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R.L. Cotterman, D. Dimitrelis, and J.M. Prausnitz

April 1984

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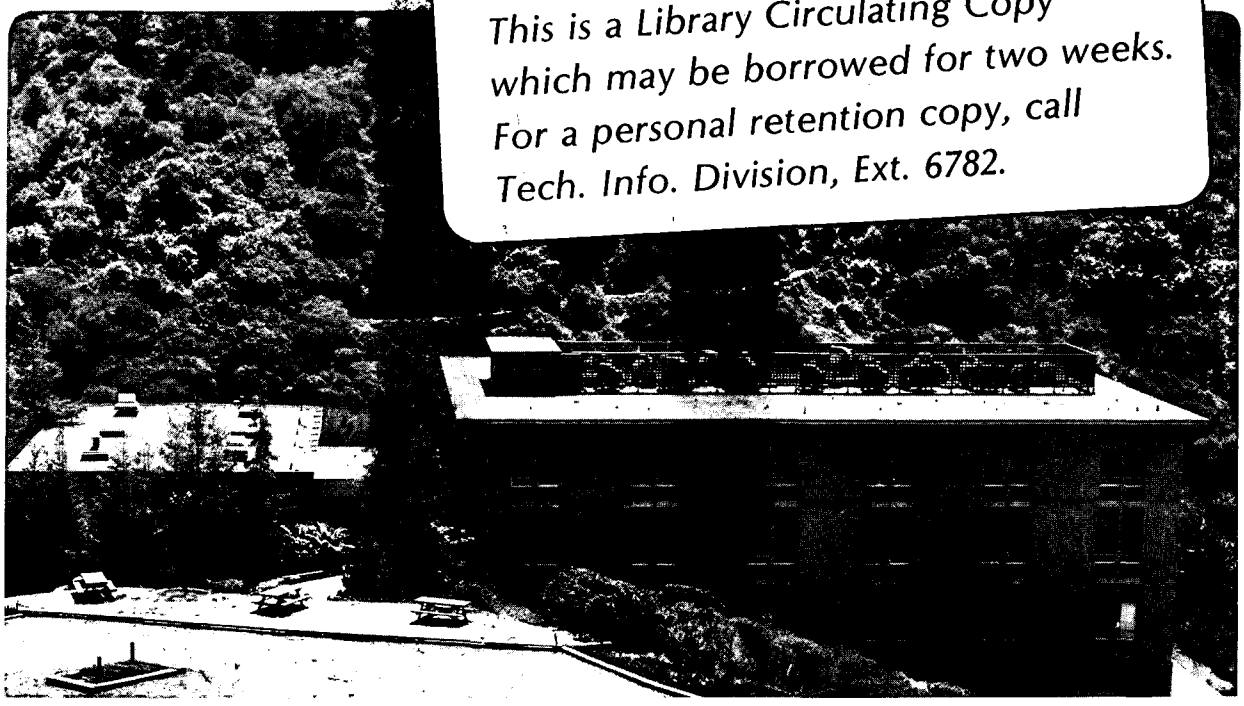

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SUPERCRITICAL-FLUID EXTRACTION CALCULATIONS FOR HIGH-BOILING PETROLEUM FRACTIONS USING PROPANE. APPLICATION OF CONTINUOUS THERMODYNAMICS

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ABSTRACT

Supercritical-fluid extraction is a useful process for upgrading heavy multicomponent mixtures such as high-boiling petroleum fractions. Design-oriented calculations are reported for an extraction process using propane to extract intermediate components from a petroleum fraction with molecular weights in the range 150-500.

The composition of the heavy-hydrocarbon mixture is described by two continuous distribution functions of molecular weight, one for paraffinic and one for aromatic components. Process calculations are based on a recently developed thermodynamic framework for mixtures with very many components, coupled with an equation of state of the van der Waals form.

Particular attention is given to multicomponent phase equilibria in the retrograde region where solvent recovery is favorable. Quantitative results are given for solvent capacity and selectivity as a function of operating conditions.

1. Introduction

Supercritical-fluid extraction is a useful process for upgrading heavy crude petroleum residua, for extracting polymer blends or for purifying natural products such as vegetable oils [1,2,3,4]. A common characteristic of these systems is that they are mixtures with very many components. While the study of binary or ternary mixtures [5,6,7] is important for understanding the effects of process variables on supercritical-fluid extraction of desired products, for engineering design it is often necessary to describe the properties of mixtures with very many components.

Figure 1 shows a schematic of a supercritical extraction process (e.g. propane deasphalting). A heavy crude residuum is to be upgraded using a supercritical solvent. In a typical extractor, supercritical propane may extract from the crude the lighter components; it is then separated from the solutes in a second step by temperature increase or pressure drop and finally, it is recycled back to the extractor. Efficient solvent regeneration is the most important advantage when supercritical-fluid extraction is compared with conventional liquid-liquid extraction.

In this work we discuss application to supercritical-fluid extraction of recent work [8,9] on the framework of continuous thermodynamics (i.e. thermodynamics of mixtures with very many components). Continuous thermodynamics provides a useful method for calculating phase equilibria for those mixtures where conventional quantitative chemical analysis is not available but where the mixture's composition is given by some statistical description. We present illustrative calculations to indicate the effect of operating conditions (temperature T and pressure P) on supercritical extraction of a continuous mixture consisting of two ensembles (paraffins and aromatics). We

also discuss conditions leading to preferential extraction of lighter hydrocarbons and selective extraction of paraffins relative to aromatics.

2. Procedure

2.1 Thermodynamic Framework

Figure 2 contrasts the compositions of a discrete and a continuous mixture. On the left, the composition of a mixture with a finite number of components (in this case ten) is characterized by mole fractions x_i (for each component i) indicated by a bar; the sum of all mole fractions equals unity. For a continuous mixture (i.e. a mixture with very many components), shown on the right of Figure 2, we describe the composition of the mixture in terms of a distribution variable I (e.g. molecular weight); instead of mole fractions, we now have a distribution function F(I) such that F(I) ΔI is the fraction of moles within the range I to $I+\Delta I$. The normalization condition is now given by an integral shown at the bottom.

Suppose that we have a liquid phase (L) and a supercritical phase (SF) at equilibrium; as discussed elsewhere [8], the conditions for equilibrium for the case of a semi-continuous mixture are

$$T^L = T^{SF} \quad , \tag{1}$$

$$p^L = p^{SF} \quad , \tag{2}$$

for every discrete component i

$$f_i^L = f_i^{SF} \quad , \tag{3}$$

and for every continuous component

$$f^L(I) = f^{SF}(I) \quad \text{for all I,} \tag{4}$$

where fugacity f can be calculated from an equation of state; for the fugacity of a continuous component in the liquid phase, we have

$$\ln \frac{f^L(I)}{F^L(I)\ P} = \int_{V^L}^{\infty} \left\{ \left(\frac{\delta(P/RT)}{\delta(n_T^L\ F^L(I))} \right)_{T,V,I^\dagger} - \frac{1}{V} \right\} dV - \ln \frac{P\ V^L}{n_T^L\ F^L(I)\ RT} \quad (5)$$

where n_T^L is the total number of moles of continuous component and V^L is the volume of the liquid phase. Symbol δ stands for the functional derivative operator [8,10]. A similar relation holds for the fugacity in the supercritical phase.

Flash calculations are essential for engineering design of supercritical-extraction processes, as indicated in Figure 3. Given the temperature, pressure and feed composition, it is necessary to calculate compositions and relative amounts of the two outlet streams. The outlet streams are assumed to be in thermodynamic equilibrium; further, feed and outlet streams are related through material balances. Material balances and phase equilibria must be solved simultaneously using numerical methods as discussed elsewhere [9].

