QUICK APPROXIMATIONS FOR HE_3 POINTS OF STATE

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While studying steady state, very low temperature refrigeration which would be required to permit operation of superconducting RF waveguides, it became evident that operation at about 1.0°K would be more economical than at 1.8°K. This is because the RF losses fall off exponentially in this temperature region. Thus small He_3 refrigerators, together with He_4 cold gas heat shield refrigerators, could be used at 1.0°K rather than large He_4 refrigerators as have been used to attain 1.8°K. Thermodynamic data of He_3 were required to check out these possibilities.

AFML-TR-67-175 Thermodynamic Data of Helium-3, by R. M. Gibbons and D. I. Nathan, covers a temperature range of 1.0°K to 100°K and 1.0 atm to 100.0 atm. This is fine for refrigeration cycles exhausting at or above 1.0 atm, but not for operation at temperatures below 3.2°K. The He_3 data were graphically extrapolated up to 400°K and to very low pressures. Use of the charts was simple but accuracy was questionable. The fit between gas data and liquid data appeared to defy thermodynamic theory.

In further checking of the He_3 data it occurred that one could do better if one could make more use of data for He_4 which is available over a wide range of points as in NBS Report 9762 Provisional Thermodynamic Functions for Helium 4 for Temperatures from 2 to 1500 K with Pressures to 100 MN/m^2 (1000 Atmospheres), by R.D. McCarty. This is to say that much can be inferred from the similarities between He_3 and He_4 data rather than concentrating only on the differences.

First, the sources were reconciled. The He_3 data were converted to the same units used for the He_4 data. The He_3 data appear to be based on 0.0 J/Mol at 0.0°K. The NBS data are not so based and 58.61 J/Mol are added to all values due to the starting point used. Thus, 146.328 J/Mol – 4.22°K x 20.78575983 J/Mol – $^{\circ}$K = 58.61 J/Mol. The Cp value used is for 0.0 atm and is the same for He_3 and He_4. It follows that at 300.0°K and 0.0 atm, the enthalpy for both He_3 and He_4 can be listed as 6335.73 J/Mol + 58.61 J/Mol or 6294.34 J/Mol.

Variation of enthalpy from 1.0 atm to very low pressures at 300.0°K is linear. Thus values are readily established for any isobars of interest between 0.0 atm and 1.0 atm.

H = 6293.34 J/Mol + 1.46 J/Mol (Patm/1.0 atm) (1)

At ambient temperatures enthalpy values decrease as pressure is lowered while temperature is constant. At very low temperatures enthalpy values increase as pressure is lowered except at extremely low pressure or at pressures much higher than 1.0 atm. It follows that there must be a temperature at which enthalpy is close to constant over a wide range of pressure.

A comparison of He_3 adjusted data with He_4 data was made at 10°K, 20°K, 40°K and 100°K for the range of 1.0 to 10.0 atm. At 10°K the differences in enthalpy were 0.3 J/Mol at 1.0 atm, 6 J/Mol at 5.0 atm and 20 J/Mol at 10 atm. At 20°K the respective differences are 0.0 J/Mol, 1.4 J/Mol and 4.9 J/Mol. At 40°K values were within 0.4 J/Mol out of 889.2 J/Mol ± 0.7 and at 100°K values were within 2 J/Mol out of 2142.5 J/Mol ± 5. Enthalpy values of He_3 and He_4 are the same for temperatures above 100°K but vary widely at very low temperatures.

At 0.0 atm the enthalpy values of He_3 and He_4 are identical at each temperature by definition. At low temperatures and higher pressures, the Cp values increase over 20.78575983 J/Mol – $^{\circ}$K. The starting point of the increase of Cp values for He_4 for the pressure range of 0.0 to 1.0 atm is at successively lower temperatures as pressure is reduced.

If the temperature of the start of increase of Cp values for each low pressure isobar is the same for both He_3 and He_4, then quick approximations of enthalpy might be made. A check at 2.0 atm showed that the increase in Cp values starts at the same temperature but that there is no decided increase for He_3 as there is for He_4. A similar check at 1.0 atm showed fairly close correspondence. It was assumed that the temperature of the start of increase of Cp values therefore would be the same for He_3 and He_4 at low pressure isobars.

