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Advanced In-situ Diagnostics for Multicomponent Gas Analysis and Material Aging

Part 2: Compact Determination of Hydrogen Isotopes

David B. Robinson
Sandia National Laboratories
Livermore, CA 94551

Abstract

This report has been accepted for publication in the journal Fusion Science and Technology, in the special issue associated with the Tritium 2016 conference, where the work was presented.

Scanning calorimetry of a confined, reversible hydrogen sorbent material has been previously proposed as a method to determine compositions of unknown mixtures of diatomic hydrogen isotopologues and helium. Application of this concept could result in greater process knowledge during the handling of these gases. Previously published studies have focused on mixtures that do not include tritium. This paper focuses on modeling to predict the effect of tritium in mixtures of the isotopologues on a calorimetry scan. The model predicts that tritium can be measured with a sensitivity comparable to that observed for hydrogen-deuterium mixtures, and that under some conditions, it may be possible to determine the atomic fractions of all three isotopes in a gas mixture.

Introduction

Experimental studies of nuclear fusion often require the handling of mixtures of gaseous isotopologues of diatomic hydrogen, as well as helium isotopes that are products of fusion or the decay of tritium. A prevalent method to determine compositions of these mixtures involves leaking a small quantity of the gas into a vacuum chamber, ionizing it, and performing mass spectrometry. A low-cost quadrupole mass spectrometer has typical detection limits for a given species of a few tenths of a percent; more expensive instruments such as magnetic sector mass spectrometers have lower limits. However, mass spectrometers and their vacuum hardware are generally bulky and consume large amounts of energy. When tritium is used, that bulky hardware becomes contaminated. The vacuum pumps produce undesirable waste streams of dilute tritium in their exhaust, and replacement of worn pump parts produces additional tritium-contaminated waste. Especially when tritium is used, it would be valuable to have methods to measure composition that do not require a vacuum system.

A previous publication proposed a method to determine composition using scanning calorimetry of a reversible hydrogen-absorbing material in a small capsule with a laser-drilled hole.[1] Experiments with hydrogen, deuterium, and helium-4, using palladium as the hydrogen-absorbing material, demonstrated that mixtures of about 1% of one gas in another yield calorimetry scans that are distinguishable from those of the pure gases. The pure hydrogen isotopes absorb into (and desorb from) the palladium at temperatures differing by tens of degrees C, with mixtures absorbing at intermediate temperatures. Helium modifies the absorption and desorption by forming a temporary blanket of helium-rich,

hydrogen isotope-poor gas in the capsule during absorption, and a helium-poor, hydrogen isotope-rich gas during desorption. This results in an increased separation of the absorption and desorption peaks, with characteristic peak shapes, aiding deduction of the helium mole fraction. This effect is not predicted to be strongly dependent on the isotopic composition of the helium. A model accounting for mass transport and the thermodynamics and kinetics of absorption predicts the positions and shapes of the calorimetry peaks. Experiments with tritium have not been performed, and the model was not applied to these in the previous work. In this report, the model is extended to account for tritium, and its predictions are evaluated for mixtures of two or three hydrogen isotopes. The effect of helium in the presence of tritium is not expected to differ significantly from the effect of helium on the other hydrogen isotopes as described in Ref. 1, so for brevity, helium is not considered here.

Model

In the scenario to be modeled, a mixture of $^{1}H_2$, $^{2}H_2$, $^{3}H_2$ is present in and around a capsule containing a small amount of palladium, as in the experimental geometry described in Ref. 1. The choice of palladium is motivated by its ability to reversibly absorb and desorb hydrogen near room temperature and atmospheric pressure; its robustness against surface fouling and bulk oxidation, which make it convenient to handle in laboratory conditions; and the existence of literature data on the equilibrium amounts of each hydrogen isotope in the solid as a function of temperature and pressure. It is assumed that the mixed hydrogen isotopologues such as $^{1}H^{2}H$ exist in their equilibrium amounts, and have an effect on the solid-gas equilibrium. Enthalpies of formation of the mixed isotopologues are typically less than 1 kJ/mol, which is similar to the reported uncertainties in the enthalpies of absorption of hydrogen isotopes into palladium, so the chemical effects of the mixed isotopologues are relatively minor.[2,3] Similarly, it is assumed that the effects of the mixed isotopologues on the physical properties of the gas (viscosity, heat capacity, diffusion coefficient) are within the uncertainty related to other approximations in the transport model, so that the mass transport equations treat all gas-phase ^{1}H as existing as $^{1}H_2$, etc.

