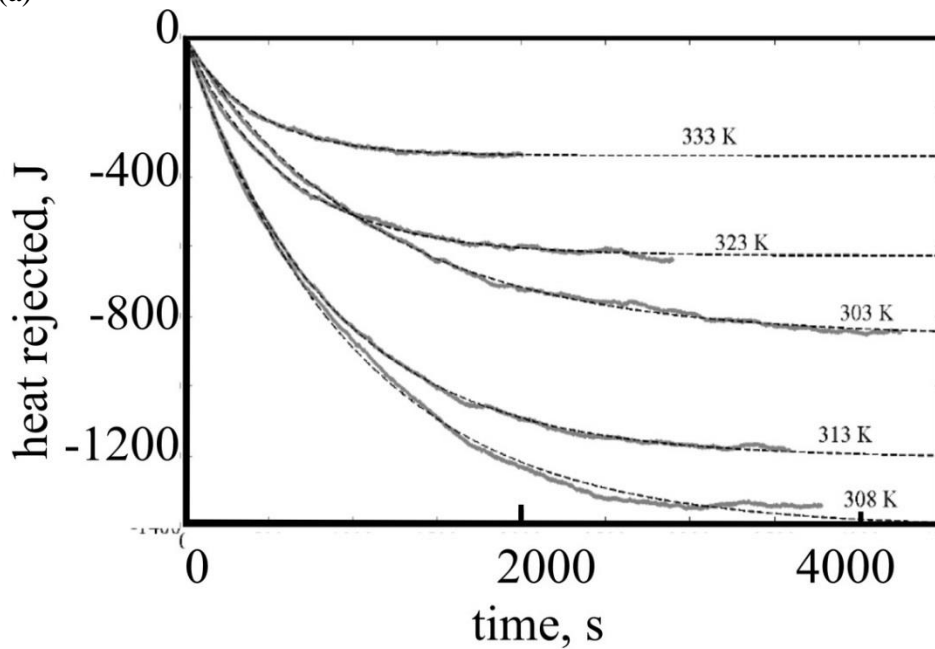
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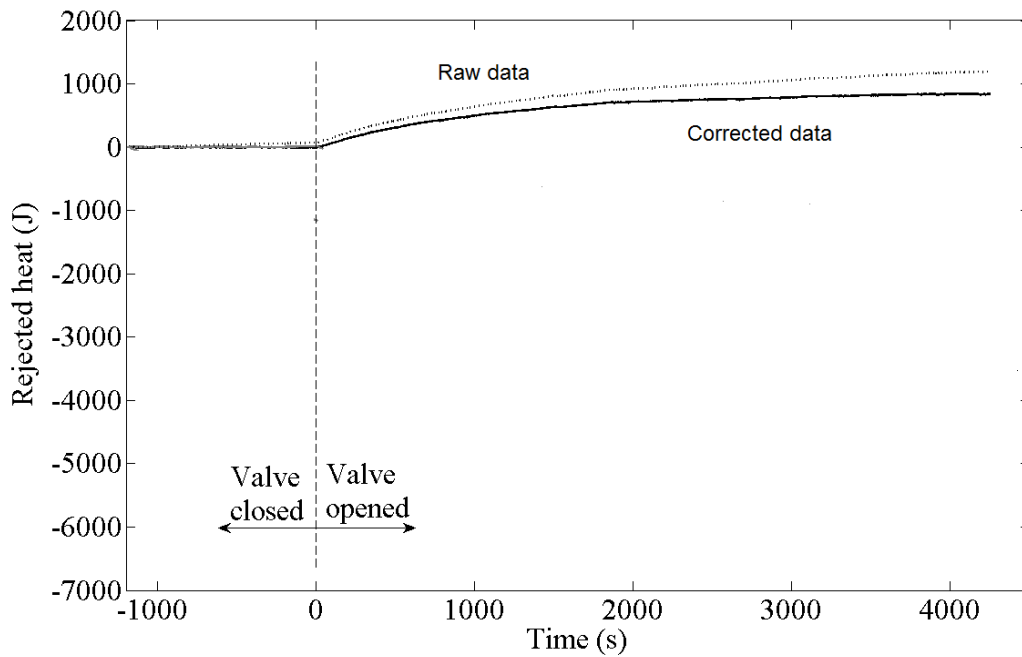
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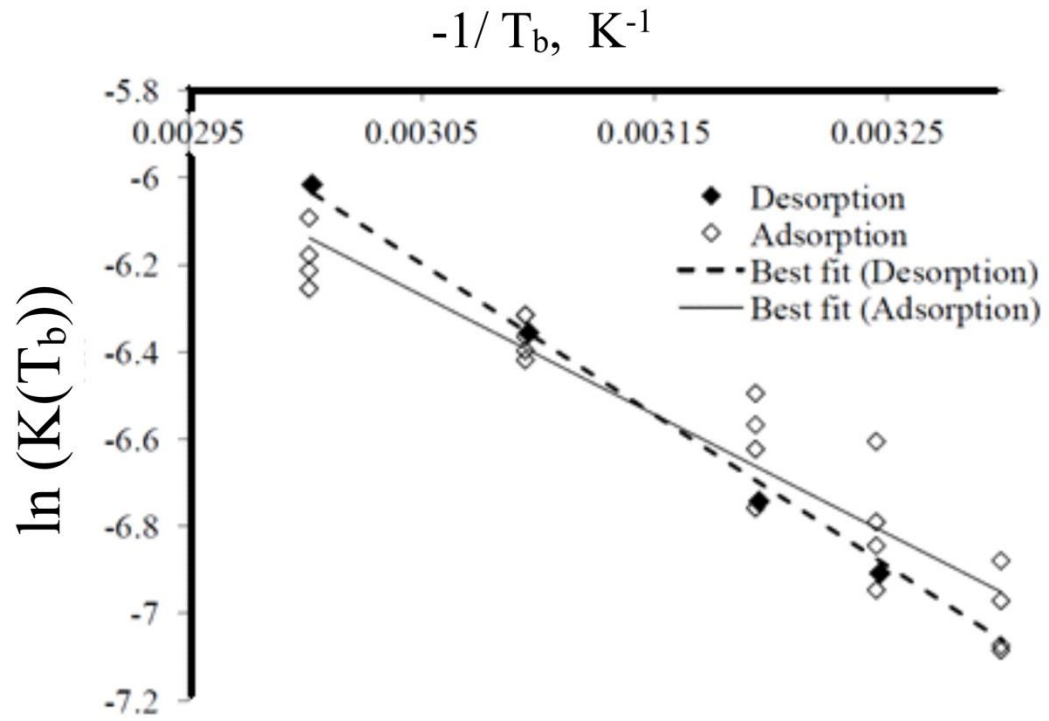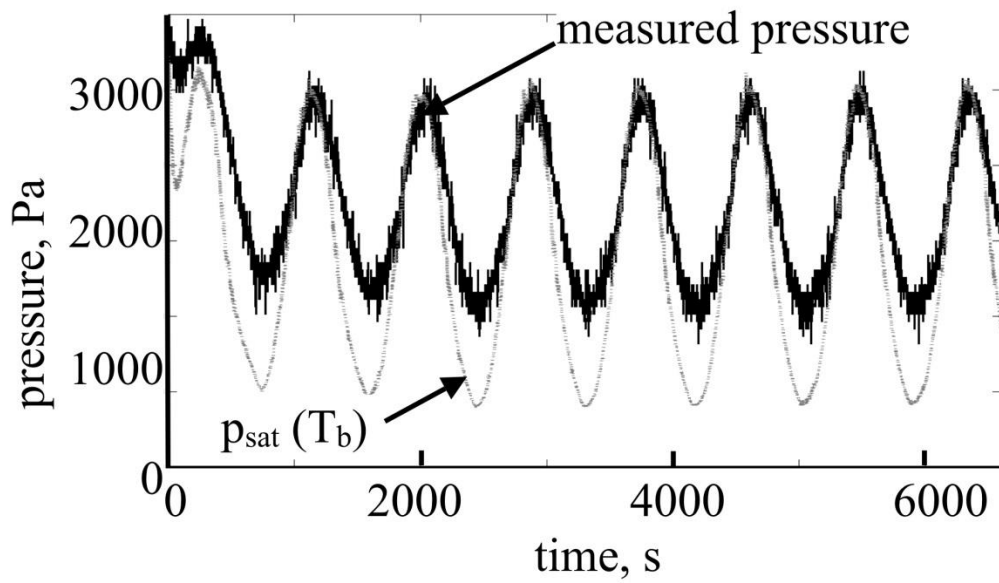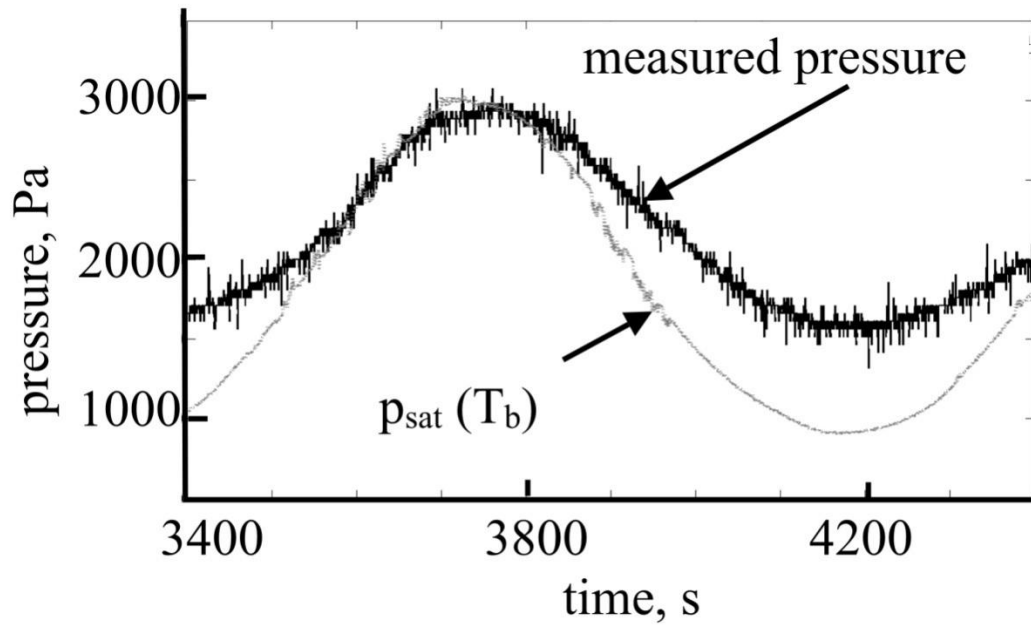
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Table 1
Measurement uncertainties and error analysis

Item no	Source of uncertainty	Justification	Error
Heat flow measurement			
1	Measured heat flow	Assessed in [9]	10.0%
