SEPARATION OF GAS MIXTURES VIA BATCH PARAMETRIC PUMPING - A THEORETICAL STUDY

BY

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ABSTRACT

An equilibrium plug-flow model, for the batch isothermal separation of a binary gas mixture in a pressure changing parametric pump, was investigated for the system propane-argon on carbon, with the aid of a G. E. Pack 4020 computer. Separation factors comparable to a temperature changing parametric pump are predicted by the model. A change in pressure of the gas mixture may be carried out very rapidly, compared with a temperature change of similar magnitude. The effects of temperature, pressure, concentration, and penetration are discussed.

APPROVAL OF THESIS

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TABLE CAPTIONS

TABLE 1 : Summary of Parametric Pumping Processes.

INTRODUCTION

Since the original work of Wilhelm and Sweed (1) describing the Parametric Pumping Process utilizing the different adsorption characteristics of two miscible fluids at different temperatures, many other alternatives and models have been studied.

An equilibrium theory of the parametric pump was presented for a temperature cycling system by Pigford, Burke and Blum (2), and the characteristics of batch, semi-continuous and continuous equilibrium parametric pumps were studied by Chen and Hill (4).

All the above work was concerned with parametric pump systems using temperature as the changing parameter.

Pressure swinging adsorption systems have been used commercially for drying air (5) and for purifying hydrogen (3), a process developed by the Linde Division of Union Carbide Corporation. Several hydrogen purifiers are in operation. They consist of two or several adsorbing columns, using pressure changes for bed regeneration (6). An excess amount of feed is necessary to purge out the system, and to provide the driving force to move the gas within the adsorbers. The continuous change in pressure, and direction of flow within the adsorber, produces the separation under isothermal conditions.

The separation of gaseous mixtures by pulsed adsorption at constant volume, using temperature as the changing parameter, and the stop-go equilibrium model proposed by Wilhelm and Sweed, was studied by Jenczewski and Myers (7). Separation of gaseous mixtures were obtained experimentally for argon-propane and ethane-propane mixtures. An equilibrium model, the parameters of which are measured independently, provides good agreement with the experimental results.

Other types of parametric pumps reported are summarize in Table 1.

A model for an isothermal parametric pump, using one adsorbing column with two reservoirs, one for expansion only and one for compression only, is described in this paper. The system studied is limited to a binary gaseous mixture with only one component adsorbed to simplify the calculations, but it should work equally well for other mixtures with different equilibrium adsorption constants. The basic distinction of the proposed parametric pump is the use of one reservoir for compression and a different reservoir for expansion. This operating characteristic may be achieved in two ways, one, with the help of a programmed cam*, as described later; and the other, using two different size reservoirs directly opposed to one another in the expansion-compression cycle.** The first method was used in the model for convenience in calculations.

The proposed system permits the separation of gases at a constant temperature using pressure changes. A change in pressure has dynamic advantages over a heat transfer operation. A temperature cycling system is limited by the high energy losses encountered in heating and cooling the equipment itself. Pressure changes, on the other hand, can be made quickly, and are limited only by the pressure drop through

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* See Figure 2.

** See Figure 3.

TABLE I

Summary of Parametric Pumping Processes

Type of Process	Constant Parameter	Changing Parameter	Type of Adsorber	Driving System	Type of Fluid	References
Batch Semicontinuous Continuous	Volume Pressure	Temperature	One Column	Two moving reservoirs	Liquid Mixture	1, 2, 4
Semicontinuous Continuous	Temperature	Pressure Volume	Several Columns	Purging at low pressure.	Gas Mixture	3, 5, 6
Batch	Volume	Temperature	One Column	Two moving Reservoirs	Gas Mixture	7
Batch	Temperature	Pressure Volume	One Column	Two moving Reservoirs	Gas Mixture	This Paper