Fig. 1 presents a graphical representation of the capsule geometry, gas concentrations, and hydride-to-metal ratios accounted for by the transport model. Table 1 describes other transport model parameters.

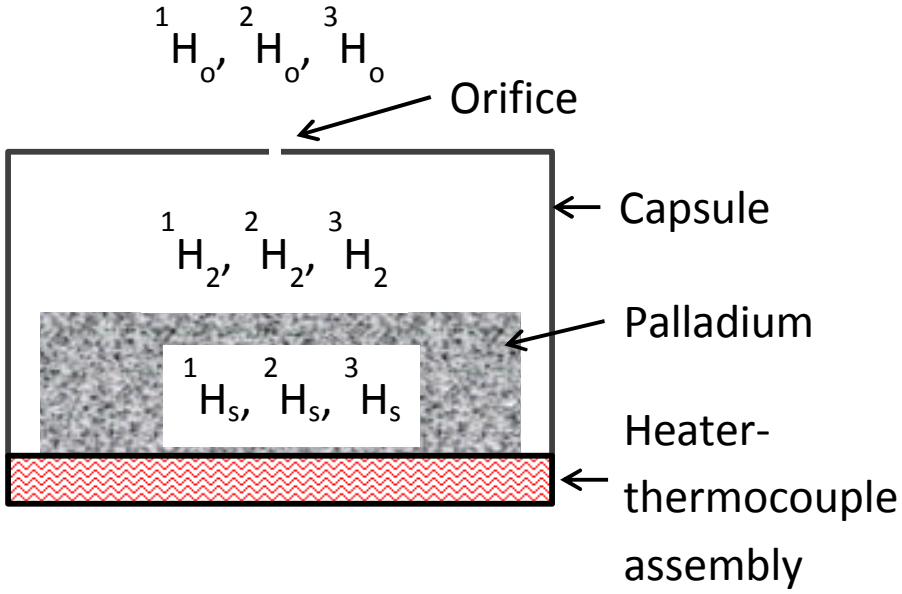

Fig. 1. The calorimetry model accounts for constant external gas concentrations $^{i}H_o$, variable concentrations $^{i}H_2$ inside the capsule, and variable solid-phase hydride-to-metal ratios $^{i}H_s$ (i = 1, 2, or 3).

Table 1. Parameters in transport model.

${}^{i}H_{eq}$	Value of ${}^{i}H_2$ that would be at equilibrium with the solid composition (mol/m^3)
n_o	Sum over *i* of ${}^{i}H_o$ (mol/m^3)
n	Sum over *i* of ${}^{i}H_2$ (mol/m^3)
T_o	External temperature (K)
T	Temperature inside the capsule (K; reported as °C in figures)
R	Ideal gas constant (J/mol K)
r	Radius of orifice that allows gas transport in and out of capsule (m)
L	Length of capsule orifice (m)
V	Volume of capsule (m^3)
m	Moles of palladium
μ	Gas viscosity (Pa s)
D_i	Diffusion coefficient of gas species *i* (m^2/s)
k	Rate constant for absorption and desorption (m^3 mol^{-1} s^{-1})
t	Time (s)

Gas transport is described in the model by a set of equations that each account for pressure-driven flow through the orifice, diffusion through the orifice, and absorption/desorption into the solid. The flow term is treated as laminar flow through a pipe, as a simple hypothesis for its dependence on orifice geometry and pressure. The diffusion term uses a one-dimensional model. The absorption/desorption rate is assumed to be linearly proportional to the concentration difference from the equilibrium state, as determined below. Because the composition of flowing gas depends on the flow direction, the transport equations take two different forms. When the first term is positive ($n_oRT_o > nRT$), gas flows into the capsule, with the composition of the external gas:

$$V\frac{d^{i}H_2}{dt}=\frac{\pi r^4}{8\mu L}\frac{{}^{i}H_o}{n_o}\left(n_oRT_o-nRT\right)+\frac{D\pi r^2}{L}\left({}^{i}H_o-{}^{i}H_2\right)-km\left({}^{i}H_2-{}^{i}H_{eq}\right) \quad (1)$$

