

# ARCHIVAL AND THEORETICAL CONSIDERATIONS FOR ISOTOPIC DEPENDENCE IN THE $e$ -H<sub>2</sub> FIXED POINTS

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## ABSTRACT

The equilibrium hydrogen ( $e$ -H<sub>2</sub>) fixed points of the International Temperature Scale of 1990 (ITS-90) are now recognized as being significantly influenced by the isotopic composition of the source gas. The text of the ITS-90 specifies only that the “natural isotopic composition” is to be used.[1] The supplementary information[2] goes further to state that the “normal isotopic composition of hydrogen” is 150  $\mu\text{mol } ^2\text{H}$  per mole of  $^1\text{H}$ . However, hydrogen isotope fractionation is known to occur by a variety of mechanisms both in the natural terrestrial environment and in the synthesis of commercial gas leading to wide variations in the isotopic content. Unfortunately, there is presently no internationally accepted value for the shift of the hydrogen fixed-point temperatures with respect to variations in the  $^2\text{H}$  concentration. In fact, there were very few historical hydrogen fixed-point realizations forming the basis of the defined temperature values in the IPTS-68 and the ITS-90 which were performed using hydrogen of any known isotopic composition. It is also unlikely that any of those gas samples were of “normal” isotopic composition.

We examine these issues for the case of the  $e$ -H<sub>2</sub> triple point (TP), and the two vapor pressure (VP) points defined near 33 kPa and 101 kPa. The archival experimental data allows predictions to be made for the shift in the TP temperature based on extrapolations of observations at large concentrations of  $^2\text{H}$ . Similarly, archival hydrogen vapor pressure measurements of pure  $^2\text{H}^1\text{H}$  allow calculation of the dependence on  $^2\text{H}$  concentration in the dilute limit for ideal solutions. These predictions alone, however, are insufficient to establish a consensus prescription for making corrections for isotopic variations in hydrogen gas samples. New experimental work in this area will be required to resolve these issues and remove the associated ambiguities from the ITS, which probably exceed 0.5 mK.

## 1. INTRODUCTION

The phase equilibria of spin-equilibrated molecular hydrogen ( $e$ -H<sub>2</sub>) from 13.8 K to approximately 20.3 K have been used to define the International Temperature Scale (ITS) since the advent of the IPTS-68.[3] Prior to that time, the fixed-points of  $e$ -H<sub>2</sub> had been determined on the four separate low temperature thermodynamic scales[4] used to derive the IPTS-68 below 90 K.[5] While these low temperature scales disagreed with each other in the hydrogen fixed-point range by as much as 58 mK, they were all very reproducible in practice and the discrepancies in the published fixed-point temperatures were generally attributed to scale differences rather than anything pertaining to the fixed-point realizations.

The hydrogen samples which were used in most, if not all, of the early (1930s to 1950s) vapor pressure and triple point determinations were produced through the electrolysis of water.[6] Starting in the 1960's, bulk hydrogen derived via methods other than electrolysis became commercially available.[7] While it is now known that the method of hydrogen synthesis significantly affects its isotopic composition, this variation had no practical impact on any fixed-point measurements being made in this early time period given the limited accuracy of the instrumentation. The first international comparison of Sealed Triple Point Cells (STPCs),[8] however, was carried out with sufficient resolution for the dispersion in the results for the  $e$ -H<sub>2</sub> TP to be affected by isotopic variations that probably existed amongst the different hydrogen samples included in the study.

Any sample containing hydrogen will contain both  $^1\text{H}$  and  $^2\text{H}$  (*i.e.* deuterium, or ‘D’) isotopes. The relative natural abundance can be highly variable due to the strong mass fractionation effects which accompany any chemical reaction or phase change. The isotope ratio,  $R_D \equiv [\text{D}]/[{}^1\text{H}]$ , of molecular hydrogen found in the terrestrial environment varies between approximately  $25 \mu\text{mol/mol}$  and  $184 \mu\text{mol/mol}$ . [9] The variations in commercial  $\text{H}_2$  tank gas, which similarly depend on the method of synthesis, are slightly less than this range. [10] This is in contrast to the common handbook value of  $150 \mu\text{mol/mol}$  which is in fact relevant only to the hydrogen found in fresh continental surface water.

