

Specific Heats of Delta-Phase Zr-H and Zr-D†

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The specific heats of fcc $\text{ZrH}_{1.58}$ and $\text{ZrD}_{1.58}$ have been measured in the temperature interval 30–500°C. The data are interpreted in terms of a harmonic oscillator model for the hydrogen and deuterium specific heat contributions. This model is in accord with recent inelastic neutron scattering studies and predicts an isotopic depression of the deuteride Einstein temperature by a factor of $1/\sqrt{2}$ relative to the hydride value. Over the interval 30–200°C, the data and model are quantitatively consistent. At higher temperatures, the deuteride specific heat is somewhat smaller than anticipated. Quantities of noncubic γ -phase material are known to be present in the samples used, particularly in the deuteride, and this is thought to be a likely cause for the deviations. The hydride Einstein temperature calculated from the difference between deuteride and hydride specific heats at 150°C is $1500 \pm 300^\circ\text{K}$, as compared with the inelastic neutron scattering value of $1500 \pm 60^\circ\text{K}$.

I. INTRODUCTION

HYDROGEN and deuterium readily react with zirconium at elevated temperatures until the limiting compositions ZrH_2 and ZrD_2 are approached. In the resulting material, the zirconium completely occupies the sites of a lattice which has its symmetry and scale determined by temperature and gas concentration, while the gaseous component exists as a mono-nuclear species within the interstices of the resulting structure. For example, ZrD_2 is known to have all the tetrahedral interstices of the fct zirconium structure occupied,¹ so that the deuterium also forms a completed structure. At lower concentrations, however, a defect structure must result, since there are more interstices of the proper type than there are gas atoms. For the present, it will not be necessary to ponder the fate of the electrons originally associated with the gas atoms. It will suffice to assume that for a given gas concentration, the gas atom nuclei are bound to the zirconium matrix by forces which are the same for hydride and deuteride, an assumption supported by their great similarity with regard to many physical properties such as crystal structure, electronic transport properties, etc.

Recent inelastic neutron scattering (INS) studies^{2–4} indicate that the lattice vibration spectrum of $\text{ZrH}_{1.5}$ closely resembles that produced by a linear diatomic lattice in the limit of very large mass ratios. Specifically, an acoustical branch with an energy cutoff corresponding to 230°K (0.02 eV) is observed in conjunction with a narrow optical branch having a mean energy corresponding to 1500°K (0.130 eV). Instrumental resolution and Doppler broadening account for very nearly all of the optical branch energy linewidth, and hence, these modes are associated with essentially a single energy (or frequency), independent of the wave propagation vec-

tor. On this basis, it appears reasonable to treat the hydrogen nuclei as independent and identical harmonic oscillators, and to predict that they will make an independent Einstein contribution to the specific heat at constant volume C_v . The thermal vibration contribution to C_v is accordingly separated into two additive parts: one due to the gas nuclei $c_v(\text{H})$, the other to the zirconium $c_v(\text{Zr})$. The zirconium sublattice will presumably make a typical Debye contribution ($\theta_D \approx 230^\circ\text{K}$) which will be very nearly saturated at the Dulong-Petit value above room temperature. Furthermore, in view of the large molar concentration and high characteristic temperature (1500°K) associated with the gas nuclei, it would appear that the optical modes should lend a strong unsaturated Einstein character to C_v above room temperature. The tenability of this conclusion should be capable of direct test by comparison of hydride and deuteride specific heats above room temperature, since the latter should suffer a predictable isotopic depression of its Einstein characteristic temperature relative to the hydride. Unfortunately, C_v values cannot be determined directly, nor is there available the thermodynamic data which would permit the conversion of constant pressure measurements C_p to constant volume. Although the change in lattice dynamics entailed by the substitution of deuterium for hydrogen undoubtedly affects the density, thermal expansion, and isothermal compressibility somewhat, it is not unreasonable to suppose that the over-all change in $(C_p - C_v)$ will be fairly small. In this spirit, it will be assumed that $(C_p - C_v)$ is not subject to an important isotope effect, but instead is common to both hydride and deuteride. Consequently, direct intercomparison of hydride and deuteride C_p data can be used to investigate the consistency between model and experiment. As will be seen, a reasonably good degree of consistency is indeed observed.