When the first term is negative, gas flows out of the capsule, and the flowing gas has the same composition as the gas within the capsule:

$$V\frac{d^{i}H_2}{dt}=\frac{\pi r^4}{8\mu L}\frac{{}^{i}H_2}{n_o}\left(n_oRT_o-nRT\right)+\frac{D\pi r^2}{L}\left({}^{i}H_o-{}^{i}H_2\right)-km\left({}^{i}H_2-{}^{i}H_{eq}\right) \quad (2)$$

The viscosity (Ref. [4]) and diffusion (Ref. [5]) coefficients were taken as an average of literature values weighted by ${}^{i}H_o$, and incorporated the temperature dependence of viscosity (Ref. [6]) and pressure dependence of diffusion coefficient (Ref. 5) from the literature. Transport of each solid-phase hydride species ${}^{i}H_s$ is given by

$$m\frac{d^{i}H_s}{dt} = 2km\left({}^{i}H_2 - {}^{i}H_{eq}\right) \tag{3}$$

where the factor of two accounts for dissociation of the diatomic gas molecules. The main case of interest in this work is where transport between solid and gas is fast, and the solid-gas system is near equilibrium. The value of *k* in this work was chosen to be large enough that model predictions are insensitive to *k*, indicating that the solid-gas system is near equilibrium, but small enough to ensure convergence during simulation. In effect, this makes gas transport through the orifice the rate-limiting step in an overall absorption or desorption process. Use of a small *k* value results in peak broadening that can obscure some of the results described in this work.

Values of ${}^{i}H_{eq}$ were obtained by literature procedures that consider that the chemical potentials between the gas and solid phase are equal under equilibrium conditions.[1,7,8] The parameters in the solid-gas equilibrium model are described in Table 2.

Table 2. Parameters in solid-gas equilibrium model.

H_s	Sum over *i* of ${}^{i}H_s$
P_{ij}	Partial pressure of diatomic gas species ${}^{i}H_s{}^{j}H_s$ (Pa)
μ_i^0	Standard-state chemical potential of solid hydride species ${}^{i}H_s$ (mol/m^3)
μ_{ij}^0	Standard-state chemical potential of diatomic gas species ${}^{i}H_s{}^{j}H_s$ (mol/m^3)
μ^{ex}	Excess chemical potential (a function of H_s) (mol/m^3)

The partial pressures of the diatomic gas species (including the mixed isotopologues) are obtained from the chemical potentials by

$$RT\ln\left(P_{ij}/1\text{ atm}\right) = \left(\mu_i^0 + \mu_j^0 - \mu_{ij}^0\right) + RT\ln\left(\frac{{}^{i}H_s \cdot {}^{j}H_s}{1 - H_s}\right) + 2\mu^{ex} \tag{4}$$

where the standard-state chemical potentials depend only on temperature and species identity as described in Refs. 1 and 9. The second term captures the entropy of mixing in the solid. The excess chemical potential term captures nonideal chemical effects at high concentrations, depends only on *H*, and is described as a polynomial empirical fit in Refs. 1 and 10. Equation 4 does not account for the phase transition between the dilute (□) and concentrated (□) phases of palladium hydride, during which the gas pressure is constant over a wide temperature range. The transition pressures were empirically correlated to the minima in Equation 4 as described in Ref. 1, and the partial pressures constrained to be monotonic functions that have values lower than the transition pressure at low *H*, and higher than the transition pressure at high *H*. Absorption and desorption each have a different transition pressure due to the work required to rearrange metal atoms during the phase transition; the system departs from equilibrium when these processes are underway.

Because the mixed gas-phase isotopologues are not accounted for in the transport equations, their atoms are treated as rearranged into single-isotope diatomic species:

$$ {}^{i}H_{eq} = \frac{P_{ii}}{2RT} + \sum_{j} \frac{P_{ij}}{2RT} \tag{5} $$

Heat flow was computed as described in Ref. 1. The main components of the heat flow are the reaction enthalpies of absorption or desorption for each isotope (obtained from Refs. 1, 3, and 9), multiplied by $d^{i}H_s/dt$. To obtain an enthalpy for tritium absorption based on Ref. 3, which only reports a value for desorption, it was assumed that the hysteresis for tritium is about the same as the other isotopes. Additional components are included to account for the heat capacity of the sorbent, capsule, and incoming gas. The model equations were solved using the implementation of LSODE (Livermore Solver for Ordinary Differential Equations) in GNU Octave.[11]