2.2 Fluid-Phase Equilibria for a Semi-Continuous Mixture of Propane with Heavy Hydrocarbons

For illustrative purposes, we represent the heavy crude residuum by a model mixture consisting of two ensembles, paraffins and aromatics. Figure 4 shows the assumed distributions that describe the feed. Throughout these calculations we assume that in the feed the molar ratio of paraffins to aromatics is 3. We further assume that the molar distributions in the feed are given by a gamma distribution function [11] with mean molecular weights of 200 and 225, and variances of 1000 and 1600, respectively . The molecular weight of the lightest paraffin is 150 and that of the lightest aromatic is 170. However, our calculational procedure is not restricted by a particular choice of distribution function. The distribution could be specified in a functional form (as is

the case here) or by numerical data at selected points in a range of the characterizing quantity I.

To represent the phase behavior of the propane/heavy-hydrocarbon mixture, we use an equation of state similar to that of Redlich-Kwong as modified by Soave [12]. This choice restricts us in the upper limit of heavies to approximately I=500 (molecular weight). Pure-component equation-of-state parameters a and b are fitted to vapor-pressure data as a function of molecular weight (MW):

$$b = b^{(0)} + b^{(1)}\ [MW] \tag{6}$$

$$a^{1/2} = a^{(0)}(T) + a^{(1)}(T)\ [MW] \tag{7}$$

for normal paraffins from C_4 to C_{40} and for alkylbenzenes from C_6 to C_{22} [9]. For the mixture we use conventional mixing rules as discussed elsewhere [8,9]. For binary interaction parameter a_{rs}, we use

$$a_{rs} = (a_r a_s)^{1/2}(1-k_{rs}). \tag{8}$$

From experimental vapor-liquid equilibrium (VLE) data, we obtain for propane-paraffins,

$$k_{rs} = -\ 0.05 + 0.1264\ \exp(-0.0068\ [MW]). \tag{9}$$

Because of the small number of VLE data available for propane-alkylbenzene binaries, k_{rs} is set equal to 0.03, independent of molecular weight. For the paraffins-aromatics interactions, we set k_{rs} equal to zero.

Figure 5 shows a pressure-temperature diagram for semi-continuous mixtures of propane with heavy hydrocarbons. Shown are the vapor pressure curve for pure propane and isopleths (lines of constant composition) for mixtures. From the locations of the calculated mixture critical points, we can conclude that there is a continuous critical locus between the critical point

of pure propane and the critical point of the 100 mole % heavies isopleth. This is consistent with experimental evidence that the first propane/n-alkane system which exhibits a discontinuous critical locus is for a heavy component above C_{40} [13]; our system is a Type I mixture according to the classification of Scott and van Konynenburg [14].

Our phase-diagram calculations are performed using a direct-substitution method, described elsewhere [15]. A one-dimensional Newton-Raphson iteration is used to converge for the fraction vaporized using the Rachford-Rice objective function [16]. Estimated K-factors are updated for each iteration by successive substitution. We define K-factors :

$$K_i = \frac{y_i}{x_i} \tag{10}$$

for a discrete component i and

$$K(I) = \left(\frac{\eta^{SF}}{\eta^{L}}\right) \left(\frac{F^{SF}(I)}{F^{L}(I)}\right) \tag{11}$$

for a continuous component (see Figure 3).

This numerical procedure is stable; it converges smoothly and rapidly at low and moderate pressures. However, in the retrograde region, near the mixture critical point, good initial guesses of compositions are necessary and a large number of iterations are required for convergence. More efficient computational methods are now under development [17].

3. Results

Figure 6 shows the effect of pressure on the extraction of a mixture of heavy hydrocarbons at 520 K. The feed is composed of 90 mole % propane; the

remaining 10 mole % are heavies. Results are presented for 6 and 10 MPa in the form of molar distribution functions (defined as the number of moles of continuous component in a given stream within the range I to I+ΔI on the basis of 1 mole total feed) for both ensembles, paraffins and aromatics, in the feed (specified) and in the outlet (calculated) streams. Comparing peak heights in the extract phase for both ensembles, we see an increase with rising pressure. Raising the pressure from 6 to 10 MPa, therefore, increases solvent capacity which is here defined as the mole fraction of heavies (paraffins and aromatics) in the fluid phase.

While solvent capacity is an important design variable, more important is solvent selectivity. Of interest here are two types of selectivity. The first is with respect to molecular weight and the second is with respect to molecular structure (paraffins versus aromatics).

We can qualitatively understand the effect of pressure on the preferential extraction of intermediate hydrocarbons (paraffins or aromatics) by comparing the shape of the calculated distribution function for the fluid phase at one pressure with that of another pressure. As shown in Figure 6, at 6 MPa, the fluid-phase distribution function indicates that there is essentially no extraction for hydrocarbons with a molecular weight larger than (about) 280. However, at 10 MPa, the fluid-phase distribution function indicates that there is essentially no extraction for hydrocarbons with a molecular weight larger than (about) 320. These results suggest that, in the region investigated, selectivity (of the first kind) falls with rising pressure.

For more detailed quantitative calculations of capacity and selectivity, we consider a mixture where the molar solvent-to-feed ratio is 96/4 ($z_{C_3H_8}$=0.96). While this molar ratio is high, the corresponding mass ratio is much lower.

This ratio is representative of conditions in the second stage of a multi-stage extraction process [18]. For these conditions, the retrograde region is large, as shown in Figure 7.

Figure 8 shows that at constant pressure the capacity depends strongly on temperature. At pressures near 7 or 8 MPa, which are above the mixture critical point, capacity decreases drastically when the temperature is raised slightly. For the 7 MPa isobar, a change from 420 to 430 K decreases the capacity by a factor of two. As indicated in Figure 8, it is not desirable to operate at 5 MPa because a change in temperature will not be useful for solvent regeneration.

Figure 9 shows selectivity (of the second kind) as a function of temperature; at the conditions considered here, propane prefers paraffins (P) to aromatics (A). Selectivity $\beta_{P/A}$ is defined by

$$\beta_{P/A} = \frac{(\eta^{SF}/\eta^{L})_{Paraffins}}{(\eta^{SF}/\eta^{L})_{Aromatics}}.$$

At 7 MPa, selectivity is highly sensitive to temperature. Therefore, if the purpose of the extraction is to remove paraffins from aromatics, it may be desirable to use a multistage process at 7 MPa where the temperature changes, from one stage to another, in the region 420 to 430 K.

Figure 10 presents K-factors (eq. 10) for paraffins and for aromatics as a function of molecular weight. Figure 10 shows that selectivity of the first kind is good at all these pressures but it is best at 5 MPa where the slope of the line is largest. At pressures above 8 MPa, the lines tend to flatten, giving poor selectivity of the first kind.

At a fixed molecular weight, the ratio of K-factors (paraffins/aromatics) gives the selectivity (of the second kind) as a function of molecular weight, shown in Figure 11. We see that the selectivity is low at lower molecular weights but rises with increasing molecular weight; further, selectivity is better at lower pressures.

The results shown in Figures 10 and 11 indicate that propane is a useful solvent if the purpose of the extraction is to obtain separation with respect to molecular weight; it is only moderately useful if the purpose of the extraction is to obtain separation with respect to molecular structure.

The calculations presented here are for mixtures with molecular weights below 500. In present petroleum technology, primary interest in supercritical extraction is directed at mixtures with considerably higher molecular weights. While the calculational procedures discussed here are not limited with respect to molecular weight, we have not presented results for very-high-molecular-weight mixtures because, for our illustrative purposes, we used an equation of state of the Redlich-Kwong-Soave form; unfortunately, that equation of state is not suitable for hydrocarbons with molecular weights appreciably in excess of 500. However, calculations for such mixtures are possible when we use a perturbed-hard-chain equation of state; such calculations are now in progress.

Supercritical extraction is most useful in the retrograde region. When propane is the solvent, the size of this region increases with the molecular weight of the heavy hydrocarbons [19]. A large retrograde region is desirable because it permits flexibility in setting temperature and pressure for optimum operation.