II. THEORY

The characteristic frequency ν_E , Einstein characteristic temperature T_E , force constant K , and reduced mass m of a quantized, three-dimensional harmonic

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¹ S. S. Sidhu, LeRoy Heaton, and M. H. Mueller, J. Appl. Phys. **30**, 1332 (1959).

² I. Pelah, C. M. Eisenhauer, D. J. Hughes, and H. Palevsky, Phys. Rev. **108**, 1091 (1957).

³ A. Andresen, A. W. McReynolds, M. Nelkin, M. Rosenbluth, and W. Whittemore, Phys. Rev. **108**, 1092 (1957).

⁴ W. L. Whittemore and A. W. McReynolds, Phys. Rev. **113**, 806 (1959).

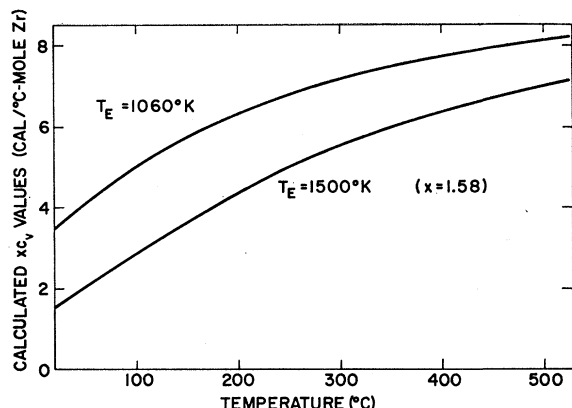


FIG. 1. Harmonic oscillator contributions calculated on the basis of 1.58 moles of oscillators. The Einstein temperatures 1060°K and 1500°K are appropriate for $\text{ZrD}_{1.58}$ and $\text{ZrH}_{1.58}$, respectively.

oscillator are related by

$$h\nu_E = kT_E = \hbar(K/m)^{1/2}, \quad (1)$$

and the specific heat of one mole of such oscillators is

$$c_v = 3R(\frac{1}{2}Y)^2 \sinh^{-2}(\frac{1}{2}Y), \quad (2)$$

with

$$Y = T_E/T, \quad (3)$$

where R is the universal gas constant. Due to the large relative mass of zirconium, only negligible errors are incurred by not using reduced masses for the oscillators. Also, since the force constant K is assumed to be determined by the electronic properties of the atoms involved, and hence to be the same for hydride and deuteride, Eq. (1) indicates that

$$T_E(\text{H}) = \sqrt{2}T_E(\text{D}), \quad (4)$$

i.e., the deuteride characteristic temperature is depressed by a factor $1/\sqrt{2}$ relative to that of the hydride for materials having the same gas-to-metal atom ratio x . Figure 1 presents plots of Eq. (2) for 1.58 moles of oscillators (or 1 mole zirconium in $\text{ZrH}_{1.58}$), the two temperatures used being consistent with the INS hydride value and Eq. (4). The INS Einstein temperature for $x=1.5$ is taken to apply also for $x=1.58$.⁵

Assuming that (1) there is one harmonic oscillator per gas atom nucleus, (2) every such oscillator makes an independent and identical Einstein contribution to C_v , and (3) the zirconium contribution to C_v (plus any other contributions not explicitly mentioned) and $(C_p - C_v)$

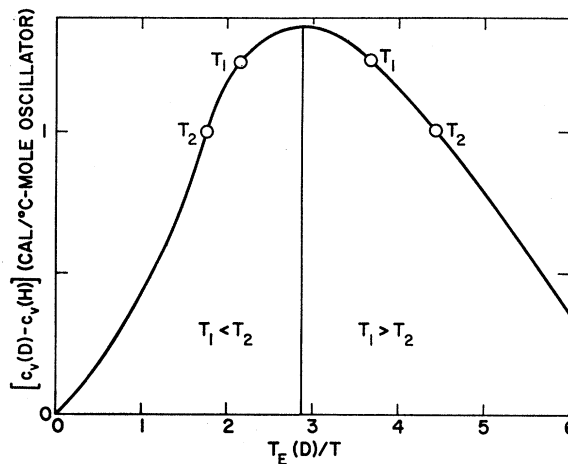


FIG. 2. Difference in harmonic oscillator specific heats (for isotopic mass ratio of two) vs ratio of Einstein temperature to actual temperature (°K). Two branches of solutions exist, due to the double valued nature of the function. The temperature T_1 is associated with the larger specific heat difference.