Results

The solid-gas equilibrium model can be checked separately from the transport model by using it to predict the results of pressure-composition isotherm experiments, and comparing to previously published results. Figure 2 shows the predictions for each pure isotope at a variety of temperatures. The isotherms show the expected behavior where the transition region is between about 0 and 0.6 hydrogens per Pd atom (H/Pd) at lower temperatures, narrowing at higher temperatures, and reaching a critical point near 300 °C and several tens of atm (Ref. [12]). At 100 °C, the transition pressure ratio for deuterium:hydrogen is about 3.4; 1.7 for tritium:deuterium, and 5.8 for tritium:hydrogen, increasing at lower temperatures and decreasing at higher temperatures. These ratios are about the same as for previously reported experimental desorption curves at 90 °C (Ref. [13]). The absolute pressures also closely match, after accounting for the temperature dependence reported in Ref. 13. Other factors such as gas purity (Ref. 13) and the effect of sample form on the amount of hysteresis (Ref. 1) can introduce variation between published reports. Examples of pressure-composition isotherms for a $^{1}H_2$-$^{2}H_2$ mixture are discussed in Ref. 1.

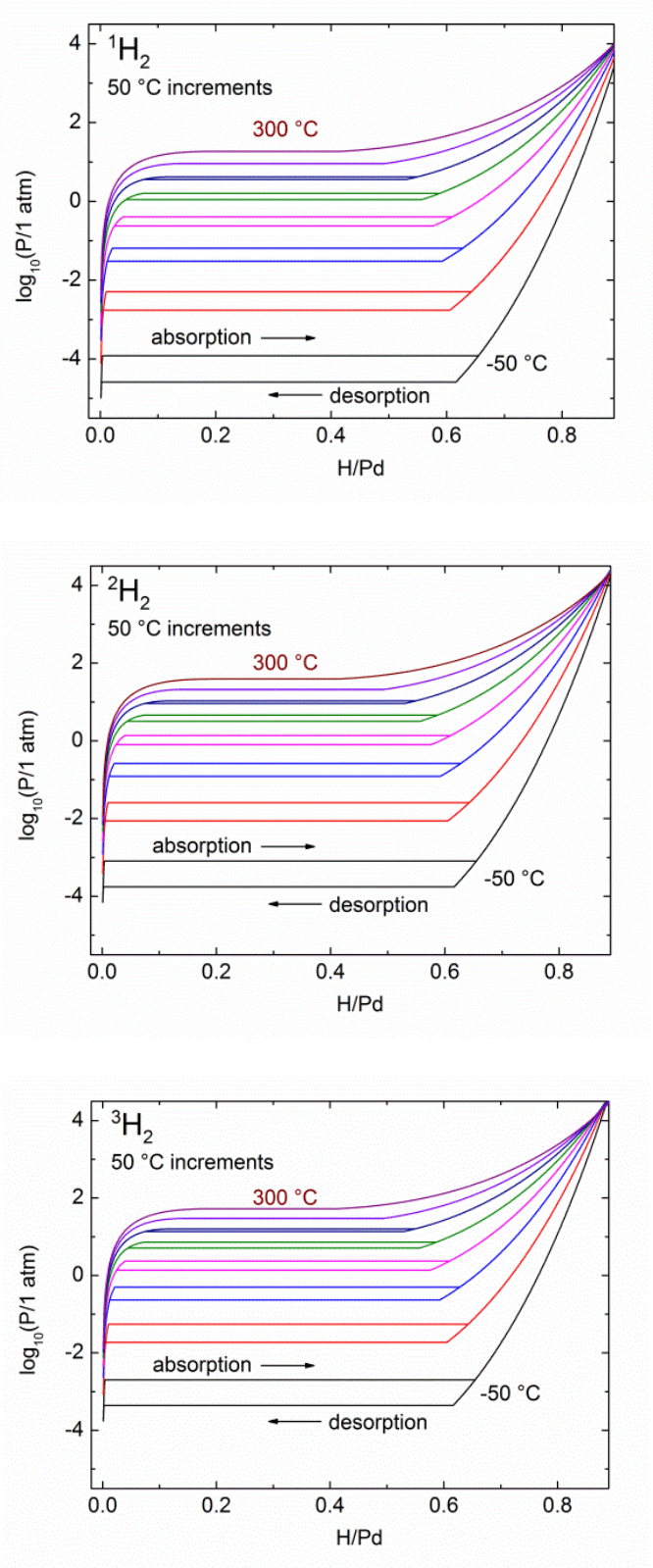

Fig. 2. Predicted pressure-composition isotherms for each pure hydrogen isotope at 50 °C intervals between -50 and 300 °C.

