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**Some Concluding Remarks  
About  
Cold Moderator Development**

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Intense Pulsed Neutron Source  
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# Some Concluding Remarks About Cold Moderator Development

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## Abstract

This is the transcription of remarks made at the conclusion of the Workshop, including some questions that emerged, some suggestions that arose and some general observations.

## I. Scattering Functions

We need inelastic scattering data for cryogenic moderator materials to enable calculations of moderator performance and thus to support informed design decisions and interpretation of measurements. Ideally, the data would be in the form of the full scattering law  $S(Q,\omega)$ , represented in some format appropriate for input to Monte Carlo and other neutron transport codes. The functions must accurately represent the temperature dependence of the scattering, and account properly for the possibility of thermodynamic non-equilibrium of the medium (as for example in cold ortho-para  $H_2$ .) Of course descriptions of the scattering from some candidate moderator materials already exist at some level of approximation. These need to be checked and improved (the liquid state effects are difficult to describe).

Cryogenic moderator performance depends sensitively on the internal molecular vibrational motions, the free-or-nearly-free molecular rotational motions, and on the center of mass motions.

Broadly speaking these are respectively in the ranges of tens to hundreds of millivolts, few millivolts and few-to-submillivolts. Measurements performed to support the development of scattering laws require different instruments to address these different energy transfer ranges. In a real sense, the effort is one of "bootstrapping", using existing neutron facilities to provide data needed to improve the neutron sources, as suggested by Figure 1. Peter Egelstaff showed us how to do this more than thirty years ago! It should be easy now, using existing instruments for example on the pulsed sources, chopper spectrometers for the high energy transfer ranges and crystal analyzer instruments for the low energy transfer ranges. There may be a problem convincing scientific program committees that these experiments are worthwhile, in that their responsibility is to deal with research applications of the instruments, rather than development applications such as the present suggestion.



Figure 1. Using existing neutron facilities to provide data to improve neutron facilities.

## II. Cold Moderator Materials

Both the structural material and the moderating material must be considered in cold moderator design. Table I below illustrates the matrix of choices. The x's represent implementations in at least one installation. Choice of structural material represents a compromise among properties of neutron attenuation by absorption and scattering, strength at operating temperature, radiation damage tolerance, and fabricability. The choice of structural and moderating materials is not

independent (therefore the matrix), although the nature of interactions in the choices is beyond my capability to state here.

Table I  
Moderator and Structural Materials  
for Cold Moderators

Mod'r →	Far Out →						
Struct'r ↓	L-H <sub>2</sub>	L-D <sub>2</sub>	L-(H <sub>2</sub> +D <sub>2</sub> )	S-D <sub>2</sub> O	L-CH <sub>4</sub>	S-CH <sub>4</sub>	L-H <sub>2</sub> +TiH <sub>2</sub>
Al	x	x			x	x	
Mg				x			
Steel	x						
Zr							
:							
:							

Rutherford Laboratory uses supercritical hydrogen (15 atmospheres absolute pressure) in a steel container. The entry for mixed H<sub>2</sub> and D<sub>2</sub> is intended to remind designers that a carefully-optimized mixture may be better than either one alone, depending on application. The same idea applies to CH<sub>4</sub>, say employing CH<sub>4-x</sub>D<sub>x</sub> (but see below some comments on the composition of irradiated mixtures). Far-out possibilities like heterogeneous mixtures of TiH<sub>2</sub> with liquid H<sub>2</sub> seem to offer the advantages of high proton density with the good low temperature thermalization properties of Hydrogen. These prospects need to be evaluated. John Hayter once suggested using isotopic <sup>15</sup>N<sub>2</sub>, to eliminate the large capture in natural Nitrogen and capitalize on the small rotational level spacing of N<sub>2</sub>. Inhomogeneous mixtures of solid CH<sub>4</sub> in liquid Hydrogen have been discussed to avoid the problems of "burping" in irradiated solid methane. An unresolved problem is to determine whether, to what extent and why ortho Hydrogen is advantageous over para Hydrogen. Scattering kernels need to be developed to support these assessments.

Steel is substantially stronger and easier to weld than Al or Mg, but has higher absorption and scattering cross sections. Zirconium (or Zircaloy) is also stronger and easier to weld than Aluminum or Magnesium, but like Iron has a substantially larger coherent scattering cross section. The Bragg scattering from moderator containers should probably not be greatly feared because the scattering should have little effect in an isotropic neutron field such as exists near the source.--this assertion needs to be verified by calculation or experiment.

