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ANALYSIS OF THE BURPING BEHAVIOR OF THE COLD SOLID METHANE MODERATOR AT IPNS*

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ABSTRACT

We report the results of analyses of the "burping" behavior of the cold solid methane moderator at the Intense Pulsed Neutron Source. This work follows one year's successful and productive experience with the "Model I" moderator, which exhibited periodic "burps" (spontaneous rises of the methane temperature following irradiation) and developed a small but liveable methane leak. An earlier report^[1] described the design of this moderator and summarized experience with it up to that time. The similarly-designed "Model II" moderator ran at a slightly lower temperature and burped only once, colossally, bursting to open a leak between the moderator container and the vacuum space. This occurred 2-3/4 hours after shutdown following two weeks of operation with a proton current of $\sim 14 \mu\text{A}$. The also-similar "Model III" moderator installed in May, 1986, has also developed a leak like that of Model I, despite pursuit of a program of purposely-induced burps. Examination of Model II revealed that a circumferential weld failed due to high internal pressure, such as would be caused by thermal expansion of solid methane or the release of Hydrogen gas upon spontaneous heating. This weld

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is the main object of our current attention, as we design a replacement. The present paper deals with the processes which lead to the burping behavior and outlines the analysis of some of the consequences. Our purpose is to determine conditions under which we can operate the system at the lowest possible temperature, avoiding the problems we have experienced to date.

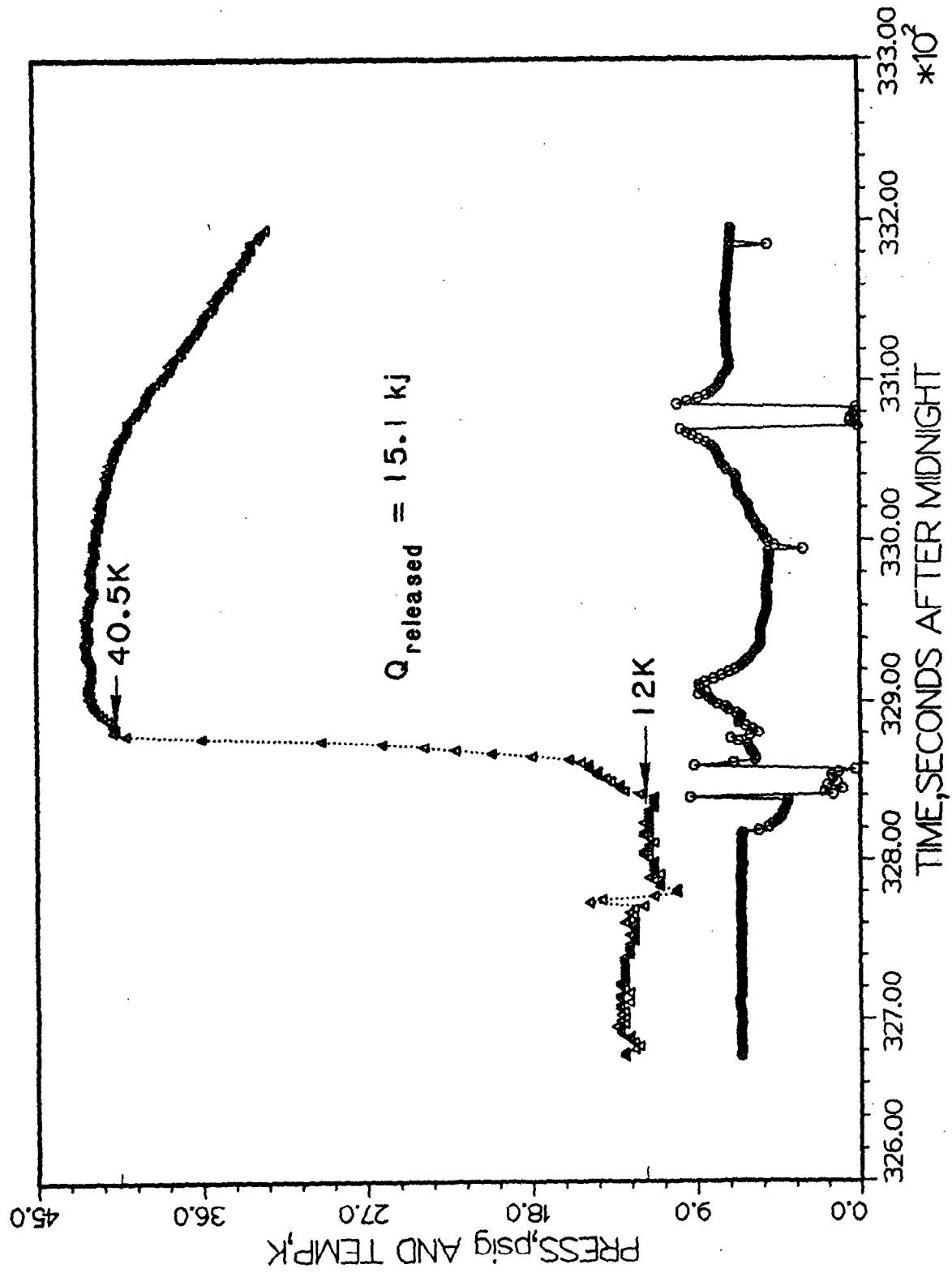
Previously we envisioned a great variety of prospective burp-causing processes that so confused the issue as to prevent the understanding of any one of them. Now it seems clear that some mechanism of radiation-damage energy accumulation and its release is the cause of the burps. We outline a simple theory purporting to describe the phenomenon, which is similar in form to that describing the well-known Wigner energy release in irradiated graphite.

The moderators operated at different temperatures (14K for Model I, 9K for Model II, 12 K for Model III). These provide the lowest measured spectral temperatures of all cold neutron sources of which we are aware, thus producing higher fluxes of long wavelength neutrons and extending the epithermal range to lower energies. It now appears, however, that these low temperatures can put the moderators into an unstable regime of operation. On the other hand KENS has operated a similar solid methane cold moderator, which has exhibited no burps. The KENS system runs at a somewhat higher temperature (~ 20 K) than that at IPNS, and at lower ($\sim \times 1/10 - 1/2$) dose rates. We show that higher temperatures allow moderators to be operated in a permanently stable regime. We suggest measurements that should be undertaken to quantify and test the results of the theory.

Burp Data

Figure 1 is the record of a typical burp of Model III, which was induced by changing the cooling conditions. The figure shows the temperature registered by the internal thermocouple and the refrigerator backpressure, an indirect measure of the heat load on the system. We interpret the irregular behavior of the temperature, and especially of the backpressure, to be indications of Hydrogen leakage into the insulating vacuum space (we have found Hydrogen to be the major component of a gas sample taken from the insulating space after a burp) which spoils the insulation and induces complex transients in the refrigerator. During the induced burp operation, there is first an initial slight decrease in temperature caused by expansion of the coolant already in the system when the coolant valve is throttled down, followed by an increase in temperature caused by the reduced coolant

MARCH 22 DATALOGGER RUN



1. A record of a typical burp of the IPNS "Model III" moderator. The upper line gives the temperature of the moderator, and the lower line records the helium backpressure in the refrigerator.

flow. However of greatest interest here is the sudden rise of temperature, which we interpret to be due to the release of stored energy. We relate this temperature rise to the released energy using the thermodynamic data below.

Thermodynamic Data

Figure 2 shows the total heat content $Q(T)$ of the box as a function of temperature T , calculated from literature values of the specific heats and phase transition energies, assuming a uniform temperature throughout the moderator. The masses of aluminum and methane in the Model I moderator box are $M_{Al} = 692$. gm. and $M_{CH_4} = 314$. gm. (We also account for the presence of the 6% dense aluminum foam [1] in the box).