In a simulated experiment described in Ref. 1, a series of calorimetry scans is performed, where the total pressure is held constant, but the ratio of $^1H_2$ to $^2H_2$ is varied for different scans. This provides a succinct summary of many predictions of the transport model under these conditions. Figure 3 shows sets of simulated scans for both the $^1H_2$ - $^2H_2$ pair and the $^2H_2$ - $^3H_2$ pair. The pure gases show relatively sharp peaks. The mixtures show broader peaks at temperatures between those of the pure gases. The broadest peaks occur at temperatures about halfway between the pure-gas peaks. For absorption, the broadest peaks are near a 1:1 gas-phase mixture, whereas for desorption (as can be observed from other simulation variables) the broadest peaks are near a 1:1 solid-phase mixture. The breadth is caused mainly by the mass transport restriction of the orifice, which causes temporary variations in composition within the capsule, as described in Ref. 1.

Just as the pure-gas pressure ratio for $^3H_2$:$^2H_2$ is smaller than for $^2H_2$:$^1H_2$, the temperature difference between their calorimetry peaks is smaller, providing a narrower range in which to determine composition of gas mixtures using peak position. However, the peak widths are not as broad, so the ability to measure small differences in composition, or small fractions of one component in another, is not severely degraded.

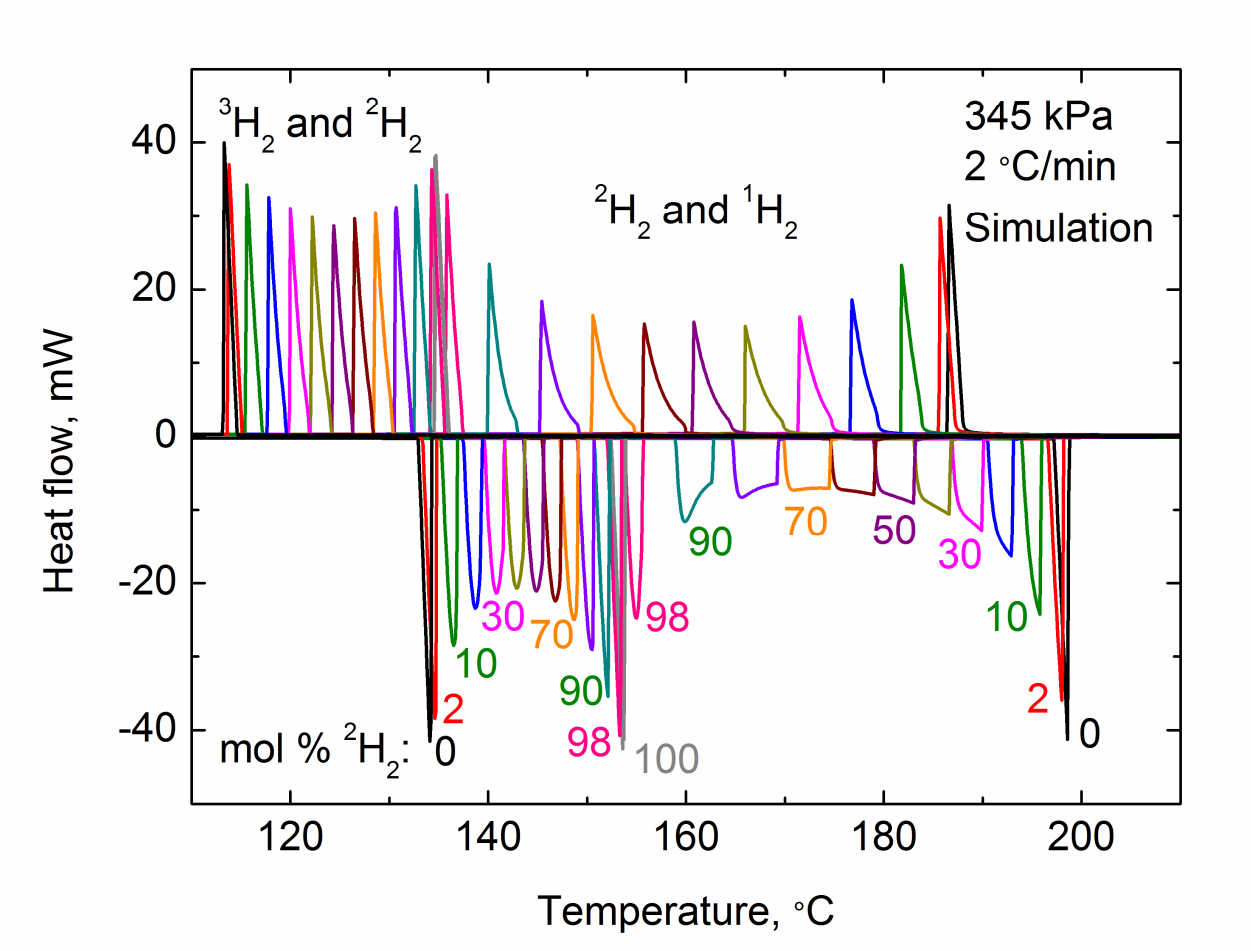

Fig. 3. Simulated calorimetry scans at a constant total pressure, but varying amounts of $^2H_2$ mixed with either $^1H_2$ or $^3H_2$ in the gas phase. Negative heat flows correspond to desorption, and positive heat flows correspond to absorption.

The case of $^1H_2$ - $^3H_2$ is shown in Figure 4. The pure-gas peaks are well separated on the temperature axis. As compared to the $^1H_2$ - $^2H_2$ case, peaks at intermediate compositions show greater broadening. Adding a small amount of $^1H_2$ to pure $^3H_2$ causes a larger peak shift, whereas adding a small amount of $^3H_2$ to pure $^1H_2$ has an effect similar to adding a small amount of $^2H_2$. The broadest peak in Figure 4 occurs at 20% $^1H_2$, as opposed to 30% for the $^1H_2$ - $^2H_2$ mixtures in Figure 3.