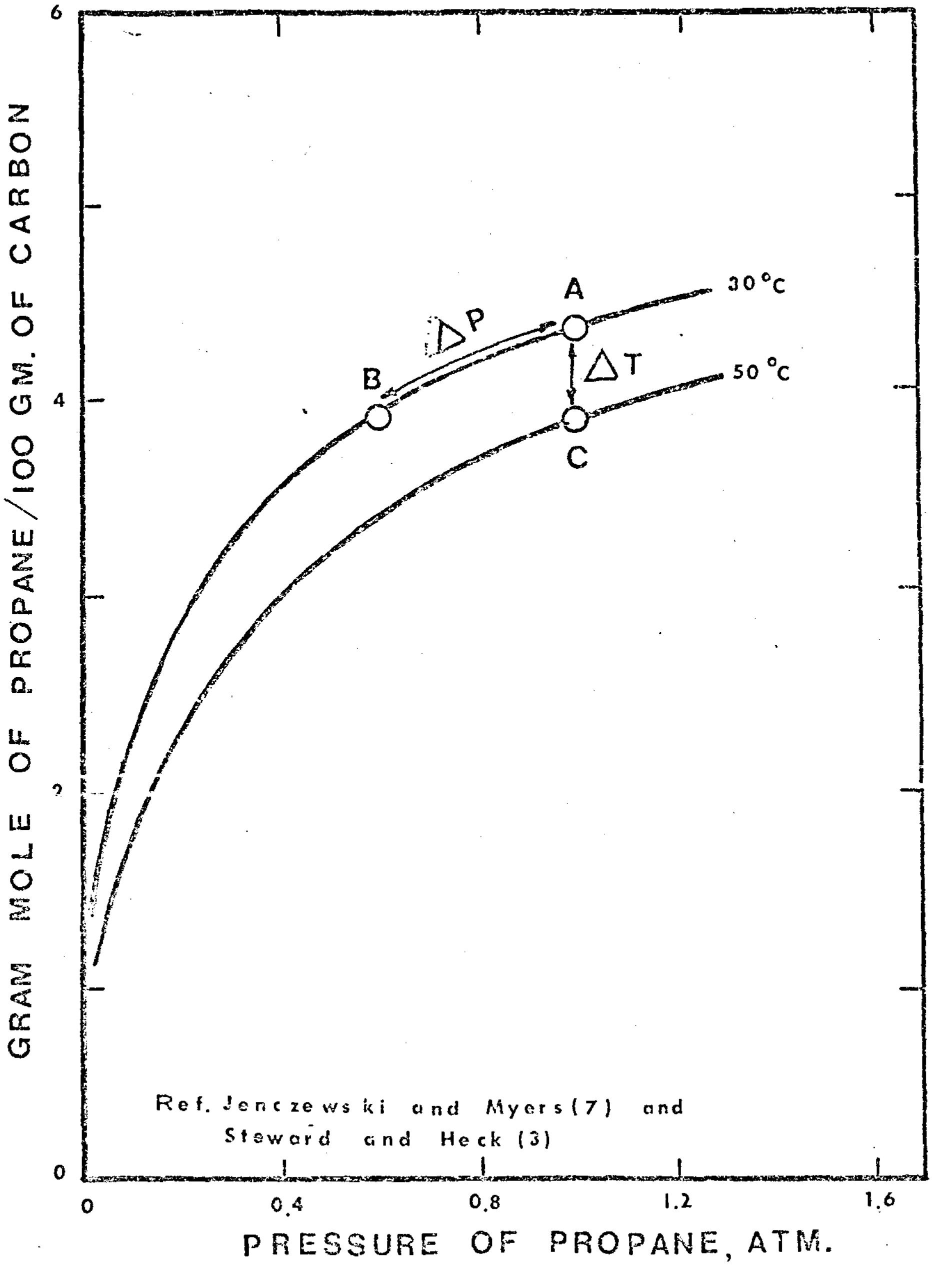
the adsorbent bed and the dynamics of the mass transfer operation.

This parametric pump may be a completely closed system. Maximum separation can be obtained by increasing the number of cycles at the expense of work.

Gases at low pressure may be separated without the need for prior compression, but the system can not take advantage of a feed that is already at high pressure.

The adsorption equilibrium isotherms of the system propane-carbon (7) used in the calculations of the mathematical model developed in this work are shown in Figure 1. They illustrate the differences between the temperature changing parametric pump and the pressure changing parametric pump at constant temperature. The equilibrium propane pressure for a given concentration of propane in the adsorbent (carbon) at two different temperatures generate two curves. If point A in the upper curve is taken as the initial conditions of a parametric pump, a change of the concentration of propane in the adsorbent may be obtained by changing the temperature T to point C at constant propane pressure. The separation of a propane-argon mixture on carbon has been reported in the literature (7) using this kind of temperature cycling parametric pump. The pressure changing model produces the concentration change of the propane at constant temperature by moving the pressure of the propane from point A, on the upper isothermal curve to point C. This change in the partial pressure of the gas is achieved by changing the total pressure of the system during the parametric pumping process.

The scope of this work is to develop a mathematical model that will describe an isothermal parametric pump using changes in pressure as the means for gaseous-mixture separation.



Ref. Jenczewski and Myers (7) and Steward and Heck (3)

FIG. 1

PROPANE CARBON ADSORPTION EQUILIBRIUM ISOTHERM

CONCLUSIONS AND SIGNIFICANCE

An equilibrium model, for a closed isothermal pressure changing parametric pump, was studied for a binary gas-mixture on a solid adsorbent. A difference in adsorbate equilibrium concentration of the two gases is necessary for the separation of the components. The gas mixture is pulsed through the adsorbent bed: upflow at high pressure and downflow at low pressure. The upflow reservoir, where expansion always occurs, is enriched by the component with the lower adsorbate equilibrium concentration. The downflow reservoir, where compression always occurs, is enriched by the other component of the gas-mixture. The length of a cycle is limited only by the mass transfer resistance from the gas to the adsorbent and by the pressure drop through the column packing when moving the gases. Since minimum heat transfer is required, it offers a significant advantage for separation of dilute gas-mixtures over the temperature changing parametric pump.

The model was investigated using the system propane-argon on carbon. Separation factors reported in the literature (7), for this system, using a constant volume temperature changing parametric pump, are slightly higher. However, a more rapid rate of separation is anticipated for the pressure changing parametric pump. The temperature, total pressure, propane concentration, the ratio of the reservoir volumes, and the maximum penetration in the column, control the rate and degree of separation.

This type of separation process in combination with the compression of a gas-mixture, in a batch, continuous or semi-continuous apparatus, may be economically attractive.