### III. Radiation Mixing of Chemical Composition

Questions arose several times during our discussions, which should at least be contemplated in the light of the realization that the high radiation fields in operating moderators can cause important configurational changes in the material which may alter their neutronic properties. We are aware of the aggradation of light hydrocarbons into  $H_2$  and heavier hydrocarbons, for example. These are inferior moderators and collect to form voids and to clog flowing systems. Additionally, radiolytic decomposition and subsequent recombination will lead to reversion of para Hydrogen to normal Hydrogen--is this a contributing factor in the mystery of why supposedly ortho Hydrogen and para Hydrogen seem to differ little in their moderating properties?. Mixtures of  $H_2$  and  $D_2$  will reform to an equilibrium mixture of  $H_2$ ,  $D_2$  and  $HD$ . Isotopically substituted methane, for example  $CH_3D$ , will reform into an equilibrium mixture of  $CH_xD_{4-x}$ .

Figure 2 illustrates the point in the case of  $H_2$  and  $D_2$  mixtures.

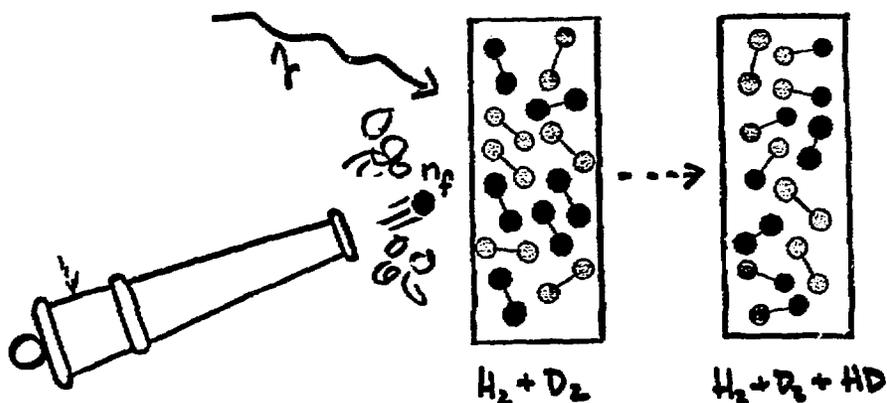


Figure 2. Radiation-induced reformation of an  $H_2$ - $D_2$  mixture.

Assuming that the binding energies of all species are identical, the equilibrium concentrations of the chemical species will reach a statistically determined equilibrium.

The relative numbers of the different atomic species are

$$p_H = N_H / (N_H + N_D) = N_{H_2}^0 / (N_{H_2}^0 + N_{D_2}^0)$$

$$p_D = N_D / (N_H + N_D) = N_{D_2}^0 / (N_{H_2}^0 + N_{D_2}^0)$$

where

$$N_H^0 = 2N_{H_2}^0, N_D^0 = 2N_{D_2}^0 \text{ and } N_{HD}^0 = 0$$

are the initial numbers.

In equilibrium the relative numbers of molecular species are

$$P_{H_2} = p_H^2, P_{D_2} = p_D^2, \text{ and } P_{HD} = 2p_H p_D.$$

Here I have not treated the dynamics of the reformation, which takes place gradually according to the rates of radiolytic decomposition and recombination.

The same reasoning applies to other situations. For example for an initial charge of  $(1 - x)CH_4 + xCH_3D$  with

$$p_H = 1 - x/4, p_D = x/4,$$

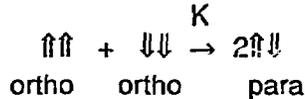
the equilibrium relative numbers of molecular species are

$$P_{CH_4} = p_H^4, P_{CH_3D} = 4p_H^3 p_D, P_{CH_2D_2} = 6p_H^2 p_D^2,$$

$$P_{CHD_3} = 4p_H p_D^3 \text{ and } P_{CD_4} = p_D^4.$$

The (questionable) assumption here is that the rates of radiolysis that affect reformation from the  $CH_4$ - $CH_3D$  mix predominate over the rates that produce the heavier hydrocarbons. In this case however, radiolysis generates a mix of other, heavier hydrocarbons,  $C_2H_6$ ,  $C_3H_8$ , . . . and their isotopically substituted analogs, which I have ignored. The final equilibrium probably consists of Carbon and  $H_2$ . The full dynamics involves a complicated transition which depends on rates of radiolysis which are unknown and on details of the system.