2	Correction for extraneous heat loss	Prior to experiment, variation from constant heat flow is $\pm$ 40 J. Produces uncertainty in correction for stray losses.	1.6%
3	Refrigerant temperature in sample section is an estimate	In Equation [1], change estimate of T_e from evaporator to vessel wall temperature	3.8%
	Total uncertainty	$\sqrt{10^2 + 1.6^2 + 3.8^2}$	10.8%
Vapour pressure measurement			
4	Gauge error	Manufacture claims repeatability of 0.2% f.s.d.	200 Pa
5	Temperature drift	Sensitivity of 0.05% full scale per Kelvin, 2°C uncertainty in gauge temperature	100 Pa
6	Data logger	Resolution of 12 bit device	20 Pa
	Total uncertainty	$\max (50, \sqrt{200^2 + 100^2}\,)$	220 Pa, 2.2mbar
Temperature measurement			
7	Sensor error	Thermocouple random error	0.5 K

Table 2
Conditions for the desorption test presented in Figure 5b (Condenser temperature = 285 K)

Desorber Temperature, K	Initial Pressure, Pa (Isolated desorber at equilibrium)	Final pressure, Pa (End of experiment)
303	2400	1400
308	3500	1400
313	3500	1400
323	3500	1400
333	3500	1400

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