are the same for hydride and deuteride:

$$C_p(\text{ZrD}_x) - C_p(\text{ZrH}_x) = x[c_v(\text{D}) - c_v(\text{H})], \quad (5)$$

where the gas contributions c_v are given by Eq. (2). The third assumption embodies the spirit of the present approximation, as mentioned earlier. It is convenient to display the consistency between model and experiment in two equivalent ways, the first of which is based on

$$xc_v(\text{D}) = [C_p(\text{ZrD}_x) - C_p(\text{ZrH}_x)] \quad (\text{experimental})$$

$$+ xc_v(\text{H}) \quad (\text{calculated}) \quad (6a)$$

$$= xc_v(\text{D}) \quad (\text{calculated}), \quad (6b)$$

where the calculated xc_v values are the functions appearing in Fig. 1. Alternatively, Eqs. (2), (4), and (5) may be combined explicitly:

$$C_p(\text{ZrD}_x) - C_p(\text{ZrH}_x) = 3R(x)(\frac{1}{2}Y_D)^2 [\sinh^{-2}(\frac{1}{2}Y_D) - 2 \sinh^{-2}(Y_D/\sqrt{2})]. \quad (7)$$

Hence, deuteride (or hydride) Einstein temperatures can be obtained directly from the difference of experimental C_p values, again enabling comparison with INS results. At first, it may appear that Eq. (7), as plotted in Fig. 2, involves a certain degree of ambiguity, in that it is a double-valued function. This difficulty is removed, however, when $C_p(\text{ZrD}_x)$ and $C_p(\text{ZrH}_x)$ are known for at least two temperatures T_1 and T_2 , since only one or the other branch of solutions is appropriate, depending on whether $T_1 > T_2$ or $T_1 < T_2$, where T_1 is associated with the larger difference of specific heats.

III. SAMPLE MATERIALS

Both hydride and deuteride specimens were prepared from AEC reactor grade, extruded sponge zirconium

⁵ A. W. McReynolds, M. S. Nelkin, M. N. Rosenbluth, and W. L. Whittemore, *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy* (United Nations, Geneva, 1958), Vol. 16, p. 297. This study indicates that the Einstein temperature (INS) remains essentially constant over the range $\text{ZrH}_{1.2}$ – $\text{ZrH}_{1.9}$. (By implication, the hydrogen in the α , δ , ϵ , and γ phases must be associated with very nearly the same Einstein temperature.)

bar stock. A typical analysis for such material is available elsewhere.⁶ Bottled hydrogen and deuterium were first reacted with uranium, then re-evolved for sample manufacture. The hydrogen content of the deuterium was determined to be less than 1 at.% by direct mass-spectrographic analysis.

Annular slugs having the approximate dimensions, 1.25 in. o.d. \times 0.25 in. i.d. \times 0.50 in., were machined from zirconium. These were subsequently reacted with hydrogen or deuterium inside a quartz tube mounted vertically in a resistance furnace. Prior to reaction, the zirconium was outgassed at either 850°C (hydride) or 650°C (deuteride) until the pressure fell below 5×10^{-6} mm Hg. During initial reaction, the furnace temperatures remained constant at the aforementioned values. Hydride and deuteride slugs were produced in about 40 and 15 hr (per slug), respectively, roughly half of the time being used to cool the samples to room temperature. The difference in preparation time between hydride and deuteride was mainly due to the necessity of admitting deuterium much faster than hydrogen, to avoid stalling the reaction as the result of very slight surface contamination. In this respect, the systems Zr-H and Zr-D seem to differ drastically, more so than would be expected from the mere decreased mobility of deuterium owing to its larger mass. During the rapid initial reaction with deuterium, the zirconium undoubtedly rose significantly above 650°C.

Mass gain and reacted gas volume (STP) were used to determine the compositions of samples as manufactured. After calorimetry, their compositions were re-determined using standard vacuum fusion techniques, good agreement invariably being obtained with the pre-calorimetry value $x = 1.58 \pm 0.02$.