PROCESS DESCRIPTION

The batch, pressure-changing parametric pump is the object of this study. Its characteristics will be easier to understand if the equipment used to effectuate this process is first described and discussed. Two posibilities are considered here; a mathematical model will be discussed for the simplest approach.

The proposed apparatus is shown in Figure 2. The equipment consists of three cylindrical sections constructed of a rigid material. The adsorber is a jacketed cylinder of length Z and constant diameter D, filled with an adsorbent material with a constant void fraction, ϵ . Heat transfer from the constant temperature jacket to the inside of the adsorber is very important, since isothermal conditions are required to meet the mechanism of pressure oscillation along the equilibrium isotherm (Figure 1). The column jacket must be supplied with a constant temperature fluid; this provides a high heat transfer coefficient and leaves the bulk of the heat transfer resistance to the gas phase inside the adsorber.

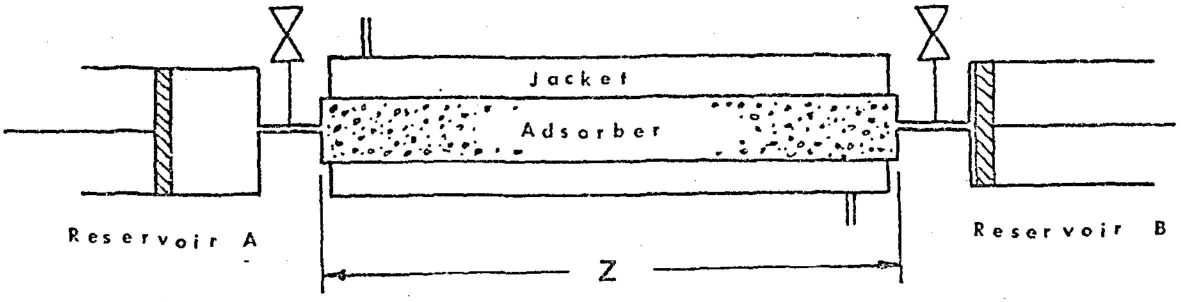
The two end reservoirs of variable volume can be constructed using leak tight flexible diaphragms, as used by Jenczewski and Myers (7) in their experiments. Two pistons are used to describe the process for the sake of model simplicity. These two pistons must move the gas phase through the adsorber bed in the following fashion:

1. Constant pressure movement of high pressure π_H gases from reservoir A to reservoir B.

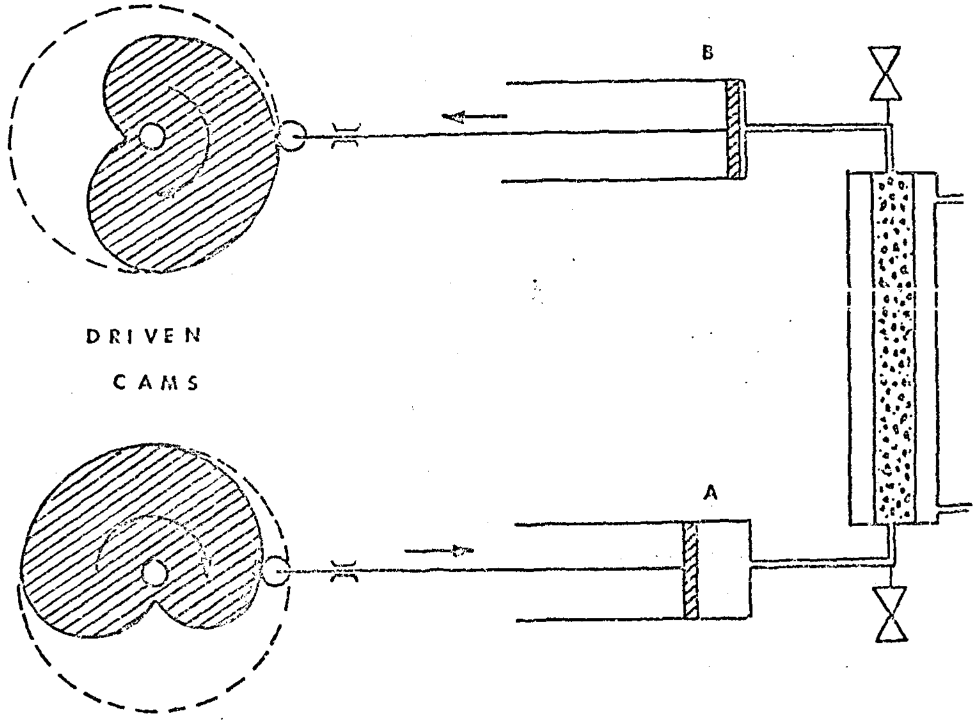
2. When reservoir A is empty, reservoir B expands to a lower pressure, π_L.
3. Constant pressure movement of low pressure π_L gases from reservoir B to reservoir A.
4. When reservoir B is empty, reservoir A compresses the gases to the initial high pressure, π_H.
5. Repeat steps 1 through 4.