This temperature of the start of increase of Cp values is easy to calculate because the graphic plot is parabolic. Let 40°K = 10 units and let 0.2 atm = 5 units and be the focus. The temperature of the start of increase is 0°K at 0.0 atm, 40°K at 0.2 atm, 56°K at 0.4 atm, 69°K at 0.6 atm and 80°K at 0.8 atm, etc., where one-half of the latus rectum is 10 units.

$$(T, {}^{\circ}K/4)^2 = 2 \times 10\ (P, atm/0.04) \qquad (2)$$

$$T, {}^{\circ}K = 4\ (500\ P, atm)^{1/2} \qquad (3)$$

This quick approximation is adequate for the range of 0.0 through 1.5 atm. The enthalpy at T start is easy to determine.

H start, J/Mol = (H, 300°K, J/Mol) – (20.78575983 J/Mol, $^{\circ}$K) (300°K – T start, $^{\circ}$K) (4)

A plot of Cp values at low pressures for He_4 versus temperature show Cp values rise above the value of 0.0 atm exponentially to a maximum value at the point of evaporation. Cp values plotted at a number of pressures are a family of hyperbolas with the real focus located at lower temperatures and Cp values as pressure is decreased. Focal axes are at 45° to constant Cp lines and the hyperbolas are close to equilateral. One asymptote is close to 20.5 J/Mol - $^{\circ}$K while the other varies between 0°K and 4°K. For 1.0 atm the latus rectum is 4 units where 1 unit equals 1°K or 1 J/Mol - $^{\circ}$K. The ratio of $^{\circ}$K,focus ÷ $^{\circ}$K,apex is close to 1.77 between 1.0 atm and 0.1 atm, rises to 2.04 at 0.5 atm and 3.0 at 0.01 atm.

The foregoing was of interest because of the possibility of determining an exponential relationship which could allow calculation of Cp at any temperature that is less than T start along a given isobar. Several factors ended this interest. The curves deviate from the model as asymptotes are approached at very low pressures. The temperatures of evaporation of He_3 are beyond the temperature asymptote of He_4 for each listed isobar. Finally, any solution which matches listed data would no longer be a quick approximation.

The average Cp between T start and T evaporation is easily determined for any listed He_4 isobar.

Cp Average, J/Mol-$^{\circ}$K = (H start, J/Mol – H evap., J/Mol) ÷ (T start, $^{\circ}$K – T evap., $^{\circ}$K) (5)

The temperature at which the average Cp occurs can be determined for any low pressure isobar by the use of an F factor.

$$\text{Tcp avg., }^{\circ}\text{K} = \text{T evap., }^{\circ}\text{K} + \text{F (T start, }^{\circ}\text{K} - \text{T evap., }^{\circ}\text{K} \qquad (6)$$

If the divergence of Cp values above 20.78575983 J/Mol -°K were linear, the F factor would be 1/3 for all isobars. The F factor for curving divergences, as are found, is always less than 1/3 except at 0.0 atm where there is no divergence. The F factor for He_4 as determined from listed data is 0.149 at 1.0 atm, 0.161 at 0.7 atm, 0.175 at 0.4 atm, and 0.205 at 0.1 atm. These points lie on a smooth curve. Let the P ordinate be from 0.0 atm to 1.0 atm. Let the F ordinate be F factors from 0.333 to 0.149.

$$F = 0.333 - 0.184\ (\text{P,atm}/1.0\ \text{atm})^{0.17} \qquad (7)$$

These quick approximations match listed He_4 data from 9.0 atm down to 0.1 atm and are reasonably close at 0.05 atm and 0.01 atm.

The enthalpy at Tcp avg. is then determined.

$$\text{Hcp avg., J/Mol} = [(\text{T start, }^{\circ}\text{K} - \text{T at avg. Cp, }^{\circ}\text{K})(20.78575983\text{, J/Mol, }^{\circ}\text{K} + \text{Cp avg.})] \div 2 \qquad (8)$$

The same procedure and F factor can be used to determine T and H values for 2 additional points along the isobar, then 4 additional points, then 8, etc. A point of interest is quickly bracketed and solved iteratively.

This approach has been used with reasonable success but has shortcomings. Further checks reveal points of temperature with more than 1 value of enthalpy which must be incorrect. There is doubt that points close to evaporation temperatures can be accurate at any isobar. Finally, the process fails to be a quick approximation and was dropped.

A review of listed data reveals that while He_3 and He_4 Cp values vary greatly at low temperatures and pressures, the Cv values are far more stable. Thus while quick estimates based on constant pressure analogies are cumbersome and inaccurate, those for constant volume are not. Fortunately the isobars of interest are few. They are 10 atm supply gas, 6 atm intermediate pressure gas to the initial liquefaction value, 0.7 atm for initial liquefaction and expansion engine exhaust, and an evaporator pressure. The latter is 0.01 atm for operation at close to 1.0°K.