Burp Data Analysis

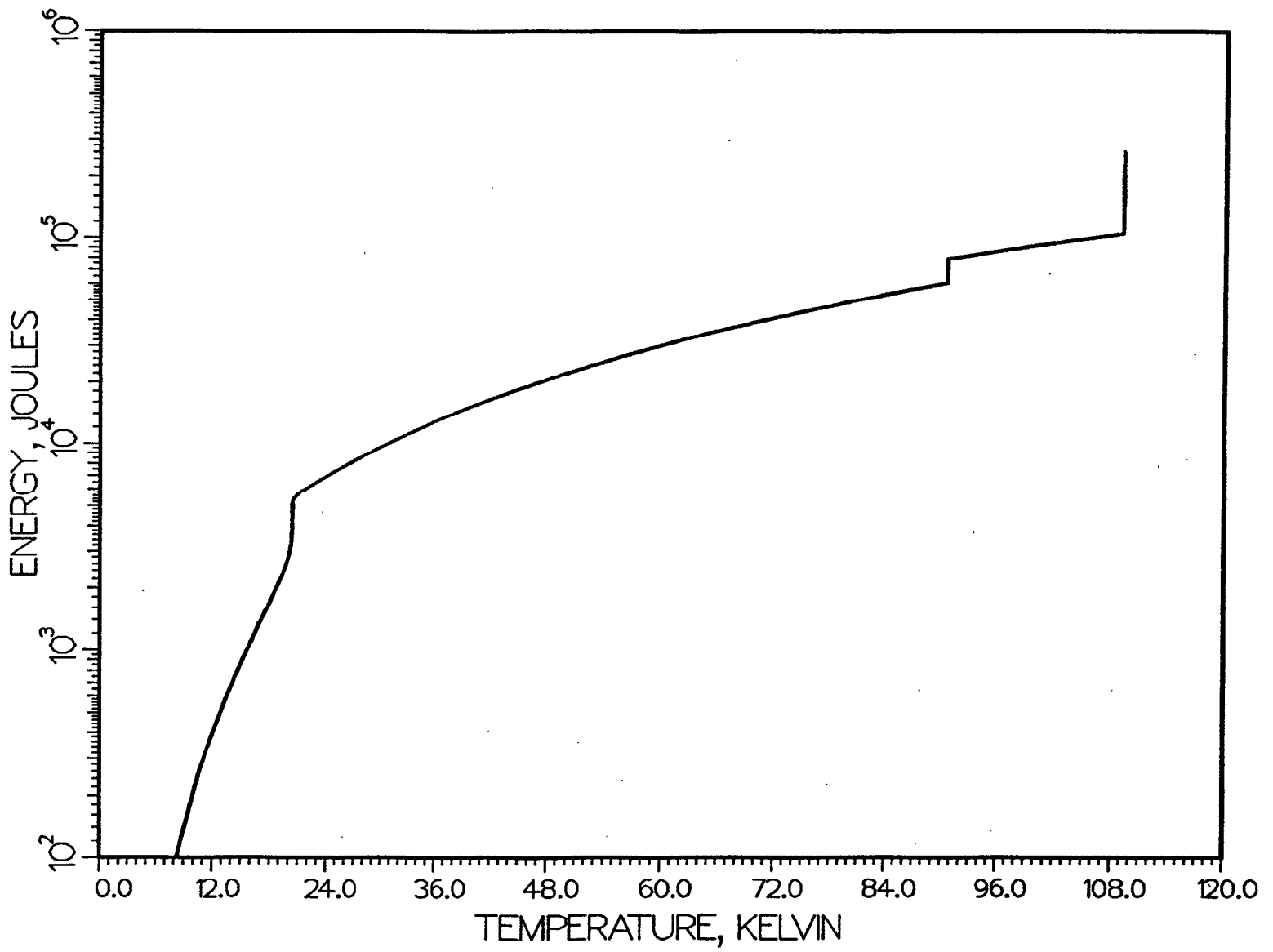
We have analyzed a series of burp data for Models I and III, noting the time intervals between each burp and the previous detected burp, and the maximum temperature reached by the internal thermocouple during the burp. Temperatures have been converted to energies using the thermodynamic data. Figure 3 shows the total energy $Q_{released}$ released, calculated from the starting temperature and the maximum temperature of each burp and plotted versus the time between burps, for Model I. Two sets of curves are drawn on Figure 3, each with the assumption that damage energy accumulates in proportion to the time since the last burp, an appropriate assumption on the basis of the simulations described later. The grand average of the $Q_{released}$ data gives a rate of damage energy accumulation of $dQ_{released}/dt = 0.4$ kjoules per hour. The steepest line that can be drawn through the data of Figure 3 (and two others which seem to be offset by multiples of about 24 hours) has a slope indicating $dQ_{released}/dt = 0.7$ kjoule per hour; these values bracket the possible values of the rate of accumulation of damage energy,

$$0.4 \text{ kj/hr (0.11 w)} < dQ_{released}/dt < 0.7 \text{ kjoule/hour (0.19 watts)}.$$

These limits pertain to the proton current during those times, about $12 \mu A$. Some of the scatter in the data would probably be eliminated if the abscissa were the total number of delivered protons rather than the irradiation times; there may have been undetected burps between the recognized ones.

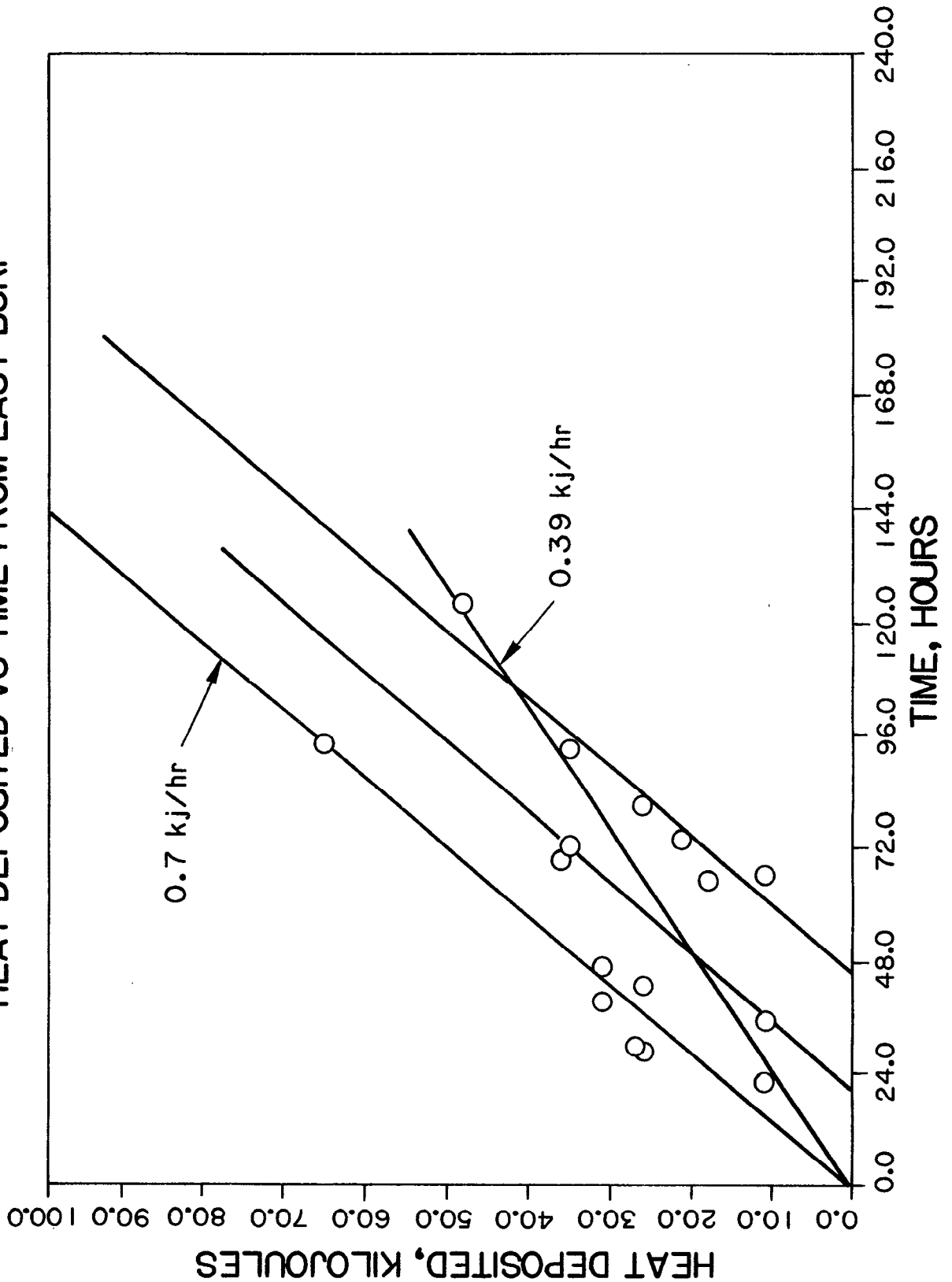
We have one more burp datum, namely that for the disastrous burp of model II, which took place after two weeks operation at a proton current of about $14 \mu A$. Taking $dQ_{released}/dt = 0.5$ kjoule per hour for this period gives $Q_{released} = 168$. kjoules. According to Figure 2, this amount of energy

TOTAL HEAT IN THE MODERATOR BOX



2. The total heat content of the methane-filled moderator box, containing 692 gm of aluminum and 314 gm of methane.

BURP DATA
HEAT DEPOSITED VS TIME FROM LAST BURP



3. The total energy deposited in the moderator box before the burp plotted against the time since the previous burp for the model I moderator. The maximum energy accumulation rate is about 0.7 kjoules/hour, and a minimum of 0.4 kjoules/hr, though other curves may be drawn assuming 24 and 48 hour offsets caused by burps that took place but were not recorded.

would melt the methane and vaporize some, with results that are consistent with what we observed.