The lower diagram of Figure 2 shows a schematic diagram of a driving mechanism that will fulfill the model requirements. This mechanism consists of two pistons and two rotating cams driven by a common shaft. Each piston has a connecting rod that travels in the axial direction, following the motion induced by a cam follower that rides on the cam surface. Each quarter-cycle of the cam surface moves each piston through one of the steps previously described. The position of the cams and pistons in the diagram is the initial position (step 1). As the shaft rotates a quarter of a cycle the piston A will be moving the gas into the column; simultaneously, the piston B will be moving the gases from the adsorber into piston B without any net volume change of the system. The two valves shown in the diagram are required to charge the column with the gases.

A similar cycle can be generated by two different size reservoirs moving opposite to each other; that is, when one piston is moving the gases into the adsorber column the other is taking the gases out of the column. Figure 3 shows the pressure changes during a typical cycle, and the movement of the gases' center of mass inside the column. The upper curves



A. SCHEMATIC OF ADSORBER



B. DRIVING MECHANISM

FIG. 2

SCHEMATIC DIAGRAM OF PROPOSED APPARATUS

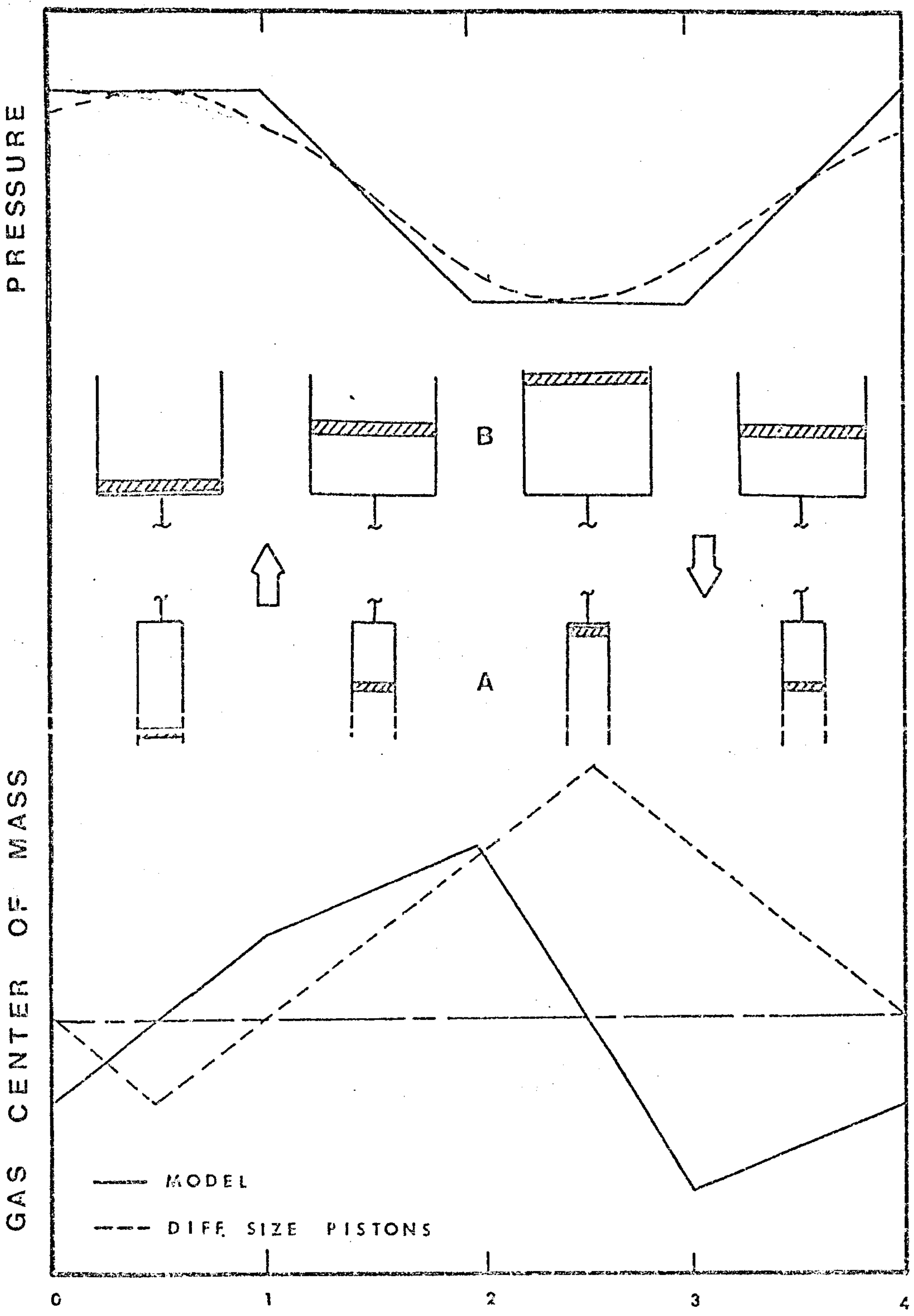


FIG. 3

DIFFERENT SIZE RESERVOIR APPARATUS VS. MODEL of Figure 3 illustrate the pressure variation of the two alternatives during one full cycle. It should be noted that the path of the two curves is similar. At the center of Figure 3 there are four pairs of pistons; each pair shows the relative positions of the large and small piston in the middle of a quarter-cycle. The two arrows show the simultaneous up and down movement of the two pistons, relative to the column. The lower two curves of Figure 3 describe the path of the gas center of mass in its axial movement relative to the column. It is obvious that there are some differences in gas movement within the adsorber, but in general the pressure and position in the two systems satisfy the requirements for the pressure changing parametric pump. The gases always expand in reservoir B and are always compressed in reservoir A. A mathematical model of the two different sized reservoirs is more involved because of the sinusoidal nature of the pressure change. For this reason the apparatus shown in Figure 2, which has a linear pressure change, is used to represent the pressure-changing parametric pump, and is the basis for the mathematical model.