The isotope ratio  $R_D(x)$  for a sample ‘ $x$ ’ of some form of hydrogen, is normally measured with respect to an isotope standard ‘ $s$ ’ having a known ratio  $R_D(s)$  and reported as a dimensionless relative deviation given by

$$\delta D_{x,s} = \left( \frac{R_D(x)}{R_D(s)} - 1 \right) . \quad (1)$$

For all forms of hydrogen, the definitive isotopic reference material is Standard Mean Ocean Water (SMOW) [11] or its practical equivalent, Vienna SMOW (VSMOW). [12] Another important isotopic reference material is Standard Light Antarctic Precipitation (SLAP). The absolute isotopic ratios of these standard reference waters have been determined [13] to be  $R_D = 156 \mu\text{mol/mol}$  and  $89 \mu\text{mol/mol}$  respectively, so that  $\delta D_{\text{SLAP,VSMOW}} = -428 \times 10^{-3}$ . In practice, the standard waters are chemically reduced using metallic Zn or U to form an  $\text{H}_2$  reference gas containing hydrogen deuteride (HD) with the same atomic proportion of deuterium as that of the water. [14] The ratio of signals at 3 u to 2 u in the reference and sample gases are then compared by mass spectrometry to derive the  $\delta D_{x,\text{VSMOW}}$  value.

All commercially prepared hydrogen is derived from reactions on hydrogen-bearing compounds such as methane, heavy petroleum hydrocarbons, or water. Temperature is the single most important variable for determining the extent of hydrogen mass fractionation which takes place in these reactions. The isotope separation temperature dependence [15] is usually exponential in  $T^{-1}$  or  $T^{-2}$ . A common gas production process is steam reforming of natural gas which involves the conversion of methane or other light alkanes in a two step process at temperatures near  $850 \text{ }^\circ\text{C}$ . The high temperature eliminates any significant mass fractionation in the process so that the hydrogen product gas (~50 % steam-derived) has  $R_D$  values typically from  $(120 \text{ to } 135) \mu\text{mol/mol}$ . In contrast, the partial oxidation process employed in some oil refineries appears to involve a low temperature step in the process of converting petroleum residuum by the addition of oxidants in the form of steam and oxygen. [16] The  $\text{H}_2$  gas produced via this process is typically very depleted in deuterium, usually ranging in  $R_D$  from  $(30 \text{ to } 60) \mu\text{mol/mol}$ . Hydrogen derived from water electrolysis appears to have a wide range of deuterium depletion due to variations in the process temperature, current density, and cell potential. If catalytic exchange is employed, the process will yield the equilibrium value of  $\delta D \approx -750 \times 10^{-3}$  at  $293 \text{ K}$  [17] for the gas relative to the water feed-stock.

## 2. ARCHIVAL DATA ON FIXED-POINTS OF HYDROGEN ISOTOPES

There is a relatively small amount of data available on the phase equilibria of isotopic mixtures of hydrogen. From what has been determined experimentally, it appears that the binary mixtures of  $\text{H}_2$  and HD form nearly ideal solutions with observed deviations in vapor pressure from ideality being no greater than 4 %. [18] The 1948 compilation of Wooley, Scott, and Brickwedde [19] (WSB) included all of the  $p$ - $T$  phase equilibria data for  $\text{H}_2$ , HD, and  $\text{D}_2$  in several ortho/para ( $o$ - $\text{H}_2/p$ - $\text{H}_2$ ) variations between  $10 \text{ K}$  and  $23.57 \text{ K}$  from previous measurements performed at the National Bureau of Standards (NBS). Most of these vapor pressure measurements were later repeated by Hoge and Arnold [20] (H&A) including some condensation point measurements on isotopic mixtures. The vapor

pressures in the  $n\text{-H}_2\text{+HD}$  binary system were also investigated by Newman and Jackson[18] (N&J), whose pure component results agreed with the earlier studies to within 10 mK for  $T < 20.5$  K.