Damage Energy and Storage Mechanisms

Radiation damage in aluminum and methane in the moderators of IPNS is presumably due mostly to fast neutrons. There has been considerable study of radiation damage in aluminum at low temperatures, partly as the object of the studies, and partly since aluminum is a common material for construction of irradiation cryostats. There, damage accumulates in the form of Frenkel pairs. For example, an aluminum cryostat irradiated at 6. K at Lawrence-Livermore Laboratory exhibited burps at an accumulated fast (14 MeV) neutron fluence of $2. \times 10^{18}$ n/cm² [2]. At IPNS the fast flux is about $5. \times 10^{12}$ n/cm²-sec, so that we would reach this fluence in about 5 days.

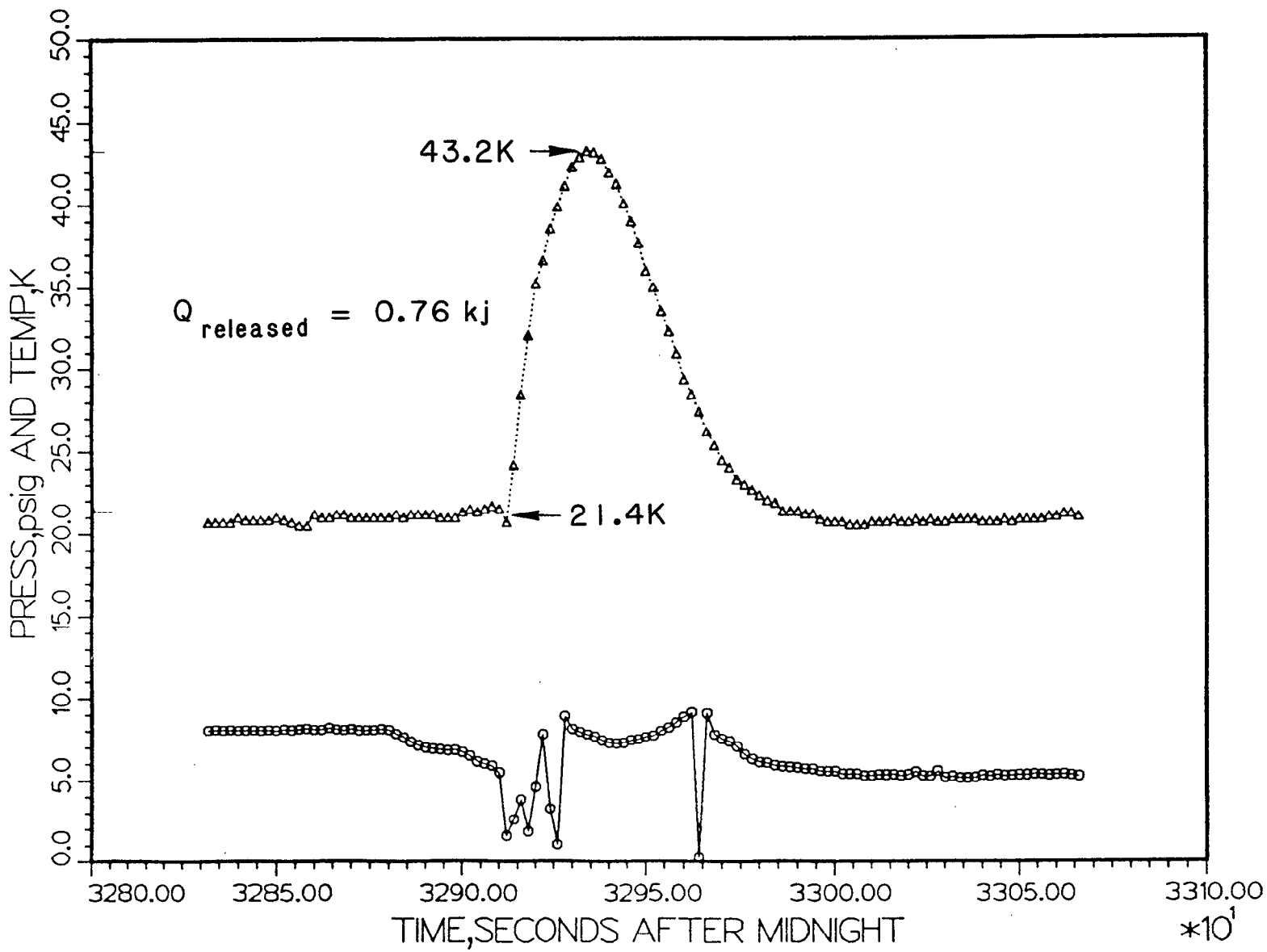
Aluminum

About 22. joules/gm of damage energy accumulates in pure aluminum irradiated to saturation at 4. K, and the release of this energy would raise the temperature of aluminum to over 100 K [3]. If, on the other hand, this energy were distributed between the metal and the methane of the moderator, (the cooling time of the moderator, and therefore the time available for this distribution, is about 15. sec), then the total energy would be about 15. kjoules. According to Figure 2 this would raise the temperature to about 36. K. This is somewhat smaller than the temperature reached in the observed burps of the Model I moderator, and much less than what is needed to explain the disastrous burp of Model II. However the damage energy of 22. joule/gm pertains to pure aluminum, while our moderator box is constructed of 6101 alloy, in which the pinning of defects by impurities is expected to lead to the accumulation of a somewhat higher density of defects.

To investigate the effect of damage energy accumulation in Aluminum, we irradiated the empty moderator container to a dose corresponding to $7. \times 10^{18}$ protons on target (about one day). Figure 4 shows the record of the subsequently induced temperature transient. Taking the temperature change from 21.4 to 43.2 K to represent a rise in the average temperature, this represents about 1.1 j/gm, roughly consistent with expectations.

We conclude that radiation damage energy accumulation and release in aluminum may be one mechanism responsible for the burps, but only may and only one, since the rate of energy accumulation is somewhat too small to explain what we have observed in the small burps of Models I and III and the

APRIL 1 DATALOGGER RUN



4. The record of the temperature transient induced following irradiation by $7. \times 10^{18}$ protons on target, of the empty Model III moderator box (Aluminum only).

titanic Model II burp in the methane-filled box. Although radiation damage in aluminum is only one of several possible mechanisms for energy storage in our moderators, it may be the triggering mechanism for release of the stored energy.

Methane

We know a great deal less about the details of radiation damage in methane than we know about radiation damage in aluminum, and this relates mostly to the chemical effects. However it is certain that the primary effect is the knocking off of protons from methane molecules, with the consequent formation of a diffuse damage cascade leaving behind protons, CH_3^+ or other fragments, and lattice deformation defects in the methane crystal lattice, each of which represents some stored energy. From chemical analyses of the products collected after several periods of irradiation of the solid methane moderator [1], we know that the long-term rate of conversion of methane to H_2 is about 5.4 mole % H_2 per week relative to CH_4 . (Since the mobilities of various species in the solid are expected to be significantly different from those in the liquid, radiation damage data for the liquid should not be considered to be relevant to the problems in solid methane). Even though there may be several relevant species involved, we compute the rate of accumulation of damage energy from neutral hydrogen $\text{H}^{(0)}$ only.

The energy released in the reaction $\text{H}^{(0)} + \text{H}^{(0)} \rightarrow \text{H}_2$ is 4.5 eV [4]. According to the long-term rate of production of H_2 in gases analyzed after warmup ($\text{H}^{(0)}$ can be produced and stored at a higher rate during cold irradiation, and recombine to produce species other than H_2 upon warmup, so that the relevant rates could be even higher than this estimate), we estimate the rate of accumulation of damage energy as $\text{H}^{(0)}$ to be

$$dQ^{(\text{H}_2)}/dt = 2.74 \text{ kJoules/hr (0.76 watts).}$$

This rate is substantially greater than the rate $dQ_{\text{release}}/dt \approx 0.7$ kJoules/hr, and does not include the energy stored as other species (CH_3^+ , etc) which would increase it. On the other hand, this figure is based on the assumption that all the H_2 evolved after warmup is stored as $\text{H}^{(0)}$ between burps--this is certainly not true, in view of the inhomogeneity of the damage cascade, and the consequent initially-rapid annihilation of defects. Lacking further information, we assume that we have identified mechanisms adequate to explain the burping behavior on the basis of energy stored as radiation damage induced defects in aluminum and methane, which is released by thermally-activated mechanisms.