THEORY

At a given temperature and pressure, the amount of gas adsorbed when equilibrium is established depends on the nature of the adsorbent and adsorbate. The separation of a binary mixture of gases in a batch isothermal pressure-changing parametric pump depends on the differences of adsorption equilibrium constants of the components. When the total pressure of the system is changed, the partial pressure of the adsorbate is also changed, and a driving force is established to reach the new equilibrium concentrations.

The cycle is carried along the isotherm line as shown in Figure 1 (A to B). In a temperature-changing parametric pump, theoretically the cycles are carried on the isobar direction (A to C).

If the gases in the adsorber always move from reservoir A to reservoir B while under high pressure, and from reservoir B to A while under low pressure, a change in concentration at each end will occur. The degree of separation in a batch process is a function of the number of cycles and the maximum penetration of the gases from the reservoir into the adsorber. The optimum time required for each step of the pumping cycle will depend on the dynamics of the adsorption process and the fluid flow limitations.

The Langmuir basic theory of adsorption can be used to approximate an equation from experimental data; this is necessary for the computer calculation of the material balance at equilibrium conditions and at any given time and position in the adsorber.

The pure component isotherms for a gas can be fitted by an equation of the form,

$$Q_1 = \frac{D \cdot P_1}{E + P_1} \qquad (1)$$

where Q_1 is adsorbate density in moles of adsorbate per unit weight of adsorbent, P_1 is the equilibrium pressure of the pure component, and D and E are temperature dependent constants for the particular adsorbate-adsorbent system. Jenczewski and Myers (7) gives values of the constants that fit Figure 1 curves for propane on carbon.

The total pressure of a binary mixture of gases is equal to the sum of the partial pressures of each gas,

$$\pi = P_1 + P_2 \qquad (2)$$

If only one of the gases is adsorbed by the adsorbent, the internal material balance of the column is simplified since the partial pressure of this gas will remain constant as long as the temperature is unchanged.

Assuming ideal gas behavior, the number of moles in the gas phase can be calculated by the equation,

$$n_T = \frac{\pi \cdot V_T}{R \cdot T} \qquad (3)$$

$$V_T = V_A + V_B + V_{AD} \qquad (4)$$

$$V_{AD} = \epsilon \cdot V_C \qquad (5)$$

The concentration of any gas Y, can be calculated from the partial pressure and the total pressure at any time.

$$Y_1 = \frac{P_1}{\pi} \qquad (6)$$

In a closed system, the initial number of moles of each component remains constant at any time. Therefore, the sum of the number of moles of a component in the gas phase and in the adsorbent is a constant for any given initial conditions, although the amount in one phase or the other will change with any change in temperature or pressure which will displace the equilibrium of the two phases.

The number of moles in the reservoirs for any particular gas can be calculated using an equation similar to Equation 3, but using the partial pressure of the gas and the volume of the reservoir. The number of moles of the adsorbed gas in the column can be calculated adding the moles in the gas phase to the adsorbed moles in the adsorbent.

$$\text{Moles of 1 in column} = \frac{\epsilon . P_1 . V_C}{R.T} + \rho.(1 - \epsilon).V_C.Q_1 \qquad (7)$$

Adsorption and desorption is assumed to occur instantaneously. The diffusion of one gas through the other is assumed negligible.

The high pressure π_H is obtained when the total volume is minimum, and the low pressure π_L when the total volume is maximum.

To simplify initial conditions in the system, it is assumed that the adsorber is at equilibrium with the partial pressure of the gases at the initial conditions and at the high pressure, π_H. This assumption can be obtained in practice by purging gas at the initial concentration Y_1 through the column until the concentration of the gases at the outlet is equal to the concentration of the gases at the inlet.

A schematic diagram of a closed, pressure pulsed adsorption system is shown in Figure 4 which illustrates the four quarters of an operating cycle. The gas and adsorbed phases have been separated for clarity. The gas phase is moved relative to the adsorbed phase, as indicated by positions b, c, d, and e. The fluid-adsorbate equilibrium relationship is oscillated by oscillating the system total pressure. An operating cycle, assuming only one component of the binary mixture is adsorbed, is described in order to emphasize the characteristics of the cyclic process and the driving force of the separating effect. The system is initially in position b, for which the pressure is uniform and equal to π_H. The gas and adsorbed phases are of uniform concentration in the axial direction and in equilibrium. The gas phase is moved from reservoir A through the column into reservoir B (b). As expansion occurs in reservoir B (c), a portion of the active component is desorbed during this quarter-cycle. The gas is then moved, at low pressure π_L, relative to the adsorbent as indicated by position c. The gas volume in reservoir B is transfered through the column to reservoir A at π_L. When compression occurs in reservoir A, as represented by position d, a portion of the active component in the gas is adsorbed. After this fourth quarter-cycle is completed, a transfer back to position b initiates another cycle.