4. Conclusions

The operational advantage of supercritical-fluid extraction is efficient solvent recovery. Flash calculations using continuous thermodynamics provide detailed process information for both extract and raffinate streams at given operating conditions. We have illustrated the advantages of such calculations for extraction of a 3:1 paraffin/aromatic mixture with supercritical propane.

Using a modified Redlich-Kwong-Soave equation of state, we found that, in the retrograde region, rising pressure decreases preferential extraction of paraffins to aromatics but increases the capacity of the heavies in the supercritical-fluid phase. For paraffin-aromatic residua, propane is a good selective solvent with respect to molecular weight but only a modest one with respect to molecular structure.

The results presented for solvent capacity and paraffin/aromatic selectivity depend, in general, on the values of binary parameter k_{rs}. We found that for propane/heavy hydrocarbons, the results are relatively insensitive to reasonable values of k_{rs}. However, for other solvents (e.g. carbon dioxide), results are often sensitive to the binary parameters. In some cases, these binary parameters may affect the qualitative shape of the phase diagram (change from type I to type III) [20].

While the illustrative calculations presented in this paper are for relatively simple mixtures, the procedure can be applied to any mixture for which we can establish a suitable molecular-thermodynamic equation of state. The important conclusion of our work is that we can now make realistic calculations for supercritical extraction of mixtures containing very many components as encountered in industrial practice.

Acknowledgements

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. For partial financial support, the authors are also grateful to the Fannie and John Hertz Foundation, to Exxon Research and Engineering Company, to the Donors of the Petroleum Research Fund, administered by the American Chemical Society and to the National Science Foundation.

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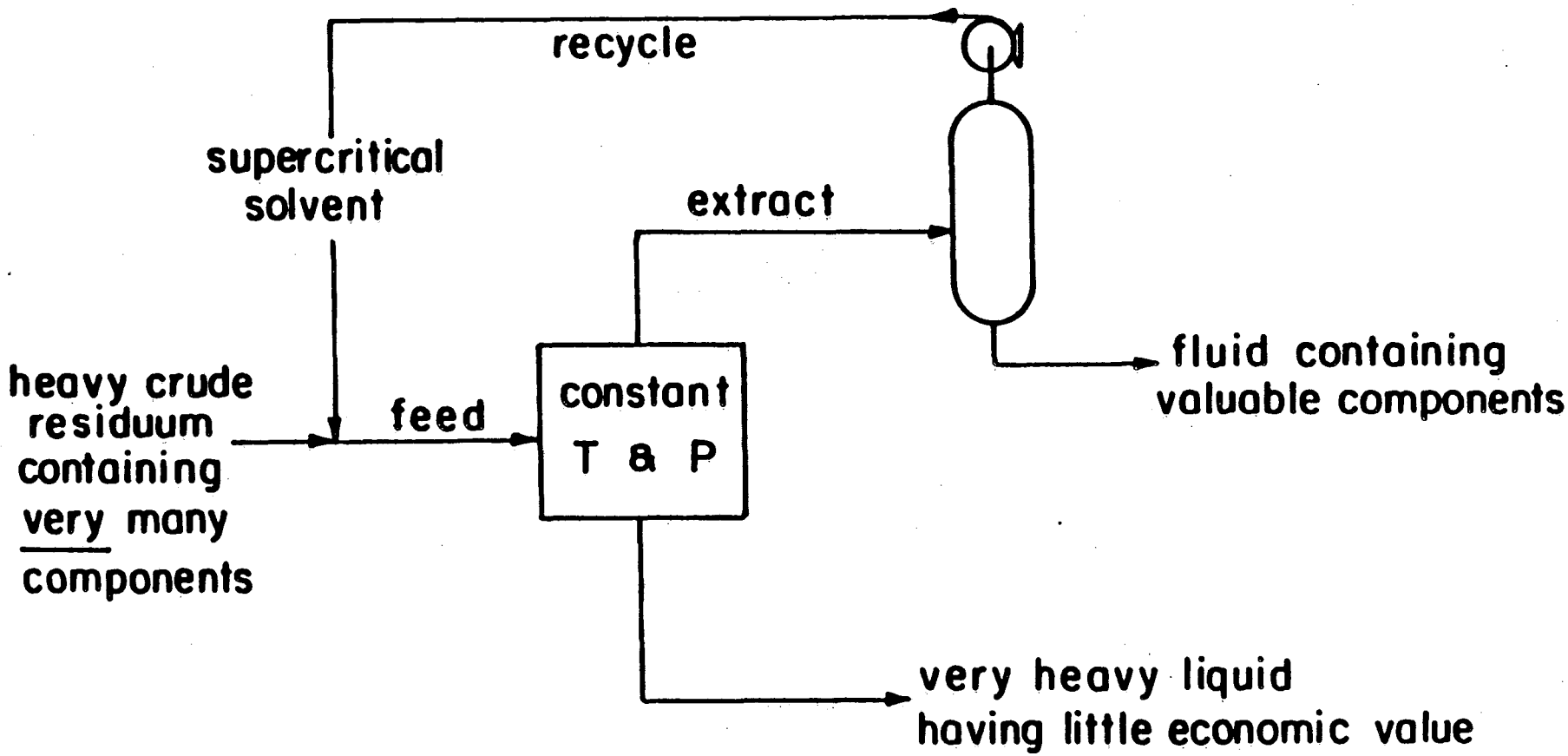
SUPERCRITICAL FLUID EXTRACTION CALCULATIONS FOR HIGH-BOILING PETROLEUM FRACTIONS USING PROPANE

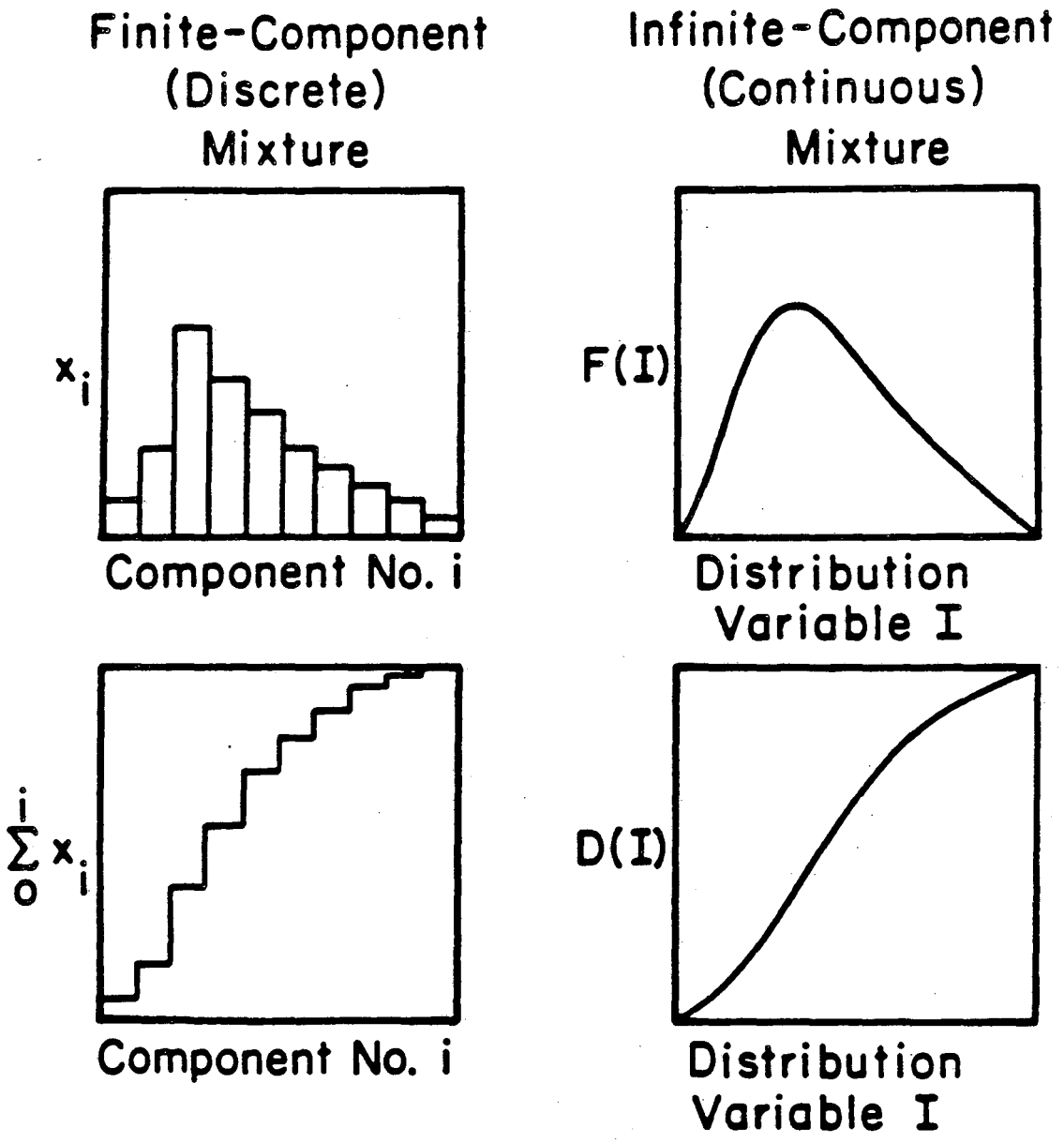
Application of Continuous Thermodynamics