Theory

Guided by the idea that energy is produced and stored in some form (Frenkel pairs, interstitial $H^{(0)}$, ...), released by some thermally-activated mechanism, we propose a simple, non-specific, lumped-parameter model of the system, based on the production and thermally-activated diffusion-controlled self-annihilation of a single type of defect, with Newtonian external cooling. There is nothing particularly novel in this approach, since it has been applied to other systems which store energy by various mechanisms while undergoing irradiation. (The best-known example is the study of the thermal annealing kinetics during the release of the stored (Wigner) energy in the form of lattice defects caused by neutron irradiation of graphite [5-10]. There various types of defects, each with different activation energies for migration and different mobilities as a function of temperature, are averaged into one species [5].)

The rate of change of the concentration $N(t)$ of defects at time t is given by the volume rate of production $R(t)$ of defects and by the rate of self-annihilation $K(T)N^2(t)$ of defects; viz.,

$$dN/dt = R(t) - K(T)N^2(t) . \quad (1)$$

(This simple model has been used to describe the release of stored Wigner energy in irradiated graphite [6], though Cottrell et al. [5] have considered a more generalized form of the defect recombination term.) The factor $K(T)$ is a temperature-dependent recombination rate coefficient having a thermal activation factor which is assumed to be of Arrhenius form,

$$K(T) \propto e^{(-\Delta E/k_B T)} . \quad (2)$$

This is arguably proportional to the diffusion coefficient describing the motion of defects. ΔE is the activation energy of the defect, which releases an energy E per defect upon annihilation, and k_B is the Boltzmann constant. (This is what Dickson et al. [7] call a constant activation energy model, though it could be generalized by a more complicated variable activation energy model which depends on the concentration of defects.)

The net sensible heating power deposited in the moderator is the summation of 1) the instantaneous nuclear heating power $P(t)$ deposited in the moderator, 2) the power $EVK(T)N^2(t)$ developed from the self-annihilation of defects, and 3) the rate of heat removal $H(T,t)A(T - T_c(t))$ by the cooling system. The factor $H(T,t)$ is the "film coefficient" describing the transport of heat across an area A from the system to the coolant. The temperature of the moderator system at time t is $T(t)$ and the temperature of the coolant is $T_c(t)$. We note that changes in the cooling conditions may alter H as well as

T_c , so designate both as externally-controlled, explicit functions of time. Hence

$$\rho C(T) dT/dt = P(t)/V + EK(T)N^2(t) - (H(T,t)A/V)(T(t) - T_c(t)) , \quad (3)$$

where $C(T)$ is the specific heat of the moderator, ρ is the density of the material, and V its volume. When reduced to minimal form, these equations have only a few unknown parameters; however, they are highly non-linear and can exhibit very irregular behavior. Drastic changes in the time behavior can be produced by relatively modest changes in the parameters. (Similar equations have been used to describe the migration and annihilation of point defects in solids, for example in the contexts of creep and radiation-induced growth [11].)

We define the following temperature and time dependent quantities in terms of dimensionless parameters relative to their values at some arbitrary reference temperature T_0 :

the defect recombination rate coefficient,

$$K(T) = K_0 k(T); \text{ so that } k(T) = e^{-(\Delta E/k_B)(1/T-1/T_0)} ,$$

the specific heat,

$$C(T) = C_0 c(T); \text{ so that } C_0 = C(T_0) ,$$

the film coefficient, whose explicit time variation we subsequently ignore,

$$H(T,t) = H(T) = H_0 h(T); \text{ so that } H_0 = H(T_0) ,$$

the defect concentration,

$$N(t) = N_0 n(t) ,$$

the defect production rate,

$$R(t) = R_0 r(t) ,$$

and the nuclear heating power,

$$P(t) = P_0 p(t) . \quad (4)$$

Hence equations (1) and (3) can now be put into a reduced form.

We further define the following constants in terms of quantities at the reference temperature T_0 :

the equilibrium concentration N_0 of defects at the reference temperature T_0 ,

$$N_0 = \sqrt{(R_0/K_0)} ,$$

the time constant τ_N (at the reference temperature T_0) for relaxation of the defect density $N(t)$ to its equilibrium value N_0 ,

$$\tau_N = 1/\sqrt{(R_0 K_0)} ,$$

the time constant τ_T (at the reference temperature T_0) for cooling of the system to its equilibrium temperature (this relaxation time is determined by the ratio of the specific heat to the film coefficient for the system),

$$\tau_T = V\rho C_0/H_0 A ,$$

the incremental temperature T_p by which the moderator temperature T would rise above the coolant temperature T_c due to a constant external power P_o ,

$$T_p = P_o \tau_T / V \rho C_o,$$

the incremental temperature T_N by which the moderator temperature T would rise above the coolant temperature T_c due to the equilibrium rate of annihilation $R_o = K_o N_o^2$ of defects,

$$T_N = ER_o \tau_T / \rho C_o. \quad (5)$$

Hence the defect concentration equation (1) and the moderator temperature equation (3) become

$$\begin{cases} \tau_N dn/dt = r(t) - k(T)n^2 \\ \tau_T c(T)dT/dt = T_p p(t) + T_N k(T)n^2 - h(T)(T - T_c). \end{cases} \quad (6)$$

The n (defect concentration) equation is a generalized Ricatti equation. When the defect production rate is constant, $R(t) = R_o$ ($r(t) = 1$, constant), and the temperature of the moderator is constant, $T(t) = T_o$, and thus the recombination rate is constant, $K(T) = K_o$ ($k(T) = 1$, constant), it has a simple solution,

$$n(t) = \frac{n(0) + \tanh(t/\tau_N)}{1 + n(0)\tanh(t/\tau_N)}. \quad (7)$$

Under these conditions, the defect concentration $n(t)$ relaxes smoothly and monotonically from $n(0)$ to 1. When $n(0) = 0$,

$$n(t) = \tanh(t/\tau_N). \quad (8)$$

(This result has been given by Newgard for defects in irradiated graphite [6]). For small times, $t \ll \tau_N$,

$$n(t) \approx n(0) + (1 - n^2(0))(t/\tau_N); \quad (9)$$

for long times, $t \gg \tau_N$,

$$n(t) \rightarrow 1.$$

When the nuclear heating rate, $p(t)$, the defect concentration, $n(t)$, and the coolant temperature, $T_c(t)$, are all constant, and $c(T) = k(T) = h(T) = 1$, independent of T , the T (moderator temperature) equation (6) has the simple solution

$$T(t) = T_{pp} + T_N n^2 + T_c + [T(0) - (T_{pp} + T_N n^2 + T_c)]e^{-t/\tau_T}. \quad (10)$$

Under these conditions, $T(t)$ relaxes smoothly and monotonically from $T(0)$ to a value $T_{pp} + T_N n^2 + T_c$.

To avoid linearizing approximations, we have coded these simultaneous first-order differential equations in reduced form for solution by Runge-Kutta methods. A few preliminary calculations with guessed parameters and constant coefficients provide some results which relax smoothly and

monotonically to stable conditions, and some which show an oscillating behavior, similar to the regular burping that we have observed. (Similar curves have been produced by Dickson et al. for describing the release of stored energy in irradiated graphite [7].) Figure 5 shows results for a stable case, for which there is a steady rise in the defect concentration $N(t)$ and the moderator temperature T to their constant equilibrium values as a function of time. Figures 6a and 6b show results for an unstable situation, where there is an initial steady rise in the defect concentration $N(t)$ until the occurrence of a precipitous release of energy (burp), with a simultaneous sudden increase in the moderator temperature, after which the moderator quickly relaxes to its earlier values. (As in the case of irradiated graphite, the onset of energy release from the moderator is very critically dependent on variations in the initial parameters, and can be initiated suddenly when some local fluctuation sufficiently raises the moderator temperature.) When the volume defect production rate, $R(t)$, and the nuclear heating power, $P(t)$, are constant, these calculations show an increase in the defect density, $N(t)$, which is nearly proportional to time up to the time of the burp. At this point there occurs a very rapid decrease of the defect density with a concurrent increase in the moderator temperature T . The calculations also show that a burp releases nearly all the energy stored in the defects. The crucial factors required for burping behavior are to have a high activation energy ΔE and a low irradiation temperature T , a high defect energy deposition rate ER_0 and a long cooling time τ_T .