Originally, it was thought that the composition $x = 1.58$ would yield a single phase, i.e., the fcc δ phase. Metallographic and x-ray evidence, however, indicates that samples prepared by the above methods actually contain amounts of noncubic material, both before and after thermal cycling in the calorimeter. Although it is difficult to make an accurate estimate, metallographic studies indicate that as much as 10 vol. % of noncubic material may be present in the deuteride. The hydride contains substantially less, probably only 2 or 3%.

Examination by polarized light suggests the presence of three classifications of material. By far the bulk of every sample consists of an optically inactive component, i.e., one which has a cubic structure. This is undoubtedly the δ phase which also produces the basic fcc x-ray powder patterns observed. Within this matrix, the noncubic (optically active) material is deposited in two characteristic modes with respect to the δ -phase grain network. One occurs within the grains (intragranular) as an array of parallel bands, while the other is deposited as irregular masses along grain boundaries

(intergranular). Of the two, the intergranular material is far less abundant, perhaps by as much as a factor of five or more.

At worst, only a suggestion of irregularity occurred in the hydride x-ray pattern (fcc). For the deuteride, however, weak lines were observed corresponding to interplanar spacings of $d = 2.72$ Å and $d = 2.48$ Å. On the basis of comparison with 11 other hydride and deuteride samples ($1.5 \leq x \leq 1.9$), as well as with pure zirconium, it was concluded that these lines did not correspond to any known fct modification, nor to free zirconium. Subsequently, it has come to the author's attention that very recent studies⁷⁻⁹ indicate that as many as three phases (α , δ , and γ) seem to coexist over much of the composition range formerly reserved exclusively for the δ phase, both for Zr-H and Zr-D. [From earlier phase diagram work,¹⁰ and from conventional phase-rule considerations, it seems likely that both α (hcp) and γ (bct) phases are metastable at $x = 1.58$.] The γ phase has been reported to have its strongest lines at $d = 2.72$ Å and $d = 2.48$ Å.⁹ In accord with the experience of others,⁹ attempts to substantially reduce the amount of γ -phase material by annealing below the eutectoid temperature (550°C) have been unsuccessful.

To summarize the situation, it would appear that relatively minor amounts of noncubic material occur in the hydride, while the deuteride may contain as much as 10 vol. %, most of which probably exists as intragranular γ phase.

IV. EXPERIMENTAL METHODS

Special experimental complications are encountered in the calorimetry of hydrides and deuterides. These stem from the fact that gas is evolved as the temperature is increased. The problem is twofold: Evolution or absorption of relatively small amounts of gas can introduce sizeable errors into the heat capacity measurements, due to the large associated latent heat; and large integrated losses of gas will significantly change the composition of the sample. Encapsulating the sample in a gas-tight stainless steel can having very little void volume is the simplest solution for both. Void volumes of the order of 10 cm³ are permissible for the samples used (approx 200 g). It is also necessary to improve the effective thermal diffusivity of the sample so as to reduce thermal-lag effects. This is accomplished by introducing $\frac{1}{2}$ atm of helium into the sample can, and by increasing heat transfer area by utilizing multiple-slug sample geometry.

⁷ S. S. Sidhu, LeRoy Heaton, and M. H. Mueller, *Bull. Am. Phys. Soc.* **5**, 461 (1960).

⁸ S. S. Sidhu, Argonne National Laboratory (private communication).

⁹ R. L. Beck, Denver Research Institute (private communication). Also: U. S. Atomic Energy Commission Rept. LAR-10, 1960 (unpublished).

¹⁰ For a review see: G. G. Libowitz, *J. Nuclear Materials* **2**, 4 (1960).

⁶ R. W. Dayton, *Reactor Handbook* (Interscience Publishers, Inc., New York, 1960), Vol. III, p. 463.

A schematic sketch of the adiabatic shield calorimeter which was used is presented in Fig. 3. Fine wires support the sample can within the adiabatic shield. Both sample can and copper shield carry platinum resistance thermometers on their surfaces. An internal electrical sample heater makes use of a vacuum-tight ceramic-to-metal seal as an insulated lead, and a ribbon heater is wound on the outer surface of the shield. Surrounding the sample-shield assembly is a vacuum resistance furnace which has its temperature regulated by means of a commercial saturable reactor thermostat. The effective temperature difference between sample-can and shield surfaces is sensed by placement of the platinum thermometers in a dc bridge circuit. After amplification, the bridge unbalance signal drives a commercial recording controller which adjusts the shield power so as to restore balance. In addition to this function, the sample thermometer can be used simultaneously as a four-terminal resistance thermometer for the determination of absolute sample temperatures.