Barber and Horsford[21](B&H) published a summary of these and other earlier results in 1963 for the  $e\text{-H}_2$  and  $n\text{-H}_2$  fixed point realizations only, together with measurements of those same species as performed at the NPL on the NPL-61 temperature scale. The B&H  $\text{H}_2$  vapor pressures were significantly higher than those of both WSB and H&A, which at a constant pressure of 101 kPa translates to between 2 mK and 7 mK lower temperatures in the B&H determination. These nominally pure  $\text{H}_2$  samples were also mixtures, but only in the dilute HD limit ( $R_{\text{HD}} \approx 2R_{\text{D}} \ll 1$ ). Compton[22] repeated some of the  $e\text{-H}_2$  vapor pressure and TP measurements in 1970 and for the first time attempted an in-situ measurement of the HD content of the vapor via mass spectrometry. His measured  $R_{\text{HD}}$  of 260  $\mu\text{mol/mol}$  was made directly, however, without the benefit of a known isotopic reference standard. Despite a significant effort by Compton to account for all possible impurities, the observed liquid volume fraction dependence of the vapor pressures was inconsistent with the measured  $R_{\text{HD}}$ .

Bereznyak, *et. al.*[23] (BBKL) studied the full range of all three isotopic binary solutions of para-hydrogen ( $p\text{-H}_2$ ), HD, and  $o\text{-D}_2$ . The data are presented graphically and their HD TP appears to be in agreement with both WSB and H&A ( $\approx 16.6$  K) to within the resolution of the graph. The slope of the liquidus line for the HD +  $p\text{-H}_2$  solutions appears nearly constant at 2.8 mK/(mmol HD/mol  $\text{H}_2$ ) throughout the full range.

In later archival works on the  $e\text{-H}_2$  fixed points, isotopic composition was generally not treated. In many cases where electrolytic hydrogen was used, we may assume that the samples were relatively depleted of deuterium. In no work that we are aware of, [8, 21-25] however, were any mass measurements related to a known isotope reference material. Nor can it be inferred that any of the ‘pure’ component hydrogen used was of a SMOW composition or otherwise close to the value of 150  $\mu\text{mol/mol}$  for  $R_{\text{D}}$  as quoted in the ITS-90 Supplement.[2]

### 3. PHASE EQUILIBRIA IN HYDROGEN ISOTOPE MIXTURES

Given the isotopic mixture  $R_{\text{HD}}\text{HD} + e\text{-H}_2$  and the assumptions of an ideal binary solution[20] of  $x_{\text{HD}}$  mole fraction of HD in the liquid phase, with partial pressures  $p_{\text{HD}}$  and  $p_{\text{H}_2}$ , the equilibrium vapor pressure  $p_v$  of the solution at the evaporation point (vanishing vapor fraction) is given by

$$p_v = x_{\text{HD}} p_{\text{HD}} + (1 - x_{\text{HD}}) p_{\text{H}_2} \quad . \quad (2a)$$

Similarly for  $y_{\text{HD}}$  mole fraction of HD in the vapor phase, the equilibrium vapor pressure  $p_c$  of the solution at the condensation point (vanishing liquid fraction) is given by

$$\frac{1}{p_c} = \frac{y_{\text{HD}}}{p_{\text{HD}}} + \frac{(1 - y_{\text{HD}})}{p_{\text{H}_2}} \quad . \quad (2b)$$