Assuming that diffusion, mixing, and convection in the axial direction are relatively slow compared to the cycle time, observation of the positions of the gas in the adsorption and desorption steps shows that the net result of one cycle is the transfer of some of the adsorbed component from the right-hand end to the left-hand end of the system. The continuation of the process through many cycles results in the establishment of a steady-state concentration gradient (7).

The possible volume relations of the column and the reservoirs are schematically represented in Figure 5. The ratio of the reservoir volume at low pressure, V_{RL}, to the column free volume V_{AD}, is defined as the maximum penetration of the gases into the column during one stroke. The abscissa of the diagram is the reservoir volume ratio, which is the ratio of the large low pressure volume of the reservoir to the small reservoir volume at the high pressure, V_{RL}/V_{RH}.

Two operating zones are possible, Zone I is for maximum penetration greater than 1, and Zone II is for maximum penetration less than 1. The effect of the volume relations in the separation of the gases is included in the discussion of the results.

It is important to consider some of the effects extreme conditions will have on the equilibrium relation of pressure and adsorbate concentration. The form of Equation 1 that fits the curves of Figure 1 has two posible simplifications. As P_1 approaches zero $Q_1 = K_1 . P_1$, and as P_1 approaches infinity $Q_1 = K_2$; where K_1 and K_2 are temperature dependent constants.

It is evident from these limits that a pressure cycling parametric pump is most effective at low pressure conditions. It becomes completely ineffective at higher pressure conditions because adsorbate concentration is constant, due to saturation of the adsorber. From Figure 1 it is also observed that the lower temperature will give a greater change of Q_1 with respect to P_1.