Heat capacities are measured as follows: After the calorimeter has achieved steady-state conditions for a given furnace temperature (and for a small, constant value of shield power), the bridge is balanced and thereafter permitted to control power to the shield. Under these conditions, the sample temperature drift is observed for an appropriate length of time. Electrical energy (dc) is then supplied to the sample heater at a well-known, nearly constant rate, and for a predetermined length of time. During this interval, referred to as the heating *pulse*, the sample temperature rises nearly linearly; afterwards, the new drift rate is observed. A typical temperature vs time plot is presented in Fig. 4. The effective change in sample temperature ΔT is obtained by extrapolating the prepulse and postpulse curves to the center of the heating interval as indicated in Fig. 4. For heating curves of the simple variety encountered, this method compensates for changes in effective drift rate which occur during the pulse. Among possible causes for such changes are temperature de-

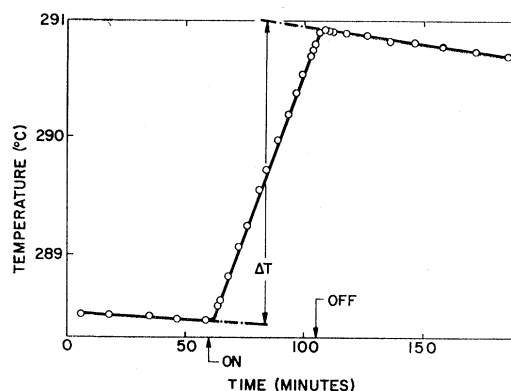


FIG. 4. Sample temperature vs time for a typical heat capacity determination. The time at which ΔT is evaluated corresponds to the center of the heating interval.

pendence of the bridge balance point, and thermal effects associated with certain types of phase reapportionment. After evaluation of the total heat ΔQ developed in the sample heater, the heat capacity of sample plus addendum is calculated from $\Delta Q/\Delta T$. Later, the sample is removed from the sample can, and the procedure repeated for the resealed sample can alone. Taking the difference yields the heat capacity of the sample. This procedure has the usual merit of compensating for systematic errors common to both sets of measurements.

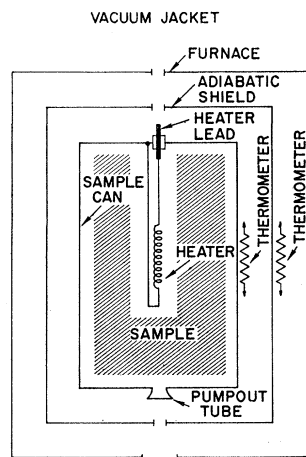
Prior to making hydride or deuteride measurements, the specific heat of very pure copper was determined several times at 300° and 500°C. All results were within $\pm 1\%$ of accepted values, corresponding to an uncertainty of ± 0.3 cal/°C in the heat capacity.

Several attempts were made to determine the room temperature compressibility of hydride and deuteride samples by measuring the elastic constants via the ultrasonic pulse-echo method. These were unsuccessful, presumably because of strong crystalline boundary scattering of sound waves. It should be possible to perform such measurements using the piezoelectric composite oscillator technique, since the wavelengths involved are much longer. Obtaining the compressibility is the major experimental problem in the direct comparison of hydride and deuteride ($C_p - C_v$) values.

V. RESULTS AND DISCUSSION

A summary of the specific heat measurements is presented in Fig. 5, with a somewhat stylized curve being drawn through the deuteride data to emphasize the possibility of a relatively rapid change in slope occurring near 150°C. These data have been combined via Eq. (6a) to produce the results of Fig. 6. This treatment is tantamount to using the hydride data [in conjunction with Eq. (2) and the INS value $T_E = 1500^\circ\text{K}$] to evaluate all contributions to C_p which are common to hydride and deuteride, i.e., all contributions save that arising from the vibrations of gas atom nuclei. Subsequent subtraction from the deuteride data yields the

FIG. 3. Schematic of adiabatic shield calorimeter.



