

Box 4 - The critical solvent

Isothermal compression of water vapour at several temperatures is represented by Andrews curves (figure B4.a). The liquid with its meniscus appears from the vapour at the dew point B and vapour disappears in D. The projection of BD on the (P,T) plane gives the liquid-vapour coexistence curve, comprised between the triple point and the critical point (see figure 2). The critical temperature T_c , the associated critical pressure P_c and critical volume V_c are defined when the B and D points coalesce (figure 28). Then, the fluid is in the supercritical state, intermediate between a liquid ($\rho > 0.3 \text{ g cm}^{-3}$) and a gas which fills completely the vessel.

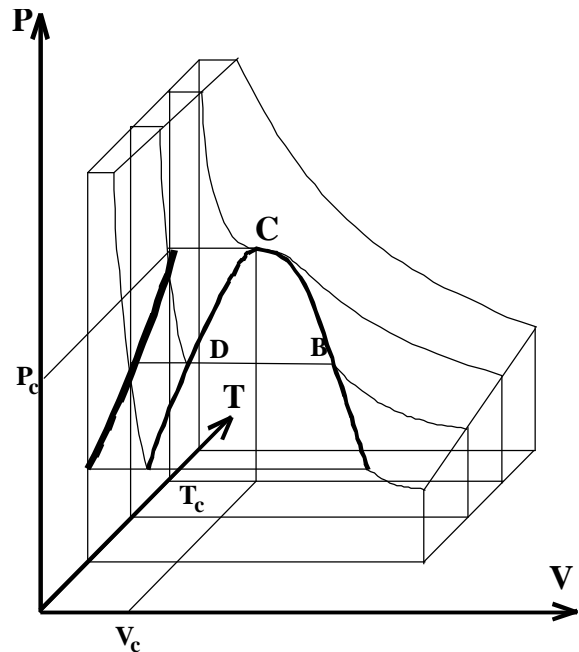


Figure B4.a - Isothermal compressibility of a solvent for various temperatures (Andrews curves)

For water, the critical values are $T_c = 647.13 \text{ K}$, $P_c = 22810^5 \text{ Pa}$, $V_c = 55.3 \text{ cm}^3 \text{ mol}^{-1}$ or $\tau_c = 0.322$ (τ =filling rate of the vessel at room temperature).

A representation of $P = f(T)$ can be given as a function of volume for a given amount of water or, preferably, as a function of filling rate τ (water in the vapour phase above the liquid is neglected). Kennedy curves are obtained (figure B4.b). At the critical filling rate $\tau_c = 0.322$, the level of the meniscus remains constant on heating, and disappears at T_c . At $\tau > \tau_c$, the liquid fills the vessel at $T < T_c$, and is supercritical at T_c . At $\tau < \tau_c$, the liquid disappears at $T < T_c$, the autoclave boils dry.

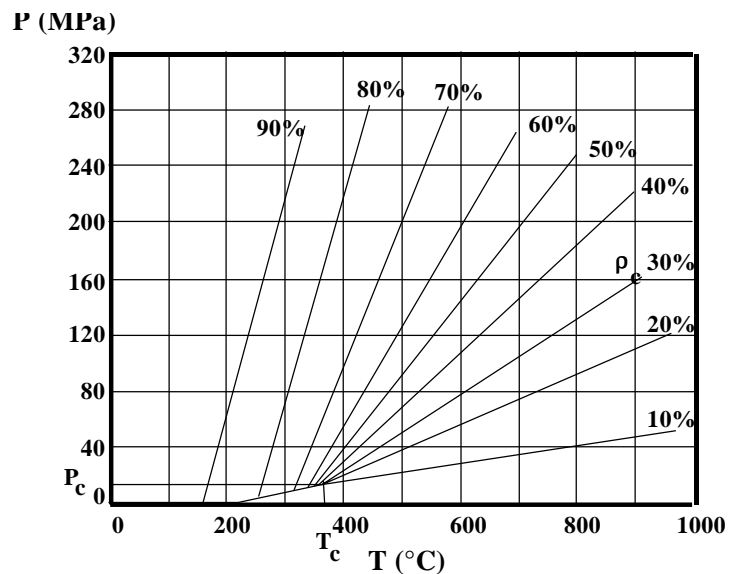


Fig B4.b - Variation of water pressure with the temperature for various filling rates of the autoclave.

The extreme parts of the Andrews curves are fairly well reproduced by the Van der Waals equation with : $a = 5.564 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 3.049 \cdot 10^{-2} \text{ L mol}^{-1}$:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}. \text{ These functions present a minimum, an inflexion point and a maximum which}$$

coalesce at the critical point ($\frac{dp}{dv} = \frac{d^2p}{dv^2} = 0$). Then, the critical constants are related to the Van der

$$\text{Waals constants : } T_c = \frac{8a}{27Rb} = 647 \text{ K}, P_c = \frac{a}{27b^2} = 21710^5 \text{ Pa}, V_c = 3b = 91.5 \text{ cm}^3 \text{ mol}^{-1}.$$