The above pressures allow a reasonable expansion ratio of 12 to 1 through the expansion engine which is close to existing He_4 reciprocating machines of standard design and the use of a single pressure reducing valve between 10 atm and the initial liquefaction pressure of 0.7 atm. If the latter is raised too much, initial yield would not be 100%. If it is lowered only to 0.5 atm, a second pressure reducing valve would be required. The establishment of a single pressure of 0.7 atm for initial liquefaction does much to simplify the determination of proper enthalpy values of low pressure isobars of He_3.

For a constant volume process it is necessary to use listed data for an isobar higher than and close to the one of interest and then calculate values for the lower pressure isobar. The recognized formulas apply.

$$T_2,\ ^{\circ}\text{K} = T_1,\ ^{\circ}\text{K}\ (P_2,\text{atm}/P_1,\text{atm}) \qquad (9)$$

$$\Delta S,\ \text{J/Mol},\ ^{\circ}\text{K} = (\text{Cp, J/Mol},\ ^{\circ}\text{K})\ \ln\ (T_2,\ ^{\circ}\text{K}/T_1,\ ^{\circ}\text{K}) \qquad (10)$$

$$\Delta U,\ \text{J/Mol} = (\text{Cv, J/Mol},\ ^{\circ}\text{K})\ (T_1,\ ^{\circ}\text{K} - T_2,\ ^{\circ}\text{K}) \qquad (11)$$

$$U_2,\ \text{J/Mol} = (U_1,\ \text{J/Mol}) - \Delta U,\ \text{J/Mol} \qquad (12)$$

$$H_2,\ \text{J/Mol} = U_2,\ \text{J/Mol} + 101.325\ \text{J/atm-l}(v_2,\ \text{l/Mol})(P_2,\text{atm}) \qquad (13)$$

To obtain values of enthalpy at 0.7 atm, listed data for He_3 at 1.0 atm are transposed using the above relationships. These values are accurate down to 7.0°K but become erratic close to the temperature of evaporation. Potential problems are obviated by selecting 7.0°K as the expansion engine discharge temperature. To obtain values of enthalpy of He_3 at 0.01 atm, the listed data for He_4 at 0.05 atm are transposed using the above relationships. The values are accurate to the point of He_3 condensation. The listed value is 78.96 J/Mol at 1.0°K for He_3. The calculated value is 79.07 J/Mol and calculated temperature value is in correspondence to within 0.01°K.

It should be noted that relationship (10) above was not used directly. It did unlock the graphical problem, however. Listed liquid-evaporation data for He_3 show the critical point of He_3 to have the same S value as for He_4. Tabulated gas data for He_3 disagree by approximately 5.38 J/Mol-°K. In transposing He_3 data from 1.0 atm to 0.7 atm the 5.38 J/Mol-°K must be deducted to assure consistency with other listed data. Additional constant pressure checks from very low He_3 temperature indicate correspondence with S values of He_4 at the same isobars.

For He_3 steady state refrigerators to be operated at very low temperature or temperatures only one expansion engine need be used. The indicated isentropic efficiency between 16.0°K, 10.0 atm, 363.9 J/Mol and 7.0°K, 0.7 atm, 196.95 J/Mol is 80.5%. The solution for an He_3 refrigerator evaporating at 0.01 atm is shown in Figure One on the basis of a cold end flow of 1.0 Mol/S. Not shown is the necessary heat leak shield which would be a separate He_4 cold gas refrigeration subsystem.

A few comments relating to the He_3 cycle are of interest. Three J-T valves are used but a 2-phase cold end expander cannot be justified because yield in the 0.7 atm liquefier should be 100%. The liquid yield into the evaporator should be close to 97.4%. The suction intake of the vapor pump is 2457.0 l/s which indicates the use of small, 1-stage, rotary screw machine having internal oil mist cooling. Discharged gas would be at 0.77 atm and 376°K MAX to prevent breakdown of oil. The He_3 compressor would be a 2-stage reciprocating unit having normal oil lubrication. Discharged gas would be at 11.0 atm and 481°K MAX to prevent damage to cast iron parts.

Starting at the liquid He_3 subcooler, heat exchanger duties are 31.05W, 94.64W, 195.96W, and 9,993.62W. The entropy at the single expander throttle (10.0 atm, 16.0°K) is almost the same as at the evaporator exhaust (0.01 atm, 0.97°K). The supply gas conditions of 303.15°K, 6379.89 J/Mol are set by maximum SLAC cooling tower water temperature and a 10°F approach in intercoolers and aftercooler. Lubricating oil used for cooling and lubrication would be removed by a twin 4-stage ambient separation set including centrifugal separator, 5 micron-rough filter, 99.9999% type oil separator and activated charcoal filters to trap residual oil vapor. This hypothetical He_3 cycle was hand calculated using listed data and data derived as outlined above.