Recognizing the fact that it is possible to unequivocally identify  $R_{\text{HD}} = x_{\text{HD}}$  and  $R_{\text{HD}} = y_{\text{HD}}$  in these two limits only, the resulting condensation and evaporation lines for the mixtures can be calculated. In comparing vapor pressure realizations of differing isotopic composition, it is the effect on the isobars which is most important. Figure 1 shows the evaporation and condensation isobars near 33 kPa and 101 kPa calculated in the dilute HD solution limit. In practice, vapor pressure fixed-point realizations are performed at liquid/vapor ratios closer to the evaporation limit rather than the condensation limit, so the slopes of the evaporation isobars may be more relevant. These slopes are approximately 1.45 mK/(mmol HD/mol  $\text{H}_2$ ) and 1.25 mK/(mmol HD/mol  $\text{H}_2$ ) at 101 kPa and 33 kPa respectively. For isotopic variations typically found in commercial tank  $\text{H}_2$  gas, this translates to lower limits in the temperature elevations of the 101 kPa point from 0.084 mK to 0.40 mK with respect to isotopically

pure (light)  $e\text{-}^1\text{H}_2$  (i.e.  $\delta\text{D} = -1000 \times 10^{-3}$ ). The range between the condensation point and the evaporation point would be as large as 0.32 mK in the case of the heaviest of the tank gases. Similarly, lower limits on the elevations of the vapor pressure point near 33 kPa will vary between 0.073 mK to 0.34 mK with a maximum evaporation to condensation range of 0.40 mK for the heaviest tank gas.

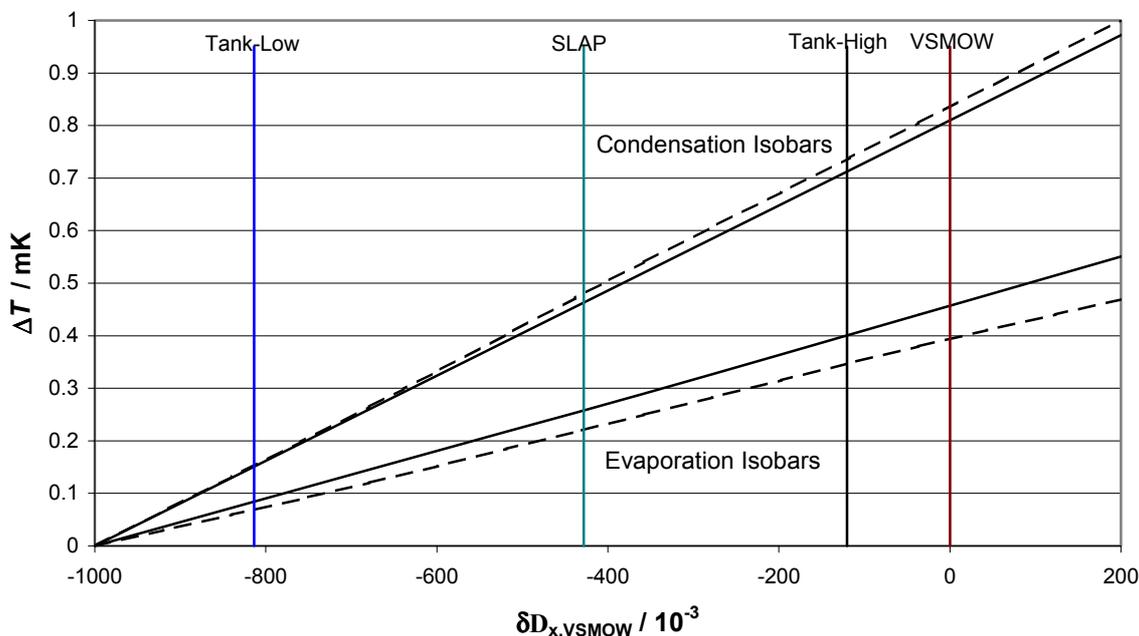


Figure 1. The calculated elevation in the 33 kPa (dashed lines) and 101 kPa (solid lines) isobars for condensation and evaporation in the dilute limit of an ideal  $e\text{-H}_2 + \text{HD}$  solution. The compositions of SLAP and VSMOW are shown along with the range of reported tank gas compositions as scale markers (vertical lines).