The solvent is supercritical to facilitate solvent recovery

Figure 1

DISCRETE AND CONTINUOUS COMPOSITION FOR A MULTICOMPONENT MIXTURE



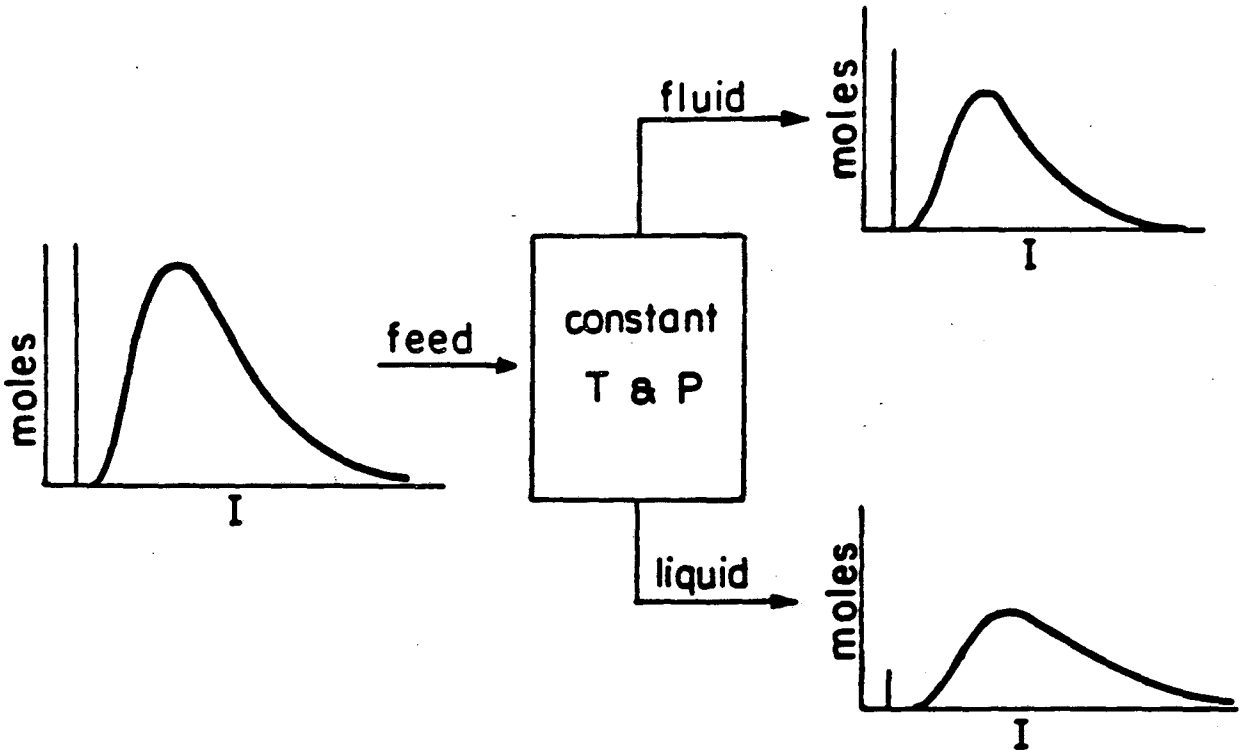
$$\sum_{\text{all } i} x_i = 1.0 \qquad D(I=\infty) = \int_0^\infty F(I)dI = 1.0$$

x = Mole Fraction F = Distribution Function

I is a characterizing quantity, e.g., molecular weight.

Figure 2

FLASH CALCULATION FOR A SEMI-CONTINUOUS MIXTURE



Must satisfy:

