Appendix 9 Krypton Operations

When the **autosorb** iQ is supplied with the krypton option (ASiQ Krypton/MP), a turbo pump and a dry diaphragm backing pump have been installed. This pumping system is oil free and does not require a cold trap to prevent oil vapors from back streaming. The degassing cold trap should however be used to prevent liberated moisture from degrading the high vacuum levels achievable during degassing. At liquid nitrogen temperature of 77.35 K, krypton is below its triple point temperature and it sublimates. Its saturation pressure over solid is about 1.6 Torr. However, for the application of the BET method the saturation pressure of supercooled liquid krypton is usually adopted. The saturation pressure of the supercooled liquid krypton at 77.35 K is 2.63 Torr which is about 300 times lower than P_0 of liquid N_2. It follows that when Kr is used in the BET analysis, the absolute gas pressure in the sample cell is much lower than in the case when N_2 is used. This makes the corrections for void volume much smaller and measurement sensitivity much higher for the analysis with Kr compared to the standard N_2 analysis. You can use a value for the equilibrium vapor pressure of supercooled liquid krypton in any of the following ways during initialization:

- Normally it is manually entered from the keyboard. Enter 2.63 Torr as User Entered P_0.
- Alternatively you can instruct the **autosorb** iQ to solidify krypton in the P_0 cell and measure the equilibrium vapor pressure of solid krypton if this value is deemed appropriate.
- Enter a calculated value other than the usually accepted value of 2.63 Torr using the calculations below.

Equation (K.4), the Clausius-Clapeyron Equation, can be used to calculate the temperature of the liquid nitrogen bath from atmospheric pressure.

$$\ln\left(\frac{P_a}{760}\right) = \frac{\Delta H_v}{R}\left[\frac{1}{77.4} - \frac{1}{T}\right] \qquad \textbf{(K.4)}$$

Where, ΔH_v is the heat of vaporization of liquid nitrogen and P_a represents the local barometric pressure in torr.

This equation is used to calculate the bath temperature from ambient pressure assuming the heat of vaporization of liquid nitrogen is 1330 cal mol^{-1}.

From the calculated bath temperature, the saturated equilibrium vapor pressure of supercooled liquid krypton is calculated from Equation (K.5):

$$\log P_0 = -899.979(1/T) - 12.55400 \log T + 34.38392 + 0.0175105\,T \qquad \textbf{(K.5)}$$

For more information about the use of krypton for very low surface area measurements, please email qc.support@quantachrome.com and request Powder TechNote 51 "Low Surface Area Analysis by Krypton Adsorption at 77.4K".

For very low surface area samples, it is recommended to use a sample cell with large bulb to accommodate a larger amount of sample.

In addition to using krypton gas for increased sensitivity for determining very low surface areas, krypton can also be used at liquid argon temperature (~87K) for determining the pore size distribution in thin mesoporous films as used in lo-k dielectric materials. For more details, please email qc.support@quantachrome.com and request Powder TechNote 39 "Characterizing thin-film low-k dielectrics using krypton adsorption"