We have also derived a number of simple and useful results from the fundamental equations in terms of measurable quantities, as guides to the understanding of the system. Fundamental to all of them is the condition that the system becomes unstable when the defect concentration $N(t)$ is so large that (neglecting $dC(T)/dT$, etc.)

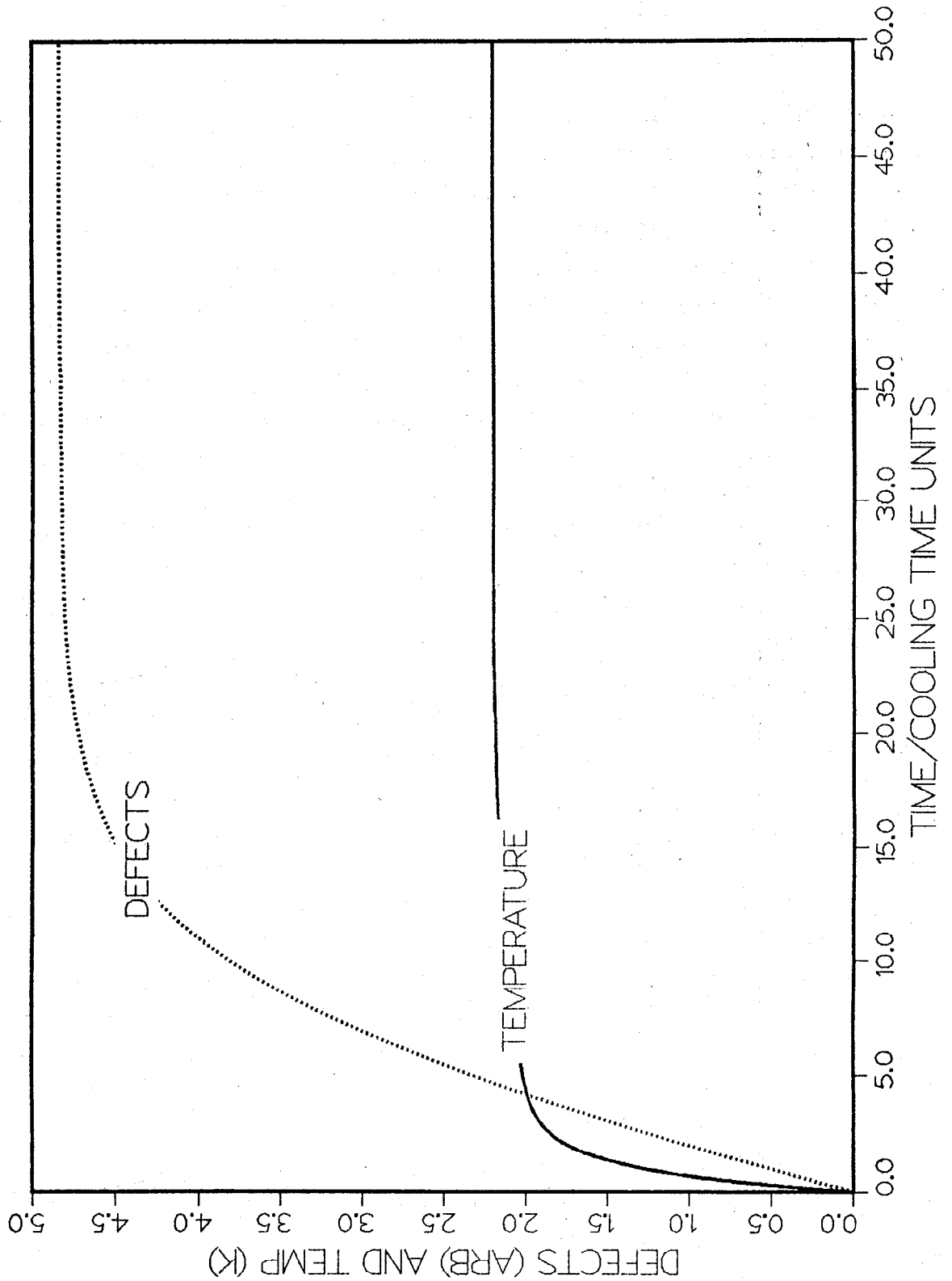
$$EN^2 dK(T)/dT = EN^2 K(T) \Delta E / (k_B T^2) > d/dT (H(T)A/V)(T-T_c) \approx H(T)A/V,$$

and $n^2 T_N (\Delta E / k_B T^2) k(T) > h(T) \approx 1;$ (11)

that is, when an increase of the moderator temperature causes an increase in the rate of release of stored damage energy which is greater than the increase in the rate of heat removal by the cooling system.

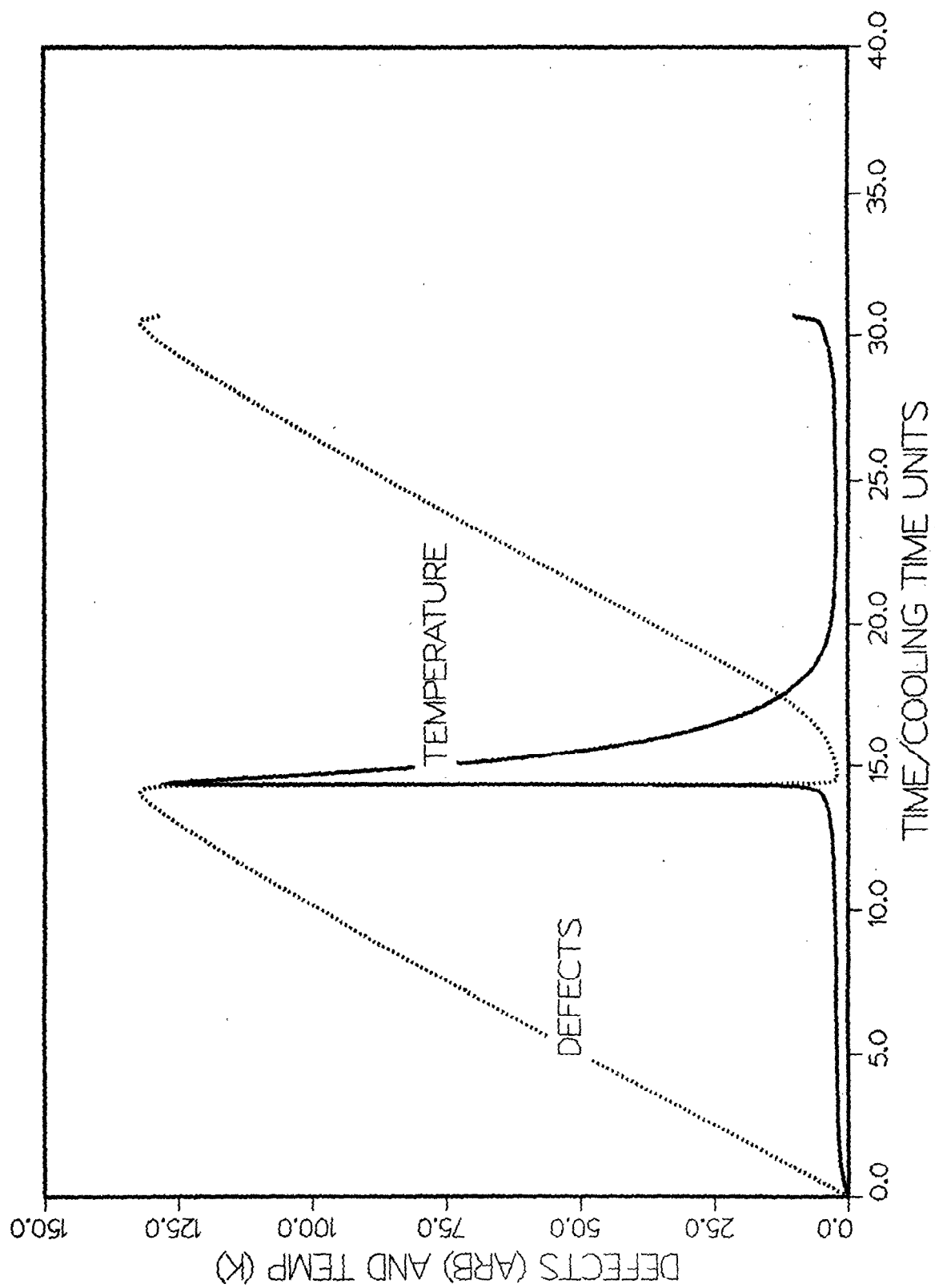
This treatment may be generalized to a defect recombination law that depends on powers of the defect density other than its square, as has been performed for irradiated graphite [5]. We present below some of the results for the expected case that the recombination takes place at a rate