In Hydrogen at low temperatures, radiation can be expected to reform the low temperature, predominantly para hydrogen into a more nearly normal hydrogen mixture. The spontaneous conversion of ortho to para Hydrogen is usually described (ignoring the backward reaction as is appropriate at low temperatures)



With the constraint on the concentrations

$$C_{\text{ortho}} + C_{\text{para}} = 1$$

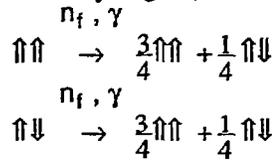
the kinetic equation is

$$\frac{dC_{\text{ortho}}}{dt} = -KC_{\text{ortho}}^2,$$

$$C_{\text{ortho}}(t) = \frac{C_{\text{ortho}}(0)}{1 + KtC_{\text{ortho}}(0)}$$

and

is the solution. When radiation decomposes either species presumably the recombination takes place at random, producing normal Hydrogen (3 ortho:1 para)



so that the kinetic equations (ignoring the back reaction, and catalytic effects which can be important) become

$$\begin{aligned} \frac{dC_{\text{ortho}}}{dt} &= -KC_{\text{ortho}}^2 - \frac{1}{4}RC_{\text{ortho}} + \frac{3}{4}RC_{\text{para}} \\ \frac{dC_{\text{para}}}{dt} &= KC_{\text{ortho}}^2 + \frac{1}{4}RC_{\text{ortho}} - \frac{3}{4}RC_{\text{para}} \end{aligned}$$

where R is the rate of destructive collisions per molecule. These equations can be reduced, using the condition  $C_{\text{ortho}} + C_{\text{para}} = 1$ , to an easily-solvable single Riccati equation similar to the equation for  $C_{\text{ortho}}$ . Some estimates based on realistic assumptions show that the effect of radiolysis and random recombination can alter the equilibrium ortho-para ratio so that the equilibrium result is nearly normal Hydrogen, even at low temperature and even at the low radiation levels characteristic of pulsed sources. Perhaps this is the basis for an explanation of why normal and what is presumed to be para Hydrogen behave similarly as moderators. It is important to recognize that the "equilibrium" here is not thermodynamic equilibrium, so the scattering function does not have the detailed balance property.

#### IV. Comparison of Some Pulsed Moderator Spectra

Figure 3 illustrates the intensity advantage of cold sources for long wavelength neutrons. The figure shows the wavelength spectra as measured with a "1/v" detector in the pulsed beams of IPNS, so that the counting rate distribution is proportional to  $\lambda\phi(\lambda)$ . The spectra are arbitrarily normalized to 1.0 at  $E = 1.0$  eV (wavelength = .28 Å), which is approximately appropriate (we cannot measure absolute spectra).

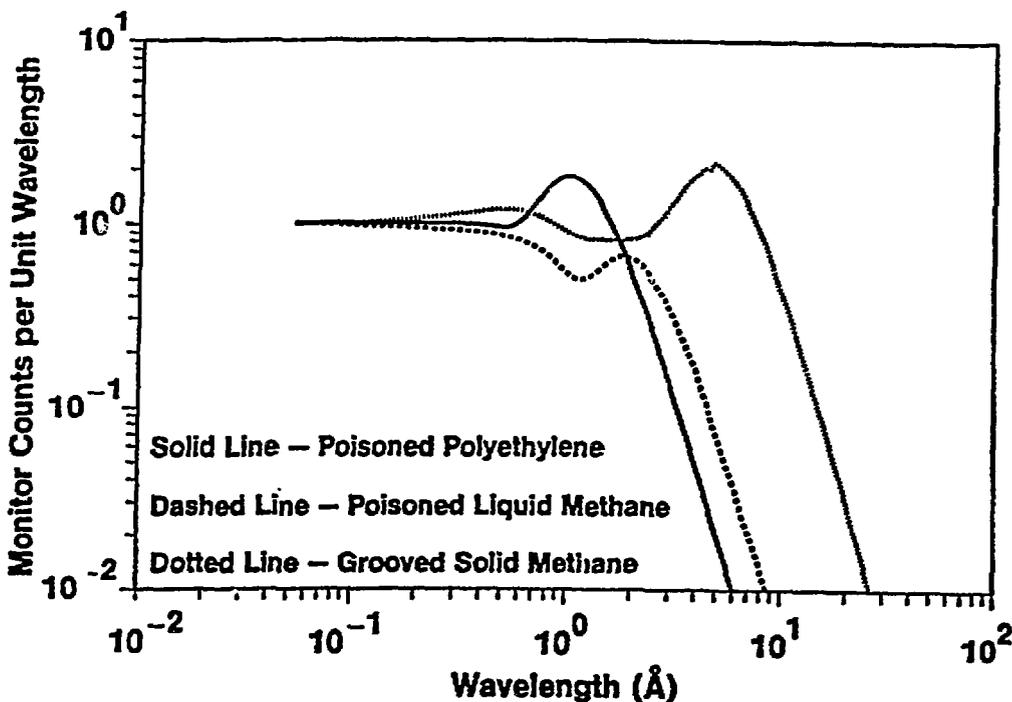


Figure 3. Comparison of flux spectra for 350 K polyethylene, 105 K liquid methane and 20 K solid methane.