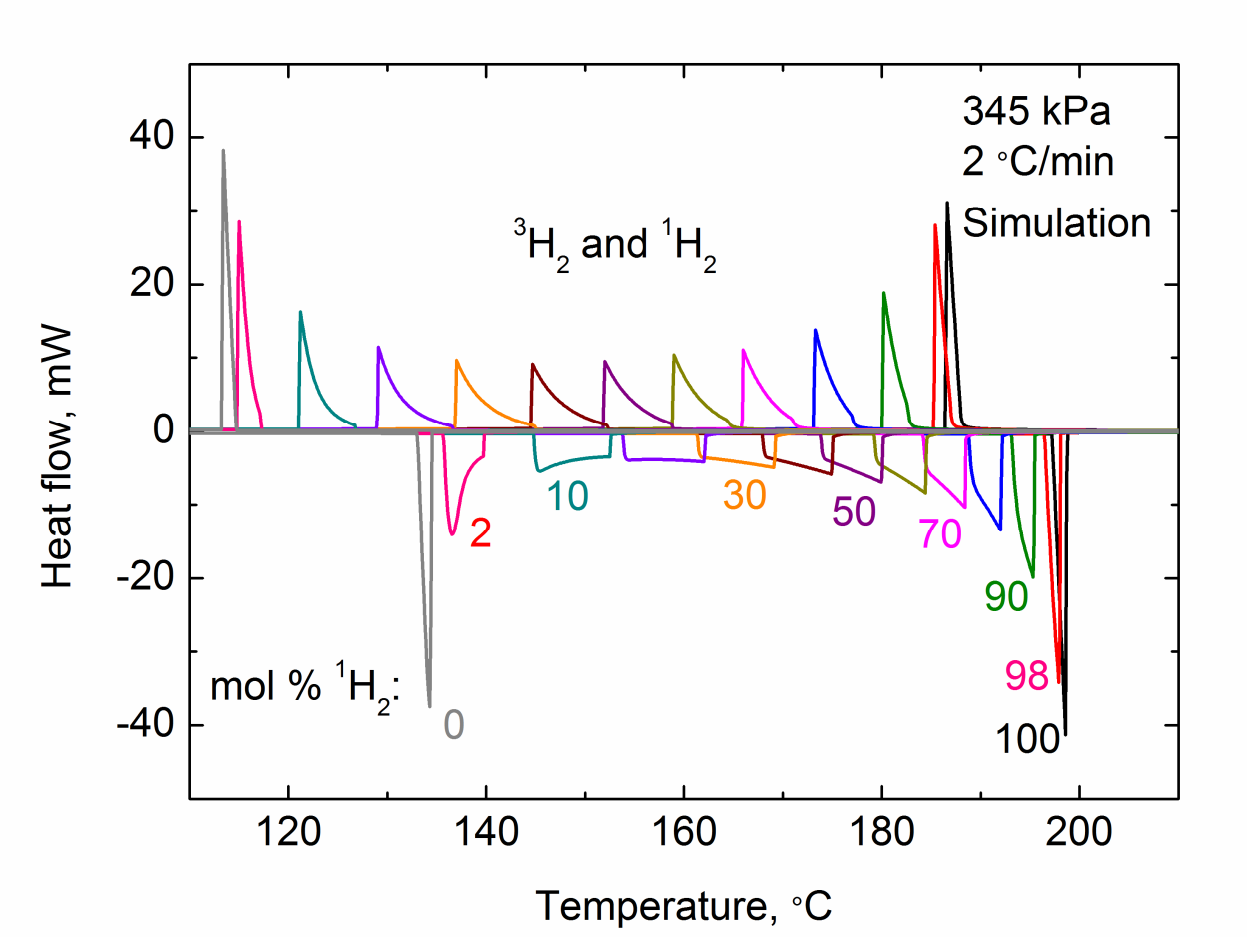

Fig. 4. Simulated calorimetry scans at a constant total pressure, but varying amounts of $^1H_2$ mixed with $^3H_2$ in the gas phase. Negative heat flows correspond to desorption, and positive heat flows correspond to absorption.

The previous results suggest that if a gas mixture contains only two known hydrogen isotopes, and the total pressure is known, the mole fractions of each isotope could be determined from a calorimetry experiment to within 2% of the total mixture. If the identity of the isotopes is not known, there is usually more than one pair of isotopes that could result in a measured peak position, but it

should still be possible to identify the pair based on peak shape, as long as there is a significant amount of each isotope (at least 10%).

In fact, the peak shape may also allow identification of ternary mixtures in some cases. Figure 5 shows an example where the relative amounts of a $^{1}H_2$ - $^{3}H_2$ mixture (of a fixed ratio) and $^{2}H_2$, each of which yield peak onsets at approximately the same temperature, are varied. The $^{1}H_2$ - $^{3}H_2$ mixture alone produces broad peaks, whereas pure $^{2}H_2$ produces narrow peaks, and intermediate compositions result in a gradual transition from one peak shape to the other. With further elaboration, it may be possible to identify a range of ternary compositions that yield unique, measurable combinations of peak position and shape that would allow their determination from unknown mixtures by calorimetry.