SOLUTION OF THE BURP EQUATIONS
STABLE CASE

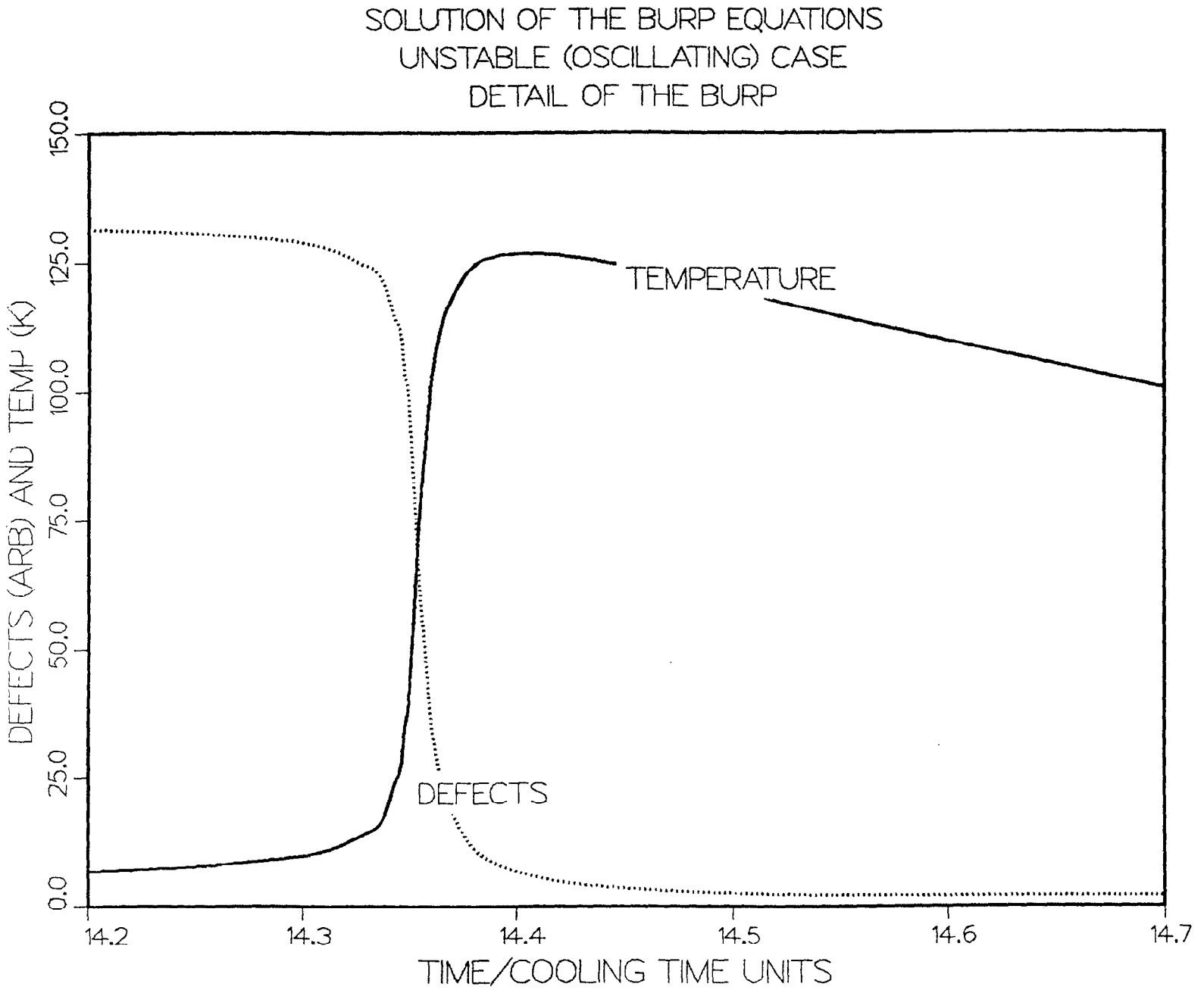


5. The solution of the burp equations for the stable case, showing the steady rise in the defect concentration and the moderator temperature to constant equilibrium values as a function of time.

SOLUTION OF THE BURP EQUATIONS
UNSTABLE (OSCILLATING) CASE



- 6a. The solution of the burp equations for the unstable (oscillating) case, showing the steady rise in the defect concentration until the occurrence of the burp, at which time the defects disappear catastrophically with the simultaneous sudden increase in the moderator temperature.



6b. The details of the burp behavior shown in Figure 6a, around the time at which a burp occurs.

proportional to the square of the density of a single species, and for constant coefficients.

Instability Time t_s and Temperature T_s

We express the results in terms of quantities which are independent of the temperature and those which depend explicitly on the temperature. We also assume that the initial defect concentration is zero, $n(0) = 0$, and that the defect production rate and cooling system conditions (namely $H(T,t)$, thus T_N) are constant. The time t_s and temperature T_s at which the moderator system becomes unstable are related by

$$\begin{aligned} \tanh^2(t_s/\tau_N) T_N k(T_s) (\Delta E/k_B T_s^2) &= 1, \\ \text{or } t_s &= \tau_N \tanh^{-1} \sqrt{(k_B T_s^2 / \Delta E T_N k(T_s))}. \end{aligned} \quad (12)$$

When $k_B T_s^2 / \Delta E T_N k(T) > 1$, eq (12) has no real solution and this is the condition for permanent stability of the system; presumably the KENS moderator operates in this regime. The stored energy accumulates more slowly at a higher temperature, and saturates at a level at which it appears steadily and stably as heat.

When $\sqrt{(k_B T_s^2 / \Delta E T_N k(T_s))} \ll 1$, the instability time t_s is proportional to the argument of the inverse hyperbolic tangent function, corresponding to the proportional regime found in the calculations; that is,

$$t_s \approx \tau_N \sqrt{(k_B T_s^2 / \Delta E T_N k(T_s))}. \quad (13)$$

We can estimate an activation energy ΔE through this equation. The burps of Model I took place at time intervals $t_{s1} = 24$ hrs at a temperature $T_{s1} = 14$ K, while the gigantic burp of Model II took place after a time $t_{s2} = 336$ hrs and at a temperature $T_{s2} = 9$ K. Hence we can estimate

$$\begin{aligned} (t_{s1}/t_{s2}) &= (T_{s1}/T_{s2}) e^{((\Delta E/2k_B)(1/T_{s1} - 1/T_{s2}))}, \\ \Delta E/k_B &= 2 \ln \left[\left(\frac{t_{s1}}{t_{s2}} \right) \left(\frac{T_{s2}}{T_{s1}} \right) \right] / (1/T_{s1} - 1/T_{s2}), \\ &= 155. \text{ K.} \end{aligned} \quad (14)$$

This result is based on numbers which are not very accurate, and, moreover, the proportionality assumption itself may not be very accurate, since we have only two data points. More accurate measurements of the instability times t_s as a function of the instability temperatures T_s would provide more useful insight into the activation energy ΔE , and therefore into what mechanism is responsible for the burps. The procedure would be to operate for various times t_s , then raise the moderator temperature until a burp occurs--this is T_s . Hence an Arrhenius plot ($\ln(t_s/T_s)$ vs $1/T_s$) would provide $\Delta E/2k_B$ from

the gradient, and the prefactor in the relationship for t_s , (parameters essential to make the theory into a model) and would lend credence to the theory if it were successful. Unfortunately the scatter in the data is so poor as to make this analysis not useful. (Measurements have been performed on irradiated graphite [10] showing a threshold effect in which a slight temperature rise over a short period causes a rapid temperature increase; an extremely slow warm-up avoids this rapid release of energy. In addition, samples irradiated at lower temperatures have much higher and quicker energy releases [5])

More generally, in case the proportionality assumption does not apply, one could instead fit the data to the relationship

$$\tanh(at_s) = bT_s e^{(c/T_s)}, \quad (15)$$

where $a = 1/\tau_N$, $b = e^{(-\Delta E/2k_B T_0)} / \sqrt{(k_B/T_N \Delta E)}$, and $c = \Delta E/2k_B$. In this case we also obtain τ_N , the time constant for relaxation of the defect density to its equilibrium value at the reference temperature T_0 . There may well be conditions where this analysis is possible.