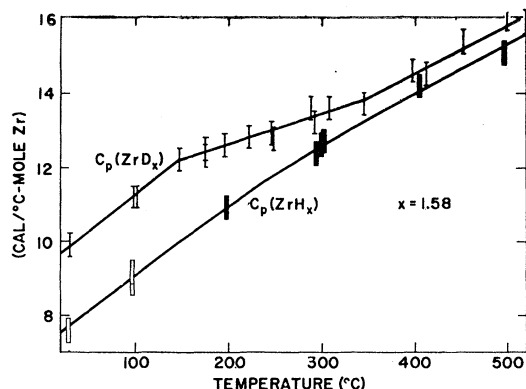


FIG. 5. Observed values of specific heat vs temperature for $\text{ZrD}_{1.58}$ and $\text{ZrH}_{1.58}$. (Filled blocks indicate two data which are unresolved.)

deuterium contribution $x c_v(\text{D})$ (bars) which can be compared with the direct predictions of Eqs. (2) and (4) (smooth curve). It is seen that within experimental uncertainty, the model is consistent with observed C_p values over the interval 30–200°C, above which there occur significant deviations towards small $x c_v(\text{D})$. Equation (7) may be used to evaluate T_E for the hydride, and again reasonable agreement is obtained over the interval 30–200°C, e.g., a value of $T_E = 1500 \pm 300^\circ\text{K}$ is obtained at 150°C, compared with the INS value of $1500 \pm 60^\circ\text{K}$. Above 200°C, the deviations of Fig. 6 are reflected in the rapid variation of deduced T_E values. By and large, however, the harmonic oscillator model seems to give fairly good account of the hydrogen and deuterium contributions to C_v , including the isotopic depression of the deuteride Einstein temperature.¹¹

The deviations noted above can only stem from two general causes: possible shortcomings of the model and/or complications in the experimental situation. Due to the potential multiplicity of possible inadequacies in the model, and because of the limited nature of available information, it appears unprofitable to consider this aspect at present. As was indicated earlier, there is evidence that the deuteride sample may contain as much as 10 vol. % of noncubic phases, which could indeed complicate matters experimentally. Furthermore, the deuteride C_p data may be interpreted as having a *break* in slope near 150°C, a feature not in common with the hydride. Predicating the validity of these observations,

¹¹ Recent electronic transport properties measurements also lend support to this conclusion: P. W. Bickel and T. G. Berlincourt, *Phys. Rev.* **119**, 1603 (1960), and P. W. Bickel and T. G. Berlincourt (private communication).

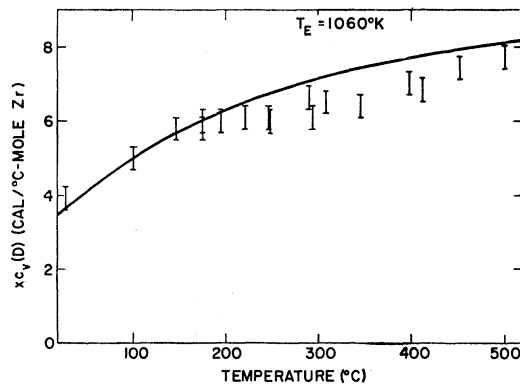


FIG. 6. Comparison of deuteride harmonic oscillator contribution to C_v as obtained from hydride and deuteride C_p measurements (bars), and as predicted directly by model using inelastic neutron scattering results (smooth curve).

a particular possibility readily suggests itself. Since there is a region in which data and model agree well (30–200°C), and since there is reason to believe that the presence of extra phases in modest amounts would not influence the average intrinsic specific heat greatly,^{4,5} it seems likely that complications due to extra phases would be caused primarily by phase reapportionment at higher temperatures. For instance, the observed deviations could be explained by the exothermic conversion of γ deuteride (assumed to be metastable) to δ deuteride. The reaction could not, however, proceed with a rate which depends only on temperature, increasing with increasing temperature. Such effects would be quite noticeable in the sample heating curve (Fig. 4), and would be subsequently compensated for (to first order) by the heating curve analysis of Sec. IV. Instead, the process would have to proceed with a rate which depends strongly on the rate of temperature change. This suggests that the amount of metastable phase present would have to depend almost exclusively on the temperature with reapportionment occurring very rapidly in time.

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