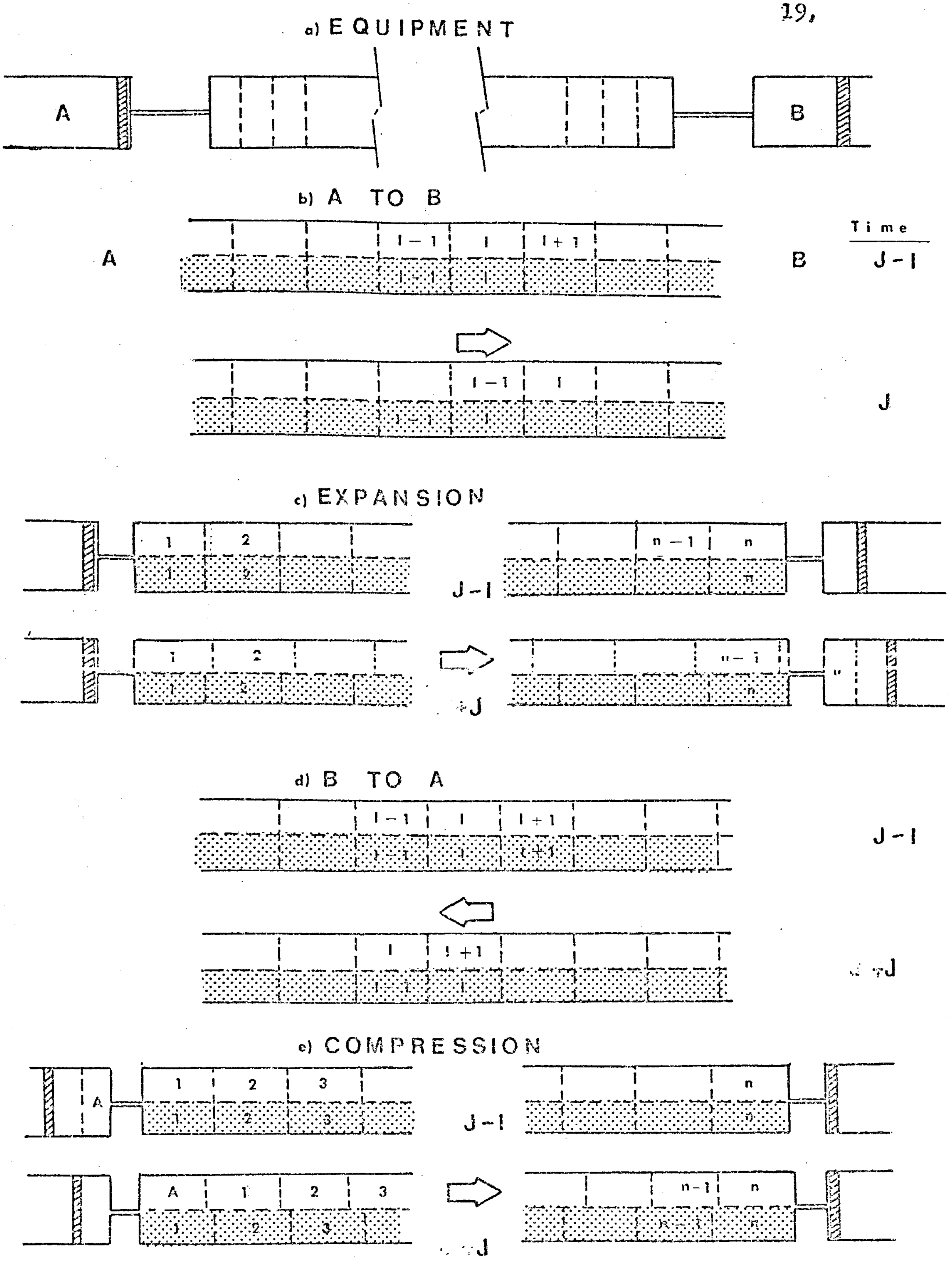
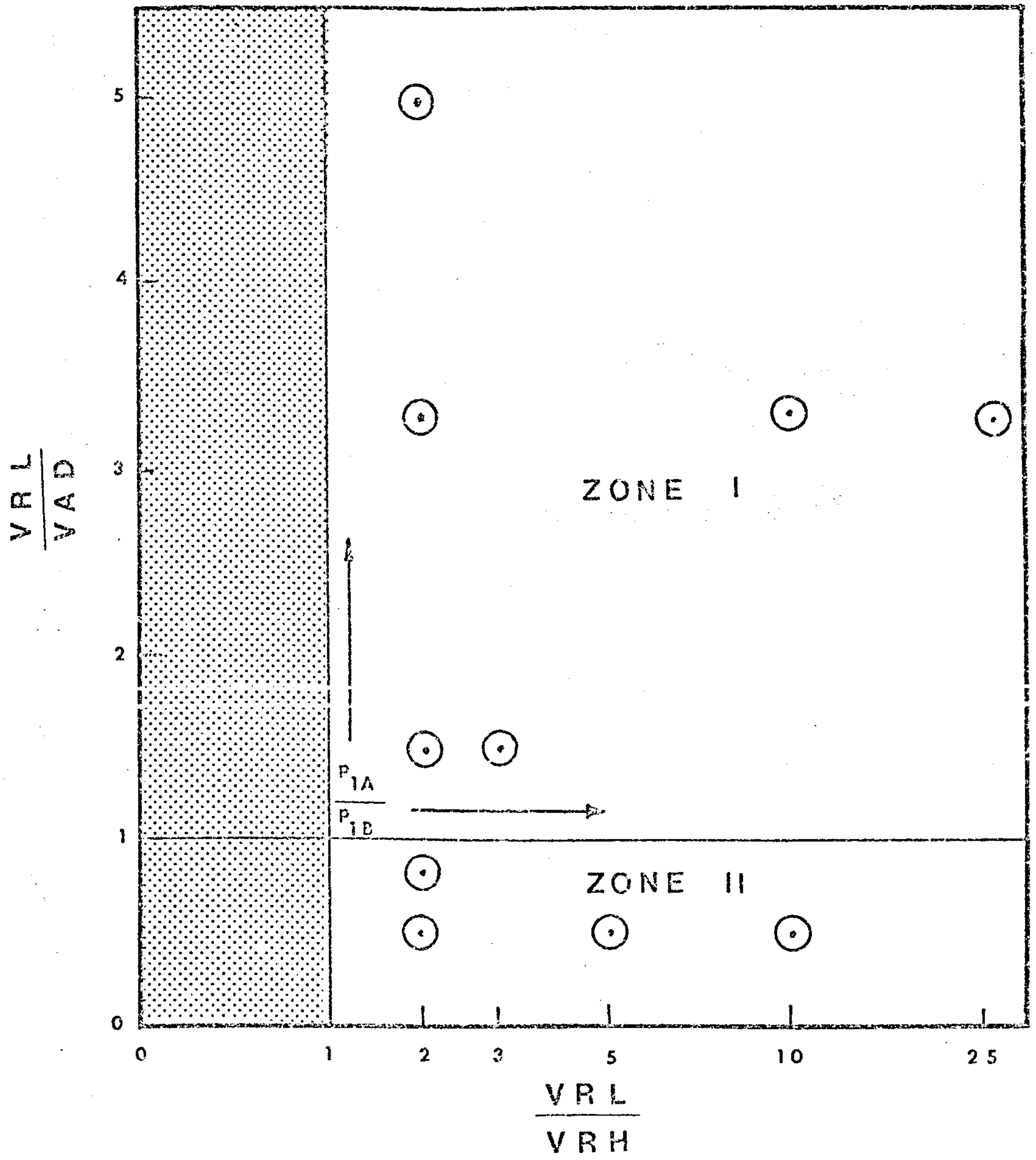


FIG. 4

SCHEMATIC DESCRIPTION OF ONE PROCESS CYCLE



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RESERVOIRS AND COLUMN VOLUME RELATION. ⊙ DATA INVESTIGATED

MATHEMATICAL MODEL

Using a model similar to Jenczewski and Myers (7) for a temperature cycling parametric pump, based on Sweed and Wilhelm stop-go model (9), an isothermal model with fluctuating pressure could be designed to approximate the batch axial expansion parametric pump previously described. An iteration process was used to solve this model with the help of a computer.

The model developed here considers an ideal binary mixture of gases that are selectively adsorbed by a solid adsorbent, with changing equilibrium concentrations in the solid as the partial pressure of each component changes. For the sake of simplicity, the particular case in which only one of the components is adsorbed and the other remains always in the gaseous phase, as in argon-propane on carbon, will be discussed. A second assumption will be made to simplify the volume changes calculation, that the concentration of the adsorbed gas is very small with relation to the inert gas.