Burp energy

On the basis of the proportionality assumption, the energy released during a burp is equal to the energy stored as defects; that is,

$$\begin{aligned} Q_{\text{released}} &= ER_0 t_s \\ &= ER_0 [(k_B/\Delta E)(V/ER_0^2 H_0 A)(T^2/K_0) e^{(\Delta E/k_B T)}]^{1/2} \\ &= \sqrt{[(k_B/\Delta E)(VE/H_0 AK_0)]} T e^{(\Delta E/2k_B T)}. \end{aligned} \quad (16)$$

The energy released increases very rapidly as operating temperature is decreased, as we have observed. The assertion that Q_{released} is proportional to the time t_s elapsed before the burp is the basis for Figure 3. More-refined measurements of induced burps, for which the maximum temperature T_{max} reached is recorded as well as the time t_s elapsed before the burp and the temperature T_s at which it begins, can refine the determination of the rate of damage energy accumulation, which is $ER_0 = T_N(\rho C_0/\tau_T)$ in the theory.

More generally, the energy released in a burp is

$$Q_{\text{released}} = \int_{\text{burp}} dt V \rho C_0 c(T) dT^{(N)}(t)/dt, \quad (17)$$

where $dT^{(N)}(t)/dt$ is the rate of change of the defect density, in the absence of nuclear heating power, heat transferred to the cooling system, and the production of defects. Thus more precisely than in the linear approximation,

$$\begin{aligned}
Q_{\text{released}} &= V\rho C_o \int_{\text{burp}} dt (\tau_N/\tau_T) dn/dt \\
&= V\rho C_o (\tau_N/\tau_T) (n_{\text{before burp}} - n_{\text{after burp}}) \\
&\approx V\rho C_o (\tau_N/\tau_T) n_{\text{before burp}} \\
&= V\rho C_o (\tau_N/\tau_T) \tanh(t_s/\tau_N). \tag{18}
\end{aligned}$$

In general this relationship should be used rather than the linear one which was invoked to interpret the data in Figure 3.

Temperature Rise During Operation and the Cooling Response Time, τ_T

The first-order effect of nuclear heating of the moderator is to raise the temperature of the system. An equilibrium condition is reached for which the moderator temperature is such that the instantaneous nuclear heating power P_o flows steadily to the cooling system. This contribution to the temperature rise is T_p . Source-shutdown transient measurements made shortly after starting up Model I, indicate that T_p is about 1. K for 12. μ A, 450. MeV operation.

Those same measurements also indicate that the thermal response time τ_T is about 60. seconds at about 14. K. The estimated instantaneous nuclear heating power based on scaling from measurements on ZING-P' moderators, is $P_o \approx 10$ -20 watts. Since $T_p = P_o \tau_T / V\rho C_o$, we would expect (identifying $V\rho C_o = dQ/dT = 148.$ joules/K at 12 K from Table 1), $T_p = (10.w)(60.sec)/(148.j/K) = 4.1$ K. This is significantly larger than the observed value $T_p \approx 1.$ K, inaccurate as it is, even though we have used the lower limiting estimate of the nuclear heating power. The cause of this inconsistency is probably the domination of the thermocouple response time in the transient measurement of τ_T . In view of the relationship between T_p and τ_T , we estimate τ_T , which is of critical importance in the theory, to be within the range $8. < \tau_T < 15.$ seconds. There is some evidence that the temperature relaxes faster than that indicated by the installed thermocouple, although this does not serve to refine the estimate of τ_T .

Hence we need better measurements of the nuclear heating power P_o , the temperature rise T_p and the time constant τ_T . This could be accomplished by using a faster thermocouple and more accurate and more frequent recordings of thermocouple emf and coolant backpressure in burp and shutdown transient measurements.

The theory and calculations show a gradual increase of the temperature of the system during steady irradiation. This is caused by the increasing

power appearing in the system due to the increasing defect density and consequently increasing defect annihilation rate. If an equilibrium is reached, this contribution to the temperature rise is $T_N k(T) n^2(t)$. In a stable system and even in an unstable system except near the time of a burp, at least a quasiequilibrium exists, in which the temperature rises by this amount. Figures 6a and 6b show this subtle effect, which was observed during operation of Model II. (The temperature rose from about 7. K to about 9. K during the two-week period of operation.)

This quasi-equilibrium, $dT/dt \approx 0$, operation of the moderator implies that the moderator temperature is given by

$$T(t) \approx T_P p(t) + T_N k(T) n^2(t) + h(T) T_0 . \quad (19)$$

When the nuclear heating power $p(t)$ is constant and the heat removal rate $h(T)$ is constant, there is an increase in the defect concentration $n(t)$, so that the moderator temperature is given by

$$T(t) \approx (1/h(T)) [T_P p(t) + T_N k(T) \tanh^2(t/\tau_n)] + T_0 . \quad (20)$$

If measurements are made at consistent relative power, $p(t)$, as a function of time in the absence of burps, then with the assumption that $h(T) = 1$, we could determine $(T_P + T_C)$ and $T_N k(T)/\tau_n^2$ in the proportionality regime, or $(T_P + T_C)$, $T_N k(T)$ and τ_n in cases for which $n(t)$ saturates.

Stresses Due to Thermal Expansion of Methane

When the methane warms up as in a burp, it expands. Figure 7 shows the lattice parameter (and hence the density or specific volume) of solid methane as a function of temperature [12]. As an example, we consider a burp which raises the temperature of the moderator from, say, 10 K to 50 K. The lattice parameter of methane changes from $a = 5.865 \text{ \AA}$ to $a = 5.925 \text{ \AA}$, so the relative expansion is

$$\epsilon = \Delta a/a = (5.925 - 5.865)/5.865 = 0.0102 . \quad (21)$$

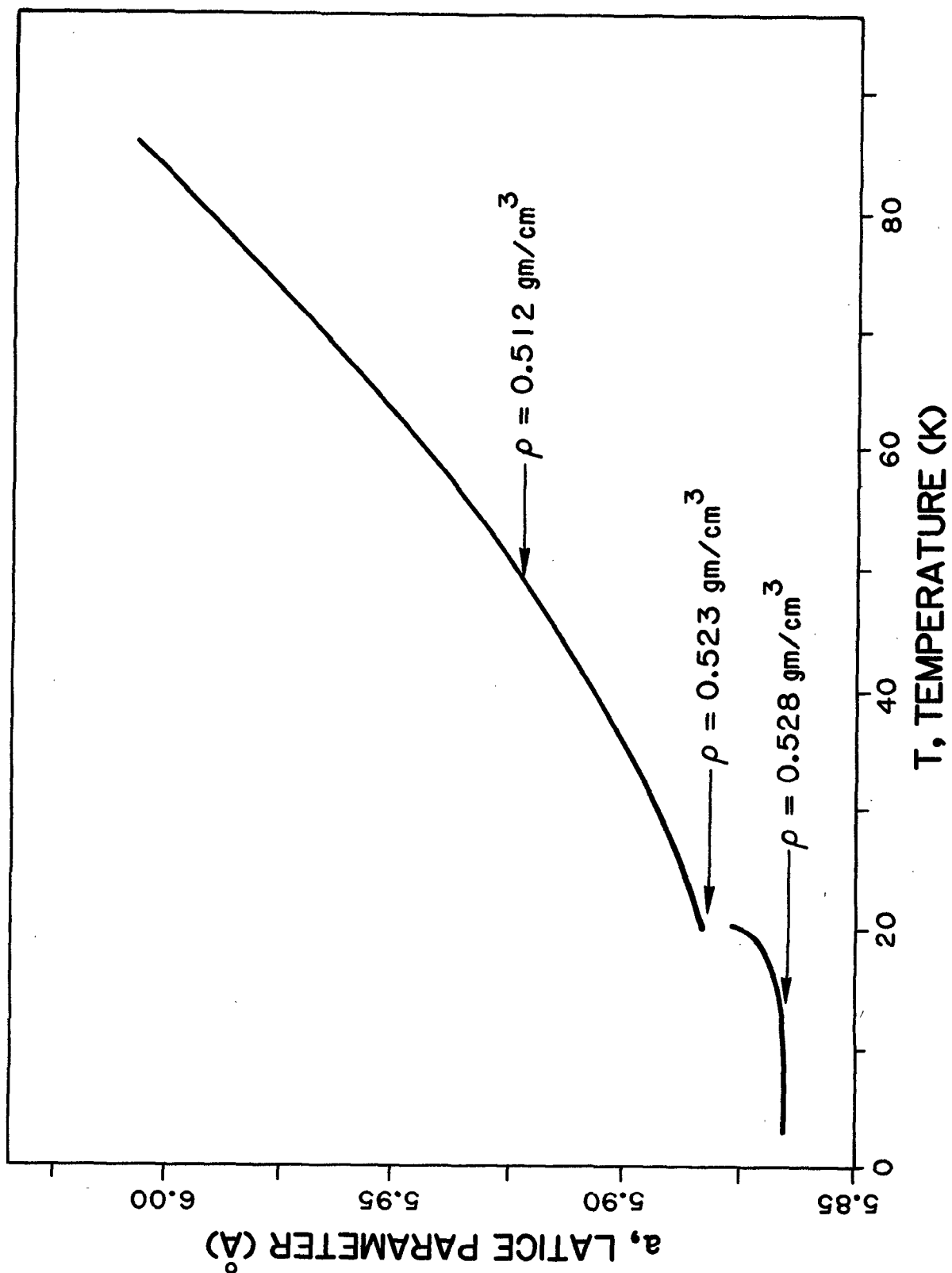
As an indicative exercise, we consider the box to be a thin spherical shell of aluminum with a radius R and thickness t , and the methane moderator to be incompressible. The strain in the aluminum shell is equal to the relative expansion of the methane, and the stress is given by