Three spectra are shown, one for ambient temperature ( about 350 K) polyethylene poisoned with .5 mm Cd 25. mm below the viewed surface, one for a 105 K liquid methane moderator poisoned 17 mm below the surface and one for a grooved, 20 K solid methane moderator. Comparing the polyethylene and liquid methane spectra in the range of the Maxwellian peak, two effects are visible: the peak of the Maxwellian is shifted in wavelength as expected according to the square root of the

temperature ratio; the more severe poisoning of the liquid methane moderator leads to a significant loss of the integrated intensity in the Maxwellian, even so the flux of long wavelength neutrons from the liquid methane is about 3x higher. Comparing the solid methane with the polyethylene reveals two effects: the 20 K moderator shifts the Maxwellian to still longer wavelengths, and the grooved, unpoisoned moderator produces a larger Maxwellian flux relative to the epithermal flux, the result is that the flux of long wavelength neutrons is more than 300 x greater!

The discontinuity at  $4.67\text{\AA}$  is due the 111 Bragg edge in Aluminum, and is one of several such features caused by scattering of neutrons from the beam by Aluminum structure in the beam; these serve as markers of the wavelength scale.

## V. Some New Ideas to Explore

A number of new ideas for improved moderators arose during the conference. Here I focus on the ones that relate to the moderation process, including some of those mentioned in previous sections of this report. Some of these might best be evaluated by tests, others by calculation.

### Hydrogen Mixtures

H<sub>2</sub> and D<sub>2</sub> might be advantageously mixed in liquid hydrogen moderators (H<sub>2</sub>O and D<sub>2</sub>O in cold ice moderators) because of their significantly different migration and diffusion lengths, and thus matched to the different requirements of cold sources of different sizes. In these instances, the effects of radiation on mixing the chemical species needs to be recognized, as discussed above.

### Premoderators and Shields

Surrounding the principal cold source with, say, H<sub>2</sub>O and/or Lead, can reduce the thermalization and gamma ray heat loads in the cold material and the container, and thus reduce the refrigeration requirements and alleviate problems in the design of the container. (Radiogenic Lead, lower in <sup>207</sup>Pb than common Pb may be useful to reduce the flux depression in reactor cold sources.)

### Composite Reflectors

In pulsed sources, as Gary Russell's calculation first showed, a composite reflector of Beryllium outside of which is Nickel, may be able to provide some tens of percents intensity advantage over simple Be or Ni reflectors. This idea is ready for test.

### Exotic Moderator Materials



John Hayter has explored the possible use of  $^{15}\text{N}_2$  as moderator, capitalizing on the fact that it has a lower capture cross section than  $^{14}\text{N}_2$ . Although Nitrogen is more massive than Hydrogen, and therefore is inferior for slowing down neutrons from high energies, this feature leads to lower rotational level spacings and more efficient thermalization to low temperatures.  $^{15}\text{N}_2$  might be useful as a premoderator surrounding conventional cold moderators, since it is easy to cool to 77 K.

### Deuterated Methanes

One of the reasons that  $\text{CH}_4$  is a superior moderator is the presence of a high density of internal rotational modes, which are nearly free even in the low temperature solid. In spite of the sacrifice in the proton density,  $\text{CH}_3\text{D}$  or other deuterated methanes might provide even better moderation to the lowest energies. The idea rests on the observation that in the coldest methane moderators neutrons with energies below about 1. meV (12 K) can lose more energy only by exciting center-of-mass translational modes. Figure 4 illustrates how the rotational band structure of deuterated methanes admits lower energy transitions than  $\text{CH}_4$ . This is partly due to the lowered symmetry of the substituted molecules and partly due to the higher moments of inertia about the unique axes in the substituted species. Monte Carlo calculations will be impractical until scattering kernels are developed for the nonspherical deuterated molecules, but tests could be done if the materials were available. The effects of radiation reformation of the mixture need to be kept in mind in practical applications.