For the  $e\text{-H}_2$  TP, assuming the nominal BBKL value of 2.8 mK/(mmol HD/mol  $\text{H}_2$ ), the liquidus values that would be expected from tank  $\text{H}_2$  gas are from 0.16 mK to 0.77 mK elevated with respect to isotopically pure  $e\text{-}^1\text{H}_2$ . Further data[26] will be available to determine the slope of the liquidus line more accurately in the dilute HD limit. Similarly, a program at the NRC will establish more accurate values for the condensation and evaporation lines for these dilute HD +  $e\text{-H}_2$  mixtures.

#### 4. POSSIBLE RE-DEFINITIONS OF THE $e\text{-H}_2$ FIXED POINTS

Considering that the modern realizations of the hydrogen-based ITS-90 fixed points, especially the triple point,[27] aim at an uncertainty lower than 0.1 mK, the problem of isotopic composition caused by the inherent ambiguity of the scale definitions is predominant. There are many possible ways in which the  $e\text{-H}_2$  fixed points of the ITS-90 could be re-defined in order to remove this ambiguity. These would in general fall into one of two categories: A.) definitions specifying a fixed isotopic composition to be used for all the realizations and requiring the use of certified gas of that composition; or B) definitions specifying an ideal composition to which all variable composition gas samples would be corrected by their measured mass values on the basis of a defined  $T$  vs HD content function. The fixed or ideal isotopic composition could be: isotopically pure light hydrogen ( $^1\text{H}_2$ ), VSMOW composition hydrogen; SLAP composition hydrogen; or any other nominal composition defined by a recognized international authority.

All of these alternatives would require measurement and or certification of the deuterium content of the sample gas. Of these choices, both pure light and VSMOW hydrogen have the disadvantage that such compositions are beyond the range readily available and would require special preparations to

produce samples. In general, the uncertainty attributed to the applied correction will increase for gases in proportion to their difference in composition from any isotopically defined gas. In this context, a SLAP definition for the  $e\text{-H}_2$  fixed-points under option B would be a reasonable compromise as it is roughly midway in the range of typical  $\text{H}_2$  tank gas isotopic compositions.

For vapor pressure realizations of most  $e\text{-H}_2$  samples, it may also be necessary to specify certain limits of the liquid to vapor ratio in order to remove the ambiguity between the condensation and evaporation points. Liquid volume fraction checks of the type performed by B&H and Compton would establish a trend which could be extrapolated to either of the two vapor pressure limits as required. Hence, while the TP would only require one correction, the vapor pressure points could require two.

Figure 2 illustrates the uncertainty variations that would arise as a result of either a VSMOW-defined or a SLAP-defined  $e\text{-H}_2$  TP. The assumptions made are: 2.8 mK/(mmol HD/mol  $\text{H}_2$ ) is the nominal correction factor to be applied; that all deuterium content measurements are on the same VSMOW relative scale; and that two uncertainty components predominate. These components are: 1.) the correction factor itself, which is assumed to be established (in the future) with a standard uncertainty of 7.7 %; and 2.) the uncertainty of the  $\delta\text{D}$  measurements for a sample, which is simply proportional to the mass difference from VSMOW according to the statistical results of the study by Brand and Coplen.[28] If necessary, the sample measurement uncertainty in  $\delta\text{D}$  can be further reduced by use of a normalized scale, VSMOW-SLAP,[29] when using a second (SLAP-derived) reference gas.