$$\sigma_{Al} = E_{Al} \epsilon = (10. \times 10^6 \text{ psi}) \times 0.0102 = 102,000 \text{ psi} , \quad (22)$$

where E_{Al} is Young's modulus for aluminum. We calculate an effective radius for the moderator to be

$$R = (3V/4\pi)^{1/3} = (3. \times 752. \text{ cm}^3/4\pi)^{1/3} = 5.64 \text{ cm} \quad (23)$$

where V is the volume of the moderator box. Taking the moderator thickness t to be 0.32 cm, the internal pressure is given by



7. The lattice parameter of solid methane as a function temperature, taken from the thesis of Aadsen (Univ. of Illinois, 1975).

$$p = 2\sigma(t/R) = 2. \times (102,000.) \times (0.32/5.64) = 11,574. \text{ psi} . \quad (24)$$

With such an internal pressure, the compressibility of the methane reduces the stress, to give a statically indeterminate problem, as the stress analysts call it.

Accounting for the thermal expansion of aluminum, the relative change in the volume of the box is

$$\Delta V_{\text{Box}}/V_{\text{Box}} = 3\alpha_{\text{Al}}\Delta T + (1/V_{\text{Box}})(dV_{\text{Box}}/dp)p , \quad (25)$$

where α_{Al} is the thermal expansion coefficient of aluminum, ΔT is the change in temperature, dV_{Box}/dp is the rate of change of the volume of the box with respect to internal pressure p . The relative change in the volume of the methane is

$$\Delta V_{\text{CH}_4}/V_{\text{CH}_4} = 3\Delta a/a - p/B_{\text{CH}_4} , \quad (26)$$

where $\Delta a/a(\Delta T)$ is the relative change of lattice constant for temperature change ΔT , and B_{CH_4} is the bulk modulus of CH_4 . Thus the pressure p is given by

$$p = \frac{3(\Delta a/a - \alpha_{\text{Al}}\Delta T)}{(1/V_{\text{Box}}dV_{\text{Box}}/dp + 1/B_{\text{CH}_4})} . \quad (27)$$

The relative thermal expansion $\alpha_{\text{Al}}\Delta T$ of aluminum at low temperature is 0.010 % between 4. K and 60. K. We take the relative expansion of the methane to be $\Delta a/a = 0.0102$ from equation (21) above, and the factor

$$\begin{aligned} 1/V_{\text{Box}}dV_{\text{Box}}/dp &= (3/R)dR/dp = (3/E_{\text{Al}})d\sigma/dp = (3/E_{\text{Al}})(R/2t) \\ &= 2.64 \times 10^{-6} \text{ psi}^{-1}, \end{aligned} \quad (28)$$

as for a spherical box. Measurements of the pressure-temperature isochores in solid methane [13] give

$$(\partial p/\partial T|_V) = (14.7 \text{ psi/bar}) \times (21.7 \text{ bar/K}) = 319. \text{ psi/K} , \quad (29)$$

and the lattice parameter measurements of solid methane [12] at 50 K (see Figure 7) give

$$(1/V\partial V/\partial T|_p) = (3/a)da/dT = 0.00095 \text{ K}^{-1} . \quad (30)$$

This allows an estimate of the bulk modulus of methane from the thermodynamic relationship

$$\begin{aligned} B_{\text{CH}_4} &= (\partial p/\partial T|_V)/(1/V\partial V/\partial T|_p) , \\ &= 319./0.00095 = 3.37 \times 10^5 \text{ psi} . \end{aligned} \quad (31)$$

Thus finally we obtain the pressure in the moderator box

$$\begin{aligned} p &= (3.)(0.0102 - 0.0001)/(2.64 \times 10^{-6} + 1./3.37 \times 10^5) \\ &= 5.40 \times 10^3 \text{ psi} , \end{aligned} \quad (32)$$

and the corresponding stress on the box is

$$\sigma = (R/2t)p = 5.64/(2 \times 0.32) \times (5.40 \times 10^3) = 47,600. \text{ psi} . \quad (33)$$

This is substantially lower than the estimate for incompressible methane, and the difference may possibly be significant in a more accurate treatment of the volume change and the stresses in the moderator box.

Stresses Due to Released Hydrogen

When the moderator warms up and burps, it releases hydrogen into a small volume which causes further stresses on the moderator system. Calculating the volume of hydrogen released during a burp from the amount found after warming up the system, namely $(0.054 \text{ mole H}_2)/(\text{mole CH}_4)/\text{week}^{[1]}$, after one day there would be

$$H_{2\text{released}} = 0.0077 \text{ mole H}_2/(\text{mole CH}_4) \times 314./16. = 0.15 \text{ mole H}_2$$

If we assume for example that 0.2 moles H_2 ($0.01 \text{ mole H}_2/(\text{mole CH}_4)$) expands into a fixed volume of $V = 30. \text{ cm}^3$ at a temperature of 50 K, then according to the thermodynamic data on H_2 , we find that the pressure in the moderator system due to the release of hydrogen gas is

$$p = 24.6 \text{ atm}.$$

Already this is sufficient to stress the box seriously, and to explain the appearance of H_2 in the vacuum insulation space around the moderator. This calculation does not account for the entrainment or solution of H_2 in CH_4 , nor the expansion of the box due to pressure. Until dV_{Box}/dp and $d\sigma/dp$ are known, and the simultaneous effects of solid CH_4 expansion and H_2 solubility are incorporated into the calculation, we cannot realistically estimate the stresses that the box must endure.

Summary

We have suggested a model for the cold methane moderator system which seems capable of explaining the observed burping behavior. Measurements suggest approximate values for the parameters in the model, although not very accurately. A number of measurements are suggested which will refine the parameters of the model, and enable a calculation of the behavior of the moderator and determine a safe operating program. In practice, the current program is to heat up the system on a daily schedule, inducing a small burp to prevent the long-term buildup of stored energy. In principle such annealing cycles require only a few minutes to complete, but in practice secondary effects that follow the release of hydrogen into the insulating space sometimes require several hours to overcome.

The purposeful periodic induction of small burps is a macroscopic fix for the burping problem, though severe stresses may be introduced into the moderator. These might be reduced by a strictly controlled operation in which a slow increase in temperature might lead to a controlled release of energy. A microscopic fix might be to introduce as an impurity, some species which would scavenge the responsible energy-storing defects at the operating temperature, and so reduce the buildup of stored energy. The theory outlined above could be modified to include this scavenging. Another microscopic fix might be to arrange that the methane does not expand so severely upon warming, thus reducing the stresses. For example, it is reported [14] that about 10 mole % nitrogen in solid methane causes a decrease in the molar volume with increasing temperature in the range 50 - 60. K.

Further measurements may show up inadequacies in the model insofar as it assumes the dominance of a single defect species. The model could be elaborated to include several species with different production rates, diffusion coefficients, activation energies, production rates and annihilation energies, and spatial variations in the stored energy (as has been done for irradiated graphite [5,7]).

It would also be useful to determine the maximum temperature of a burp that can be safely tolerated, using the maximum stress in the moderator box as the criterion for judging what is tolerable, and therefore the maximum acceptable temperature, and the number of stress cycles that can be expected during the lifetime of the box. Such an analysis needs to be more refined than the above calculations. What is required is a determination of the stress in the box given the maximum temperature (therefore the volume change) reached during the burps, and the compressibility of solid methane as a function of temperature, which plays off against the thermal expansion.

A longer version of this report^[15] contains more extensive tables and figures.

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