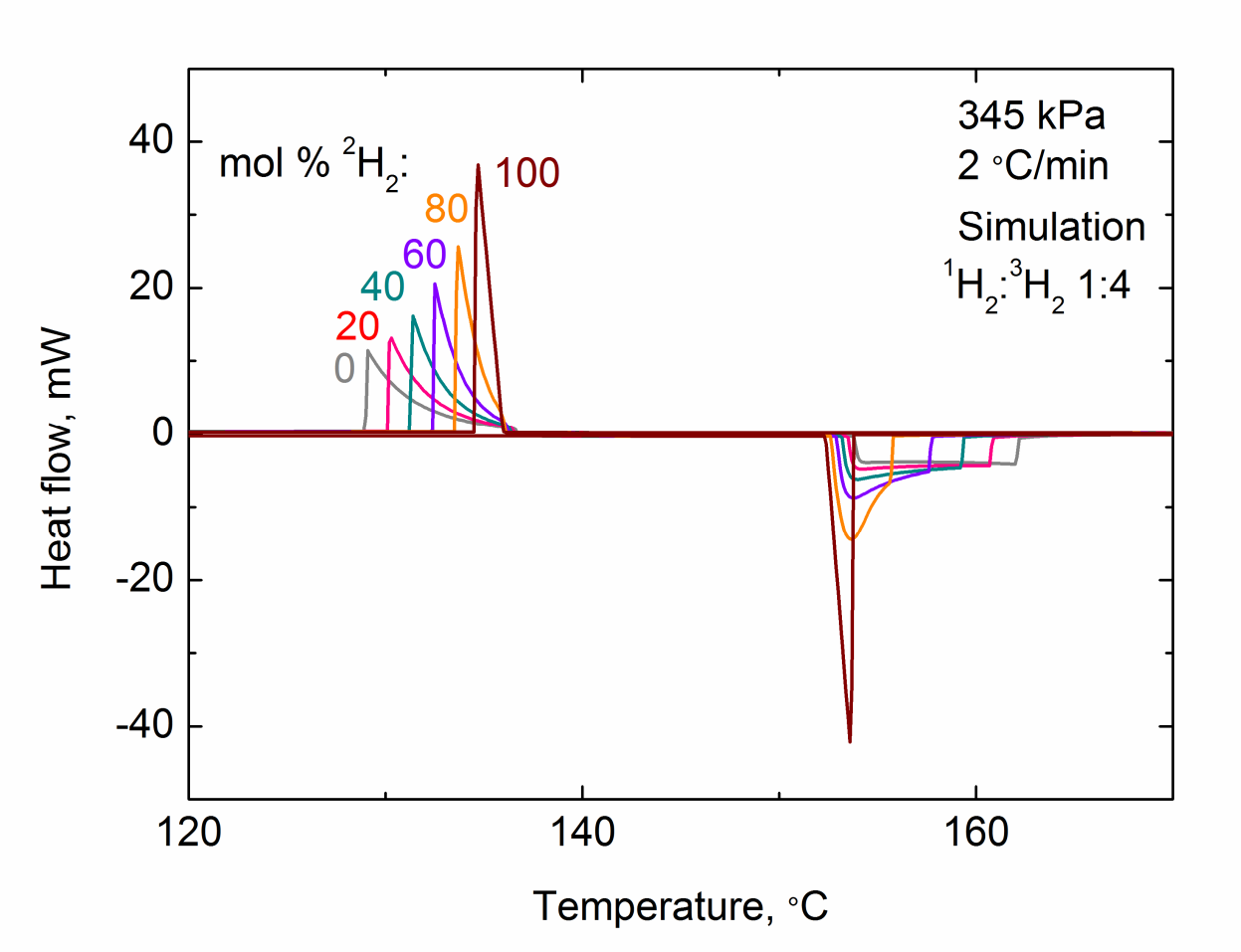

Fig. 5. Simulation of calorimetry scans on a series of gas mixtures starting with a 1:4 mixture of $^1H_2$:$^3H_2$, then adding a dose of $^2H_2$, and venting to maintain constant pressure between each scan.

Conclusion

The calorimetry model described in Ref. 1 has been extended to account for tritium. The model predicts results for $^1H_2$ - $^3H_2$ and $^2H_2$ - $^3H_2$ mixtures that are qualitatively similar to the prior predictions for $^1H_2$ - $^2H_2$ mixtures, but quantitatively unique enough in most cases to allow the isotopic pair of a binary mixture to be identified. The simulations suggest that it may be possible to uniquely quantify some compositions containing all three hydrogen isotopes. Detection limits of small quantities of tritium in another isotope, or small quantities of another isotope in tritium, are close to those described in Ref. 1 for $^1H_2$ and $^2H_2$. As described in Ref. 1, if helium were also present, the ability to identify and quantify the hydrogen components of a mixture would be compromised to a degree dependent on the helium mole fraction, because the helium imposes peak broadening that could obscure the peak shapes of the hydrogen isotope mixtures. The model presented here does not make detailed consideration of all effects that might limit response time and peak resolution, such as the heat capacity of the heating and sensing elements, slow equilibration between the gas and solid, or noise in the system. Therefore, calorimetry offers the ability to provide useful information about the composition of a gas mixture,

although there are some regions of pressure, composition, and temperature space that provide more information than others, or that provide information more quickly. This can be compared to the challenge in mass spectrometry of distinguishing $^{2}H_{2}$, $^{1}H^{3}H$, and ^{4}He; each technique has its advantages and limitations. It can be expected that the combination of calorimetry and mass spectrometry would provide a more complete description of the composition of these light gas mixtures, and allow for a reduced dependence on mass spectrometry alone. This could lead to improved system knowledge and safety, as well as reduced costs, in processes that handle tritium.

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