A graphic plot of He_4 enthalpies versus temperature at low pressure isobars indicates all these isobars have the same enthalpy at 45°K. The same must apply to He_3 although there are no listed data. A replot of listed He_4 data units and with gas data S values adjusted by 5.38 J/Mol-°K is used in Figure One. One can use the quick approximations described hereinabove without bothering to program data. This is adequate for the design of low temperature refrigerators in the absence of rigorous mathematical solutions, backed by extensive experimental data and published in suitable form.

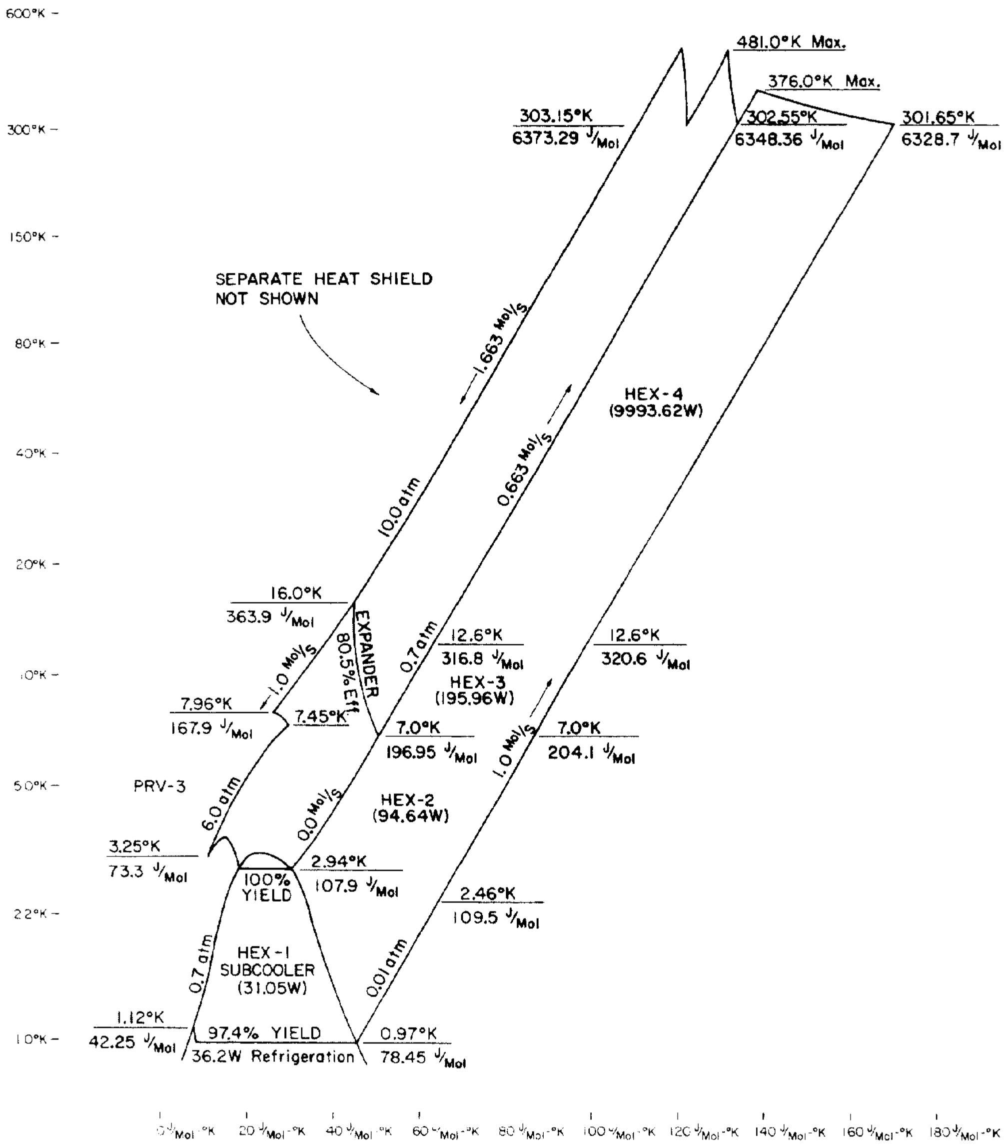

FIGURE ONE: S-LOG T DIAGRAM FOR HYPOTHETICAL HE_3 REFRIGERATION CYCLE