Fixed Points Near Room Temperature

Participants

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In our committee discussion of fixed points, we realized that several factors were of concern: Are these points equilibrium points thermodynamically? We realized that kinetics often enters into the establishment of these points. We also recognized that the apparatus plays a part in deciding where an individual person may find a fixed point in relation to his press loading or other factors.

We decided that the equilibrium value was the important value, and that we should select the fixed point data that were closest to equilibrium. Then it would be up to the individual user to worry about kinetics and apparatus factors in his own situation.

In this connection, we advise that all high-pressure workers describe their apparatus adequately. It is necessary to know what kind of device is used, and its important dimensions. If it's a piston-cylinder apparatus, the diameter of the piston and the length of the sample should be given. Materials in the cell, such as pyrophyllite, boron nitride, or silver chloride should be specified and their dimensions given. Give sufficiently detailed information so that an estimate of the pressures can be made at a later date when fixed point values become more accurate.

We decided that there were several ranges into which the pressure scale could be advantageously divided. The first range is called the Free Piston Gage Range. It was the consensus of the group that the free piston gage could be used up to pressures of about 30 kbar. The first two fixed points that we discussed—the mercury freezing pressure at 0°C and the bismuth I-II transition—lie in the Free Piston Gage Range. There may be other points that should be included.

Our assignment was concerned with pressures at room temperature. We decided that this meant 25 degrees Centigrade, and we have shown in the accompanying list of "Pressure Fixed Points" our judgment of the best values of the pressure, in kilobars, of the fixed points at 25 degrees Centigrade.

Some measurements have been made above room temperature, and we wish to include the mercury point over a range of temperatures as a fixed point, rather than just giving it as one point. It recommended that such reference pressures be based on the Simon equation, adjusted to agree with the value 7.569 kbar at 0°C as follows:

$$P = 38227\left[\left(\frac{T}{234.29}\right)^{1.772} - 1\right]$$

where T is the temperature in K on the International Practical Temperature Scale (1948), and P is the pressure in bars.

In the case of the bismuth I-II transition, it was the consensus of the group that Heydemann's value determined at the Bureau of Standards is the best value at this time and should be 25.50 ± 0.06 kbar at 25 degrees Centigrade.

We called the next range, beginning at 30 kbar, the Upper Force-Over-Area Range, with a present upward limit of about 80 kbar. In the present state-of-the-art this limit probably cannot be exceeded in apparatus such as piston-cylinder equipment. In this range, we have selected the thallium II-III transition to have a value of 36.7 ± 0.3 kbar.

The value chosen for caesium (Cs II-III = 42.5 ± 1 kbar) was the result of careful consideration. We determined who had performed experiments where the system was in a truly liquid environment, and gave considerable weight to that. We considered experiments that did not have a liquid environment but in which an attempt was made to approach a free piston condition. Here, one may have had silver chloride for the environment. We included x-ray diffraction data. We weighed these, one against the other, and came up with a good consensus as to the best value. We then tried to put some kind of an estimate on the plus or minus value. The caesium II-III value appears to be known only on an upstroke, so there could be a question as to whether or not the caesium values are equilibrium values.

The barium I-II transition was placed at 55 ± 2 kbar, and bismuth III-V at 77 ± 3 kbar, at which point we reached the limit of our upper force-over-area range.

Then we moved into a more difficult range—the 100 Kilobar Range—in which tin, iron, barium, and lead were considered. We understand that there are no shock data on the transitions in tin, barium, and lead.

There are problems, apparently, in trying to run these transitions by shock techniques. The shock data that have been obtained pertain only to iron, and according to at least one member of our panel, the iron transition is very poorly behaved. It was the consensus of the group that iron probably ought to be left out of the system, although there were a few who objected. Iron seems to be somewhat irregular in behavior, and there is an uncertainty as to the correct transition value.

It is the consensus of this group that the tin, barium, and lead points are on much less firm ground than the points in the Force-Over-Area Range, which in turn are on less firm ground than the points of the Free Piston Gage Range. We feel that pressure is probably established up to the neighborhood of 80 kbar within plus or minus 3 kbar. In the 100 Kbar Range and above there is a great deal of uncertainty. How much is difficult to estimate. Points in this range have been chosen from older work of Drickamer's and probably should be revised downward on account of the downward revision in the barium point, and the iron point.[‡]

Pressure Fixed Points

	Hg	7569±2 bars at 0°C		
Free piston gage range	Bi	I-II	25.50	± 0.06 kbar at 25°C
	Tl	II-III	36.7	±0.3 kbar
Upper F/A range	Cs	II-III	42.5	± 1 (up only)
	Cs	III-IV	43.0	± 1 (up only)
	Ba	I-II	55	± 2
	Bi	III-V	77	± 3
100-kbar range	Sn	I-II	100	± 6
	Ba		140 (up only)	
	Pb		110 to 160 (up only)	

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[‡] *Added in proof by the Editor*: In the following table are Drickamer's revised values based upon a later publication (Rev. Sci. Instr., Notes Section, Vol. **41**, No. 11, 1970):

Approximate Location of Transitions, kilobars

	Old	*New*
Bi	88	73-75
Sn	113-115	92-96
Fe	133	110-113
Ba	144	118-122
Eu	150-160	122-130
Pb	160	128-132
Rb	190	142-153
Cs*(max)	170-180	133-142
Ca*(max)	350-375	235-255
Rb*(max)	420-435	290-320
ZnS*(max)	550	410-420

*Maximum in resistance-pressure curve.