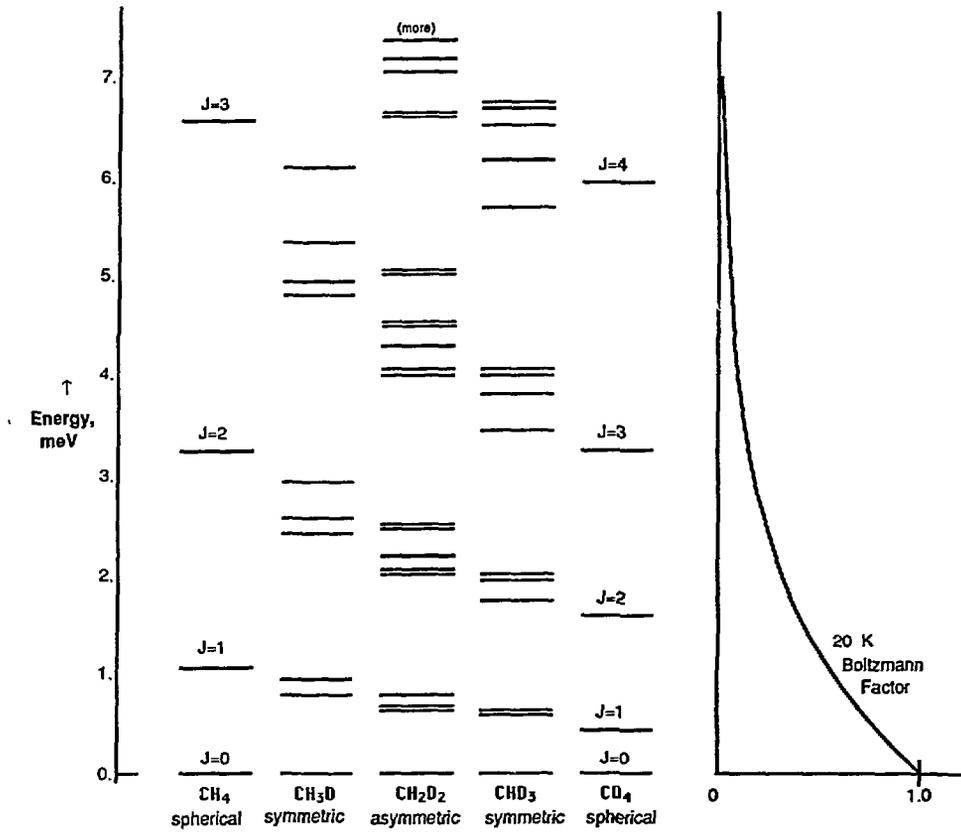


Figure 4. Rotational energy levels of methane and deuterated methanes<sup>(1,2)</sup>.

Mixed Moderator Materials

Peter Egelstaff has suggested that Kr be mixed with CH<sub>4</sub> to "free up" the molecular rotations in solid methane. This suggestion might initially be evaluated by molecular dynamics calculations.

Andrew Taylor and I once discussed the possible advantages of mixed metal hydride (e.g. TiH<sub>2</sub>) with liquid Hydrogen, to gain the advantages of high average proton density with low temperatures. The same idea might be applied to CH<sub>4</sub>. These ideas might be evaluated by Monte Carlo calculations.

Juergen Eckert suggested use of Hydrogen or hydrocarbons in zeolites. The idea, I think, is that the host might advantageously modify the motions of the principal scatterer. Such schemes might be evaluated by molecular dynamics calculations.

Circulating suspensions of solid methane in (for example) liquid Hydrogen or small spheres or thin plates of methane in liquid Hydrogen would eliminate or go far in diminishing the problems of "burping" of irradiated, cold solid methane. Such schemes present yet unsolved engineering problems, and would need neutronic evaluation.

### About Tests

There are only a few facilities where tests can be made. For pulsed moderators, The Los Alamos "Blue Room" and the Hokkaido University Linac (Sapporo) provide the needed combination of modest intensity and accessible environment. Pulsed source tests are simple and revealing, even for materials intended for steady source applications, but then the connection between the tests and the applications has to be made through calculations.

Realistic reactor tests of full scale cold sources are difficult, although some kinds of tests might be made merely by substituting materials in existing sources.

## **VI. Conclusions**

This meeting, the first addressing this subject, has been very productive in revealing progress and pointing up problems and areas of opportunity. There seemed to be general agreement that another similar meeting should be convened in two or three years.

## **VII. Acknowledgement**

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## **VIII. References**

1. E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955, p. 361 ff.
2. G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11** (1943) 27-42.