

10.40 Thermodynamics

Fall 2003

Problem Set 10

Problem 3

Estimate the critical constants (T_c , P_c), acentric factor (ω) and vapor pressure of pure caffeine as described in Problem 13.4 of the text. To solve this problem you will have to review the methods presented in Chapter 13 for predicting physical properties using molecular group contributions. (Note: Since the $>N-$ (ring) group is not listed, use the $>N-$ (non-ring) group in its place).

Solution:

Start with Joback's method for estimating critical properties. Dividing caffeine into molecular groups

Group	v_j	ΔT_c	ΔP_c	ΔV_c	ΔT_b
$-CH_3$	3	0.0141	-0.0012	65	23.58
$>C=O$ (ring)	2	0.0284	0.0028	55	94.97
$=CH-$ (ring)	1	0.0082	0.0011	41	26.73
$=C<$ (ring)	2	0.0143	0.0008	32	31.01
$-N=$ (ring)	1	0.0085	0.0076	34	57.55
$-N<$ (non-ring)	3	0.0169	0.0074	9	11.74
	$\sum v_j \Delta_j$	0.1951	0.0345	471	442.2

$n_a = 24$ (number of atoms)

$m = 194$ (molecular weight)

Using Equations (13-5) and (13-6) for the Joback method

$$T_b = 198 + 442.2 = 640 \text{ K} \quad (1)$$

$$T_c = T_b / [0.584 + 0.965(0.1951) - (0.1951)^2] = 872 \text{ K} \quad (2)$$

or alternatively using the Klincewicz and Reid formulation (Eq. (13-7))

$$T_c = 50.2 - 0.16(194) + 640 = 659 \text{ K} \quad (3)$$

Given the large discrepancy, we recommend using Joback's formulation for T_c for consistency (4)

$$P_c = 1/(0.113 + 0.0032(24) - 0.0345)^2 = 41.46 \text{ bar}$$

To estimate vapor pressure, use Eq. (13-18) with T_b , T_c , and P_c estimates substituted appropriately:

$$\ln \left(\frac{P_{vp}}{P_c} \right) = h^* \left(1 - \frac{T_c}{T} \right) \quad (5)$$

$$h^* = \frac{T_b}{T_c} \left[\frac{\ln(P_c/1.013)}{1 - T_b/T_c} \right] = \frac{640}{872} \left[\frac{\ln(41.46/1.013)}{1 - 640/872} \right] = 10.24 \quad (6)$$

$$\ln P_{vp} = \ln(32.54) + 10.24(1 - 872/T) = 3.483 + 10.24(1 - 872/T) \quad (7)$$

for the density we can use Corresponding States as a first approximation with an estimated ω and mixture pseudo-critical properties used. For pure caffeine, use Eq. (13-9)

$$\omega = \frac{3}{7} \left[\frac{640/872}{1 - 640/872} \log_{10} \left[\frac{41.46}{1.013} \right] \right] - 1 = 0.9058$$

A more accurate ω can be calculated with Eq. (13-8) and the experimental data given in problem statement 13.4.

$$\omega = -\log_{10} \left[\frac{P_{vp}(\text{at } T_r = 0.7)}{P_c} \right] - 1.0 \quad (13-8)$$

From T_c in Eq. 3, $T = 337^\circ\text{C}$ at $T_r = 0.7$. Thus, the equation for liquid caffeine is used to calculate the vapor pressure at $T_r = 0.7$.

$$\log_{10}(P \text{ in Pa}) = -3918/610 + 11.143 = 52998 \text{ Pa} = 0.53 \text{ bar} \quad (8)$$

Plugging the result of Eq. (8) into (13-8) yields $\omega = 0.894$, which is close to the result found using Eq. (13-9).