Phase Equilibria

$f_i^{SF} = f_i^{L}$

$f^{SF}(I) = f^{L}(I)$ for all I

SF = supercritical fluid

L = liquid

Material Balance

$z_i = \xi y_i + (1-\xi) x_i$

$\eta^F F^F(I) = \xi \eta^{SF} F^{SF}(I) + (1-\xi)\eta^L F^L(I)$

z_i, y_i, x_i feed, fluid and liquid mole fraction for discrete component i

ξ fraction of feed in extract

η mole fraction of the continuous component

Figure 3

MOLAR DISTRIBUTION OF HEAVIES IN THE FEED

$$\left(\frac{\text{paraffins}}{\text{aromatics}} = 3\right)$$

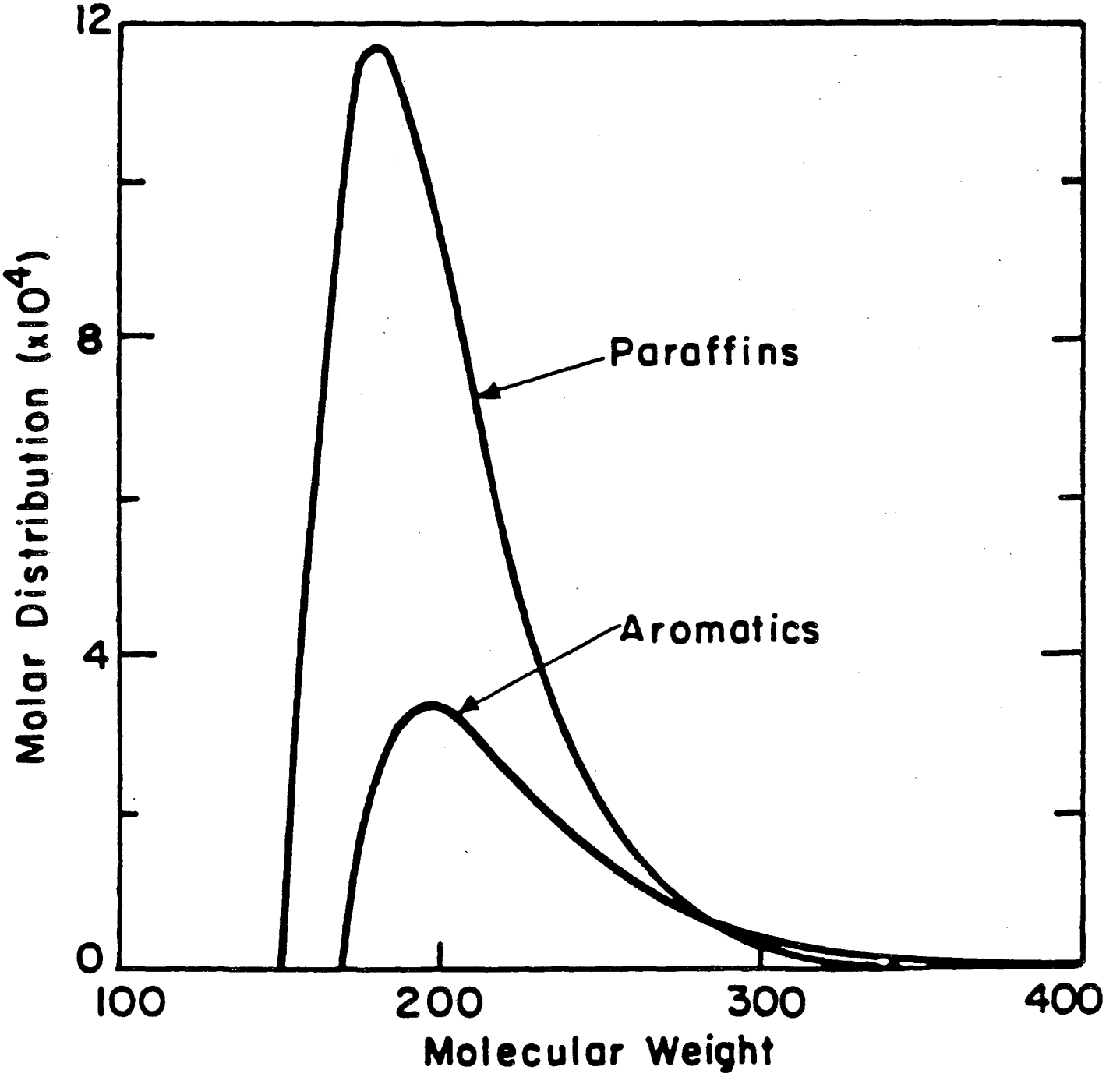


Figure 4

PRESSURE-TEMPERATURE DIAGRAM FOR A SEMI-CONTINUOUS MIXTURE OF PROPANE WITH PARAFFINS AND AROMATICS

$\left(\frac{\text{paraffin}}{\text{aromatic}} = 3\right)$

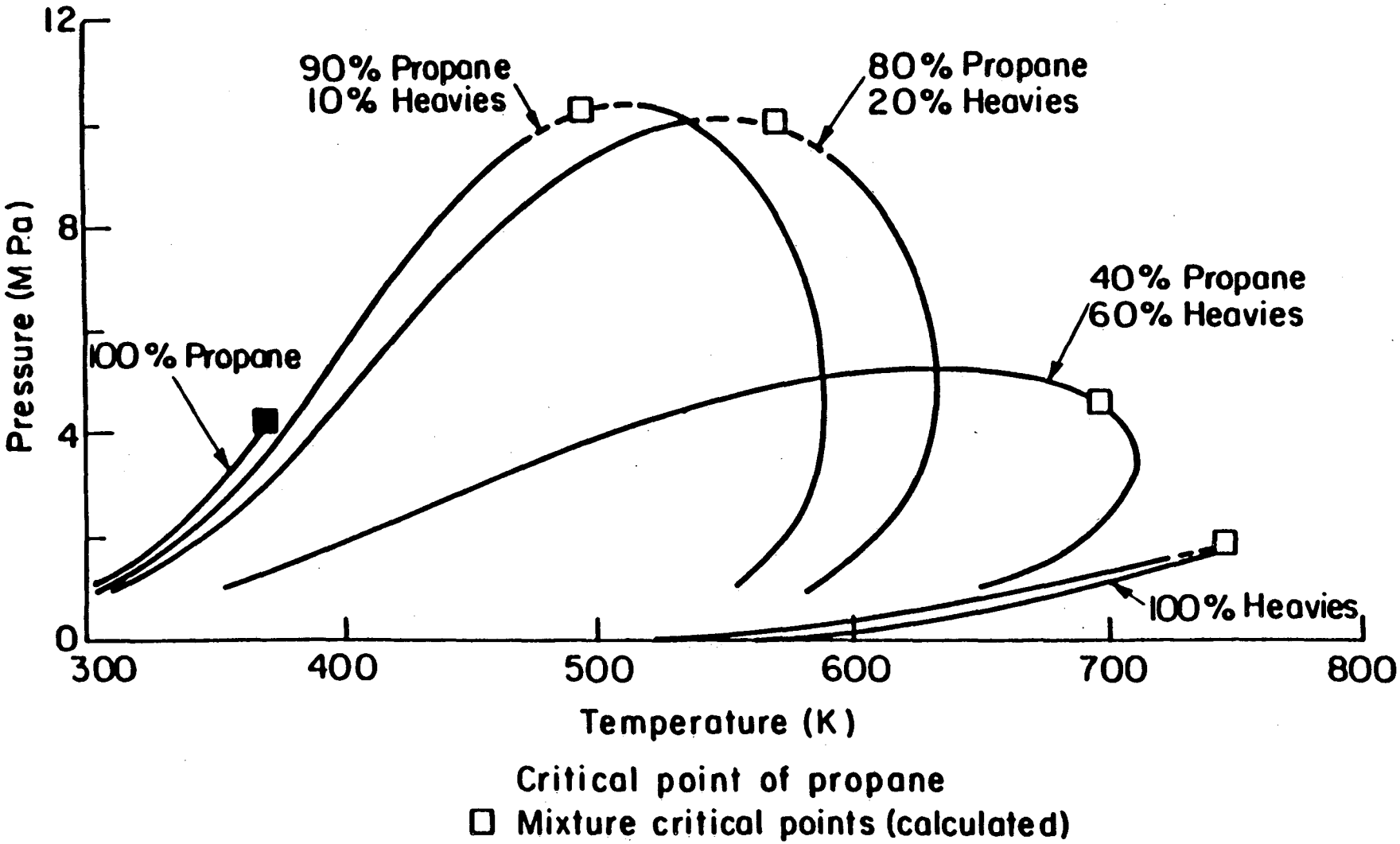


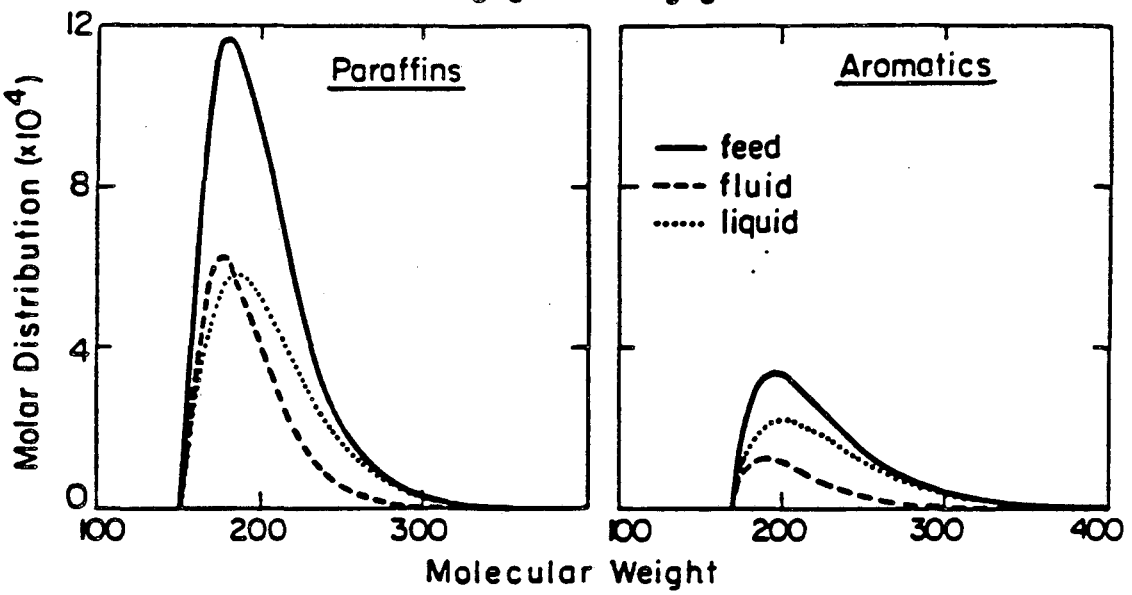
Figure 5

EFFECT OF PRESSURE ON THE EXTRACTION OF A CONTINUOUS MIXTURE CONTAINING PARAFFINS AND AROMATICS USING PROPANE AS A SOLVENT