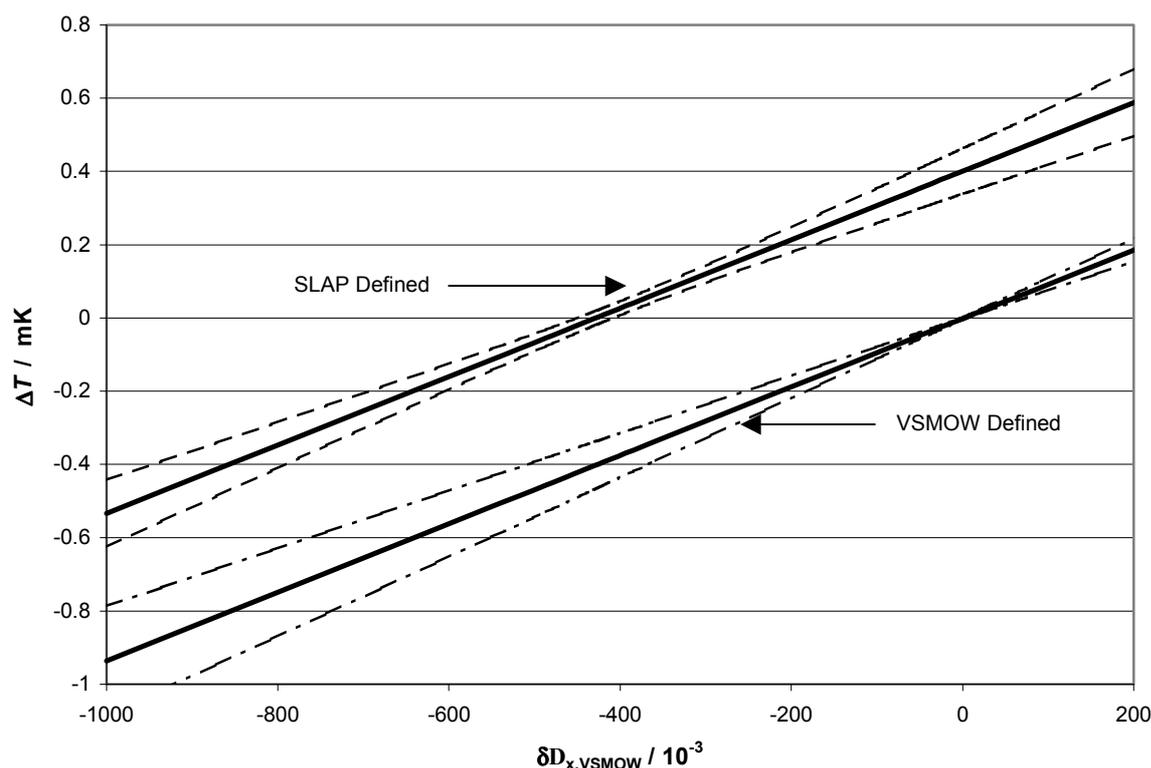


Figure 2. Theoretical corrections (solid lines) and expanded ( $k=2$ ) uncertainties (dashed lines) for a SLAP-defined and a VSMOW-defined  $e\text{-H}_2$  triple point as a function of a sample's  $\delta\text{D}$  value with respect to VSMOW.

Despite the improvement over the present situation that an amended definition could provide, it is possible that the isotopic correction would still be the largest contribution to the uncertainty budget for modern realization of these fixed points. The sample composition uncertainty should be no greater than 2 % in  $\delta\text{D}_{x,\text{VSMOW}}$ . This level of uncertainty is very difficult to achieve as an absolute isotope ratio

certification of gases, particularly for hydrogen.[30] Using either a relative VSMOW or VSMOW-SLAP mass scale, however, it is possible to achieve 0.2 % uncertainty in  $\delta D_{x,VSMOW}$ . [28] This should be a practical method to ensure sufficiently accurate and traceable results at the international level.

The impact of isotopic variations in the hydrogen fixed-points appears to be sufficiently large in practice that an amendment to the ITS-90 is justifiable to remove the current ambiguities in those definitions. The presently achievable accuracy in thermometry requires the specification of fixed-point substances with parameters less generic than terms such as “pure” or “natural composition”. The data to support any proposed correction prescriptions should be generated at various National Metrology Institutes in the near term. All *e*-H<sub>2</sub> fixed-point realizations performed in the interim should include a mass ratio measurement with respect to a VSMOW and or SLAP equivalent reference gas.

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