($T = 520K$; $z_{C_3H_8} = 0.90$)

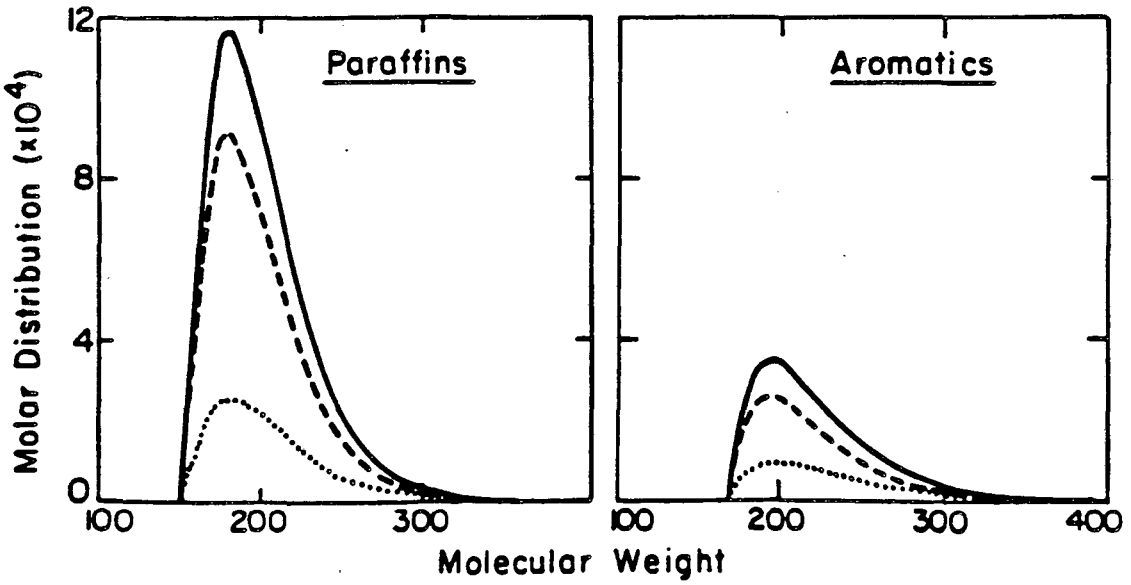
P = 6 MPa

$y_{C_3H_8} = 0.95$; $x_{C_3H_8} = 0.53$



P = 10 MPa

$y_{C_3H_8} = 0.92$; $x_{C_3H_8} = 0.79$



AS PRESSURE RISES:

- Capacity increases
- Selectivity decreases

Figure 6

PRESSURE-TEMPERATURE DIAGRAM FOR A SEMI-CONTINUOUS MIXTURE OF PROPANE WITH HEAVY HYDROCARBONS

($z_{C_3H_8}$ = 0.96)

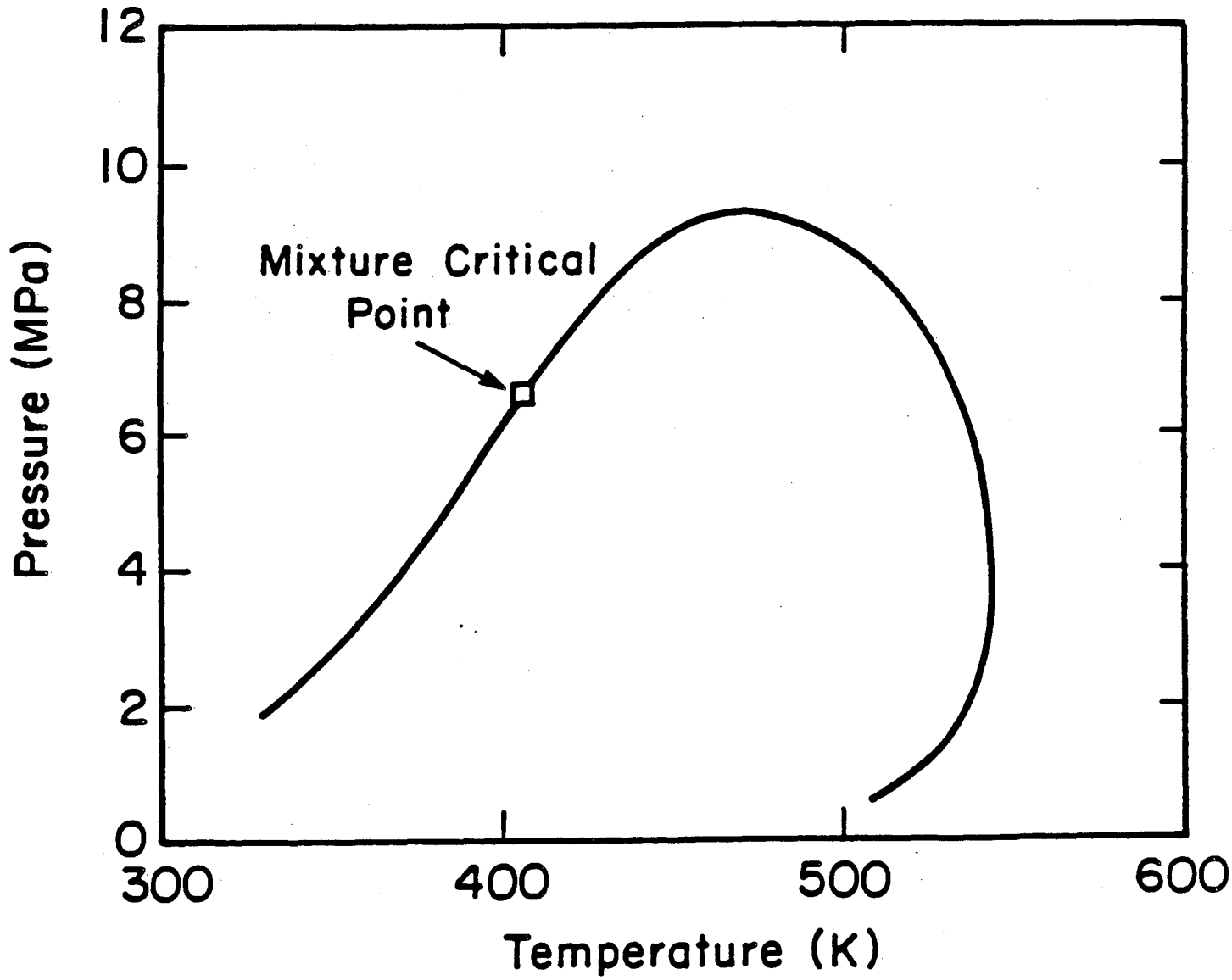


Figure 7

EFFECT OF TEMPERATURE ON SOLVENT CAPACITY AT CONSTANT PRESSURE

($z_{C_3H_8}$ = 0.96)

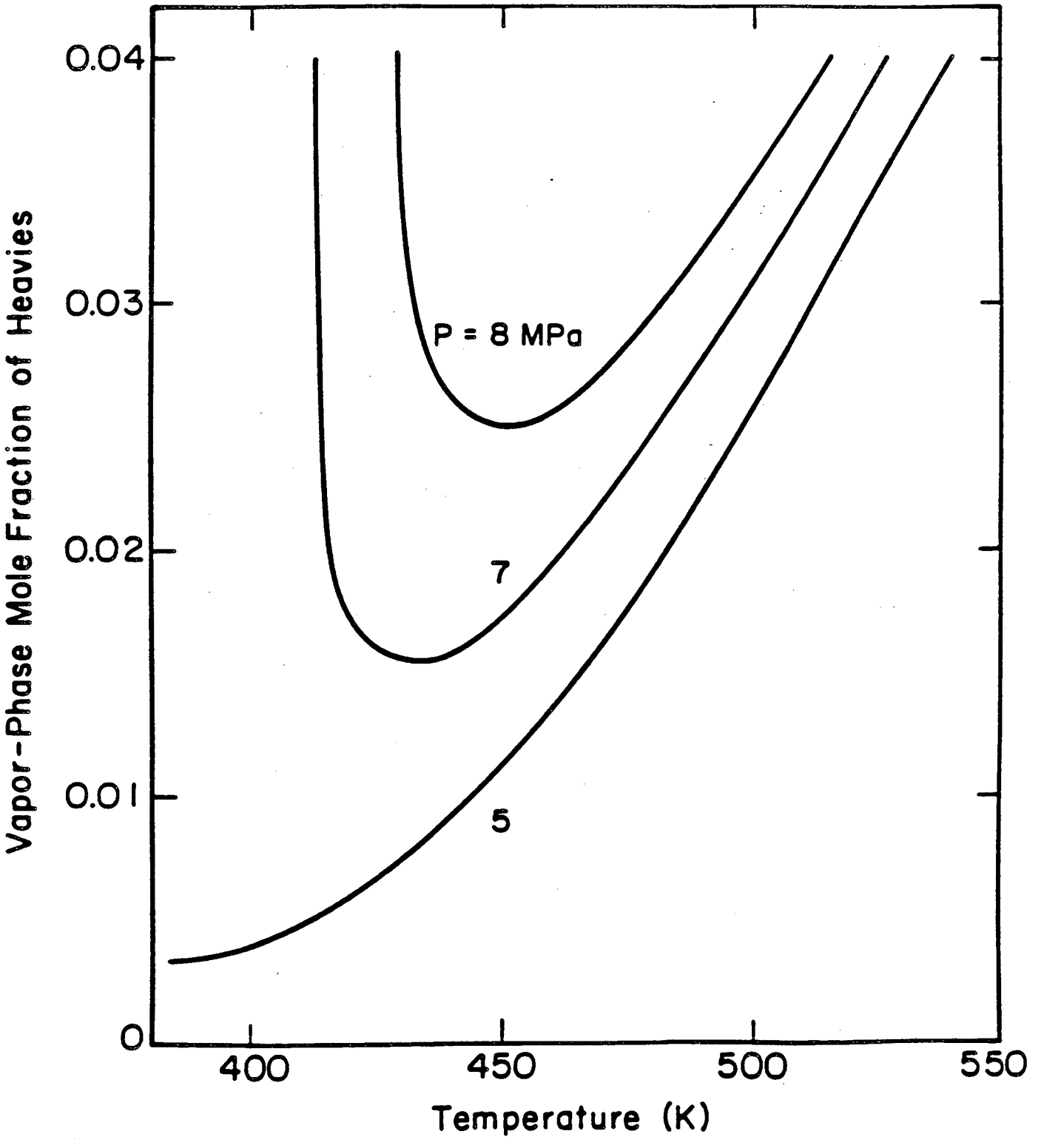


Figure 8

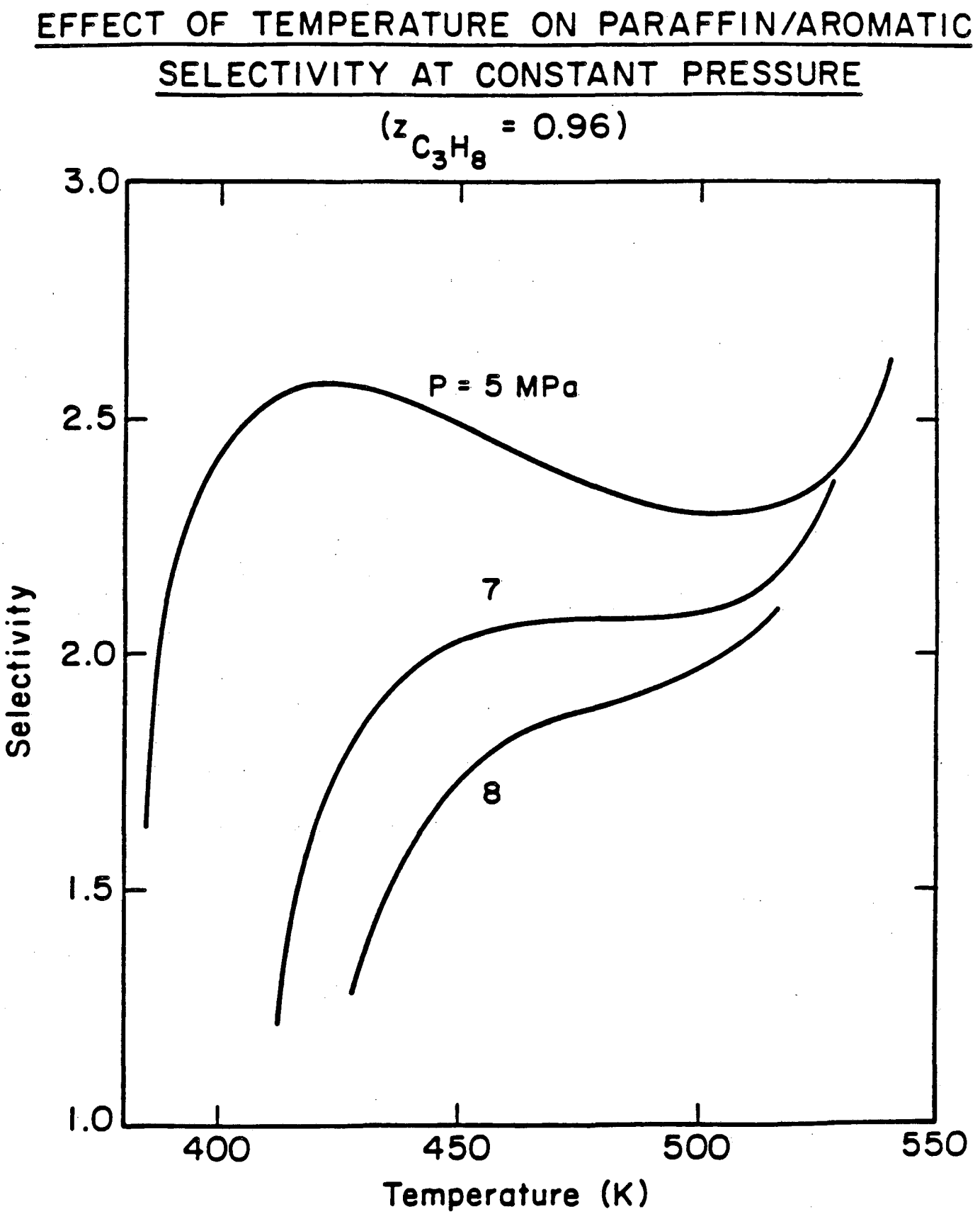

EFFECT OF TEMPERATURE ON PARAFFIN/AROMATIC
SELECTIVITY AT CONSTANT PRESSURE
($z_{C_3H_8}$ = 0.96)
3.0
2.5
2.0
1.5
1.0
Selectivity
P = 5 MPa
7
8
400
450
500
550
Temperature (K)

Figure 9

K-FACTORS OF THE CONTINUOUS FRACTIONS IN THE PROPANE/HEAVY-HYDROCARBON SYSTEM

($T = 450$ K; $z_{C_3H_8} = 0.96$)

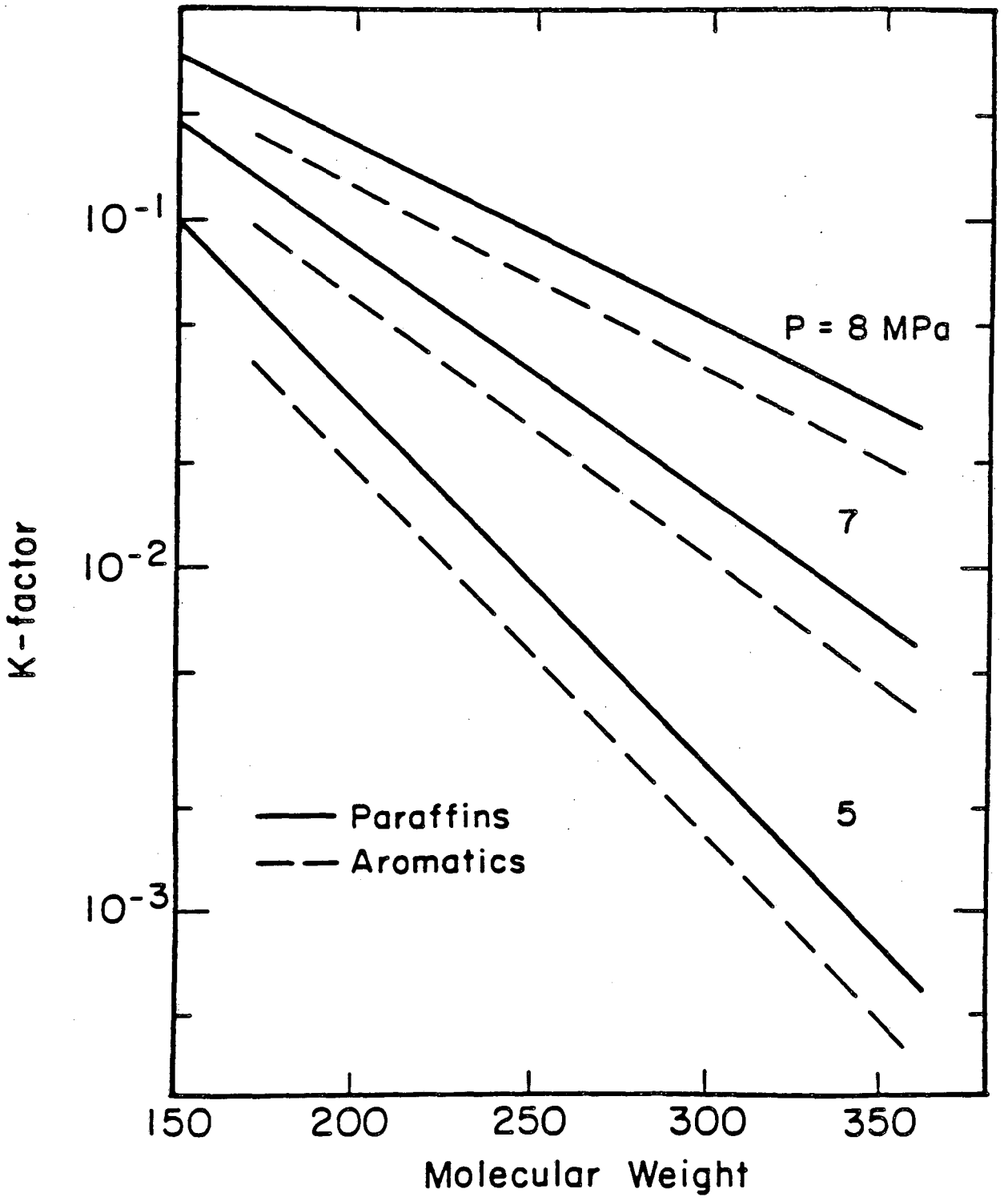


Figure 10

PARAFFIN/AROMATIC SELECTIVITY IN THE PROPANE/HEAVY-HYDROCARBON SYSTEM

($T = 450$ K; $z_{C_3H_8} = 0.96$)

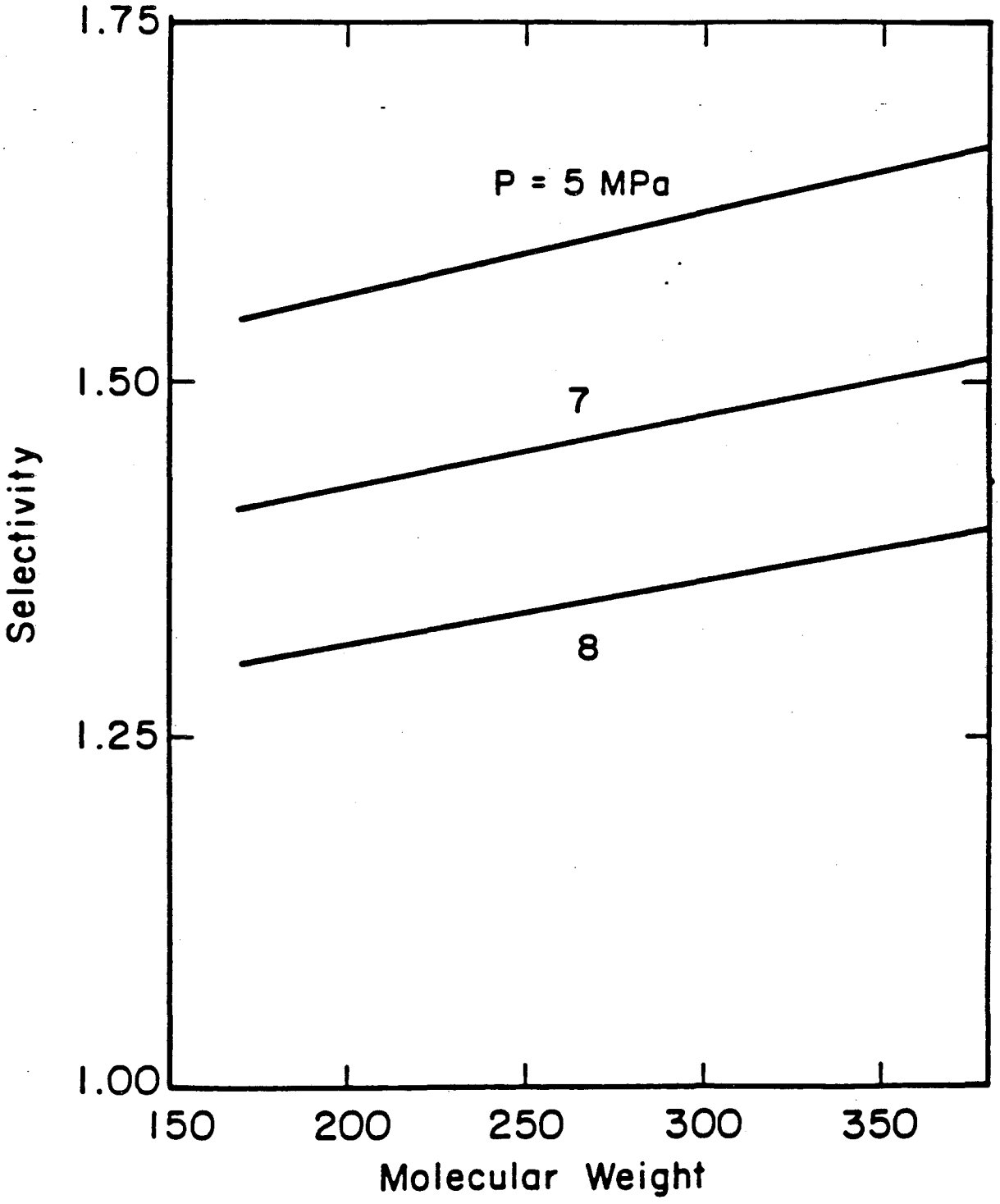


Figure 11

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