Let us assume the adsorption chamber and reservoir A are subject to an almost perfect vacuum, less than 1 mm Hg. Then the binary mixture is purged through the system at the high pressure π_H and the adsorbent (carbon) is allowed to reach equilibrium with the gases. When the composition of the out going gas is equal to the inlet composition the system is closed*.

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*See Figures 2 and 4.

The concentration of gas 1 (propane) at any position and time will be $Y_1(I,J)$, where I defines position in the adsorber and J defines time. The pistons of A and B reservoirs are moved so that the total volume is displaced from reservoir A to fill an equivalent volume in reservoir B. The initial total pressure in the apparatus is Π_H, and the gas concentration through-out it is Y_1 and Y_2, for component 1 and 2 respectively. The adsorbate density in the adsorber at initial conditions can be calculated from the equilibrium relation, Equation 1.

In order to solve the equilibrium and material balance equations for each quarter-cycle, the adsorber column is divided in n equal sections (Figure 4a). The calculation of the instantaneous number of steps required at each quarter-cycle depends on the free volume of one small section and the volume of the reservoir at the particular quarter-cycle. The number of the sequential steps required for each quarter-cycle τ is calculated as follows,

$$\tau_H = \frac{V_{RH}}{V \cdot \epsilon} \qquad (8)$$

$$\tau_L = \frac{V_{RL}}{V \cdot \epsilon} \qquad (9)$$

$$\tau_C = \tau_E = \frac{V_{RL} - V_{RH}}{V \cdot \epsilon} \qquad (10)$$

where the subscripts H, L, C and E denote the high pressure quarter-cycle, the low pressure quarter, the compression quarter-cycle, and the expansion quarter-cycle, respectively. The free volume of one step segment is the product of the volume of the segment and the void fraction, ϵ. Low adsorbate concentration (Y_1) minimizes the hysteresis effects, and permits the assumption that τ_C and τ_E are equal (Equation 10). The volume of one segment is the total volume of the column V_{AD}, divided by the number of segments, n.

The time required from J = 1 to J = τ is the time any particular quarter-cycle will need to be completed.

The stop-go model (9) assumes that the axial displacementof length Z/n is instantaneous and that the time period t is allowed for mass transfer between phases. For the case of equilibrium between phases, the problem of calculating the concentrations in each volume element at each time increment reduces to that of solving simultaneous mass balances and equilibrium relationships for each component.

The assumptions and limitations of the proposed model for the batch pressure changing parametric pump previously described are summarized as follows:

- Closed system.
- Constant temperature.
- Ideal gas law.
- Instantaneous axial displacement.
- Pressure drop negligible.
- Instantaneous equilibrium.
- Axial diffusion negligible.
- Initial conditions in equilibrium at high pressure.
- Binary gaseous mixture with only one component adsorbed.
- Very dilute concentration of active component.
- Volume fraction of active component negligible.

One complete process cycle is schematically represented in Figure 4, showing one instantaneous displacement of the gas phase for each quarter of a cycle. The adsorber column is axially divided in two layers; the upper portion represents the gas phase and the lower dotted portion, the solid adsorber. Each quarter-cycle has two sections of column; the upper section shows the relative position of the gas volume elements with respect to the adsorbent at time J - 1, before the axial displacement. An arrow between the two diagrams represents the direction of the displacement, and lower diagram shows the new relative position of the volume segments after the axial displacement, at time J.

The equilibrium and material balances for each step of a quarter-cycle may be easily understood with the diagrams in Figure 4. The four quarter-cycles are treated independently, but the last step of one quarter-cycle is always the beginning step of the next, as the end conditions of one cycle are the beginning of the other.

<u>First quarter-cycle</u>:

The first quarter-cycle consists to move the gases at high pressure π_H, from reservoir A to B at constant pressure. Figure 4b shows the relative position of typical volume elements before and after one step.

A material balance of component 1 is carried out for one volume element before and after a time step. The total number of moles of component 1 in the volume element, in both phases, is equal to the number of moles in the adsorber before the time step, plus the moles moved from the adjacent volume element. It is assumed instantaneous equilibrium of both phases.

$$\frac{\epsilon.V.P_1(I,J)}{R.T} - (1-\epsilon).V.\rho.Q_1(I,J) = \frac{\epsilon.V.P_1(I-1,J-1)}{R.T} - (1-\epsilon).V.\rho.Q_1(I,J-1) \qquad (11)$$

The physical meaning of Equation 11 is described in the theory, in the discussion of Equation 7. The concentrations at time J - 1 are known, therefore the right side of the equation can be calculated as H_1, and the left side of the equation can be expressed in terms of $P_1(I,J)$ using the adsorption equilibrium relation, Equation 1.

$$H_1 = \frac{\epsilon.V.P_1(I,J)}{R.T} + (1-\epsilon).V.\rho.\frac{D.P_1(I,J)}{E + P_1(I,J)} \qquad (12)$$

Equation 12 can be solved as a quadratic equation for $P_1(I,J)$.

$$P_1(I,J) = \frac{-b + \sqrt{b^2 - 4.a.c}}{2.a} \qquad (13)$$

where,

$$-b = H_1 - \frac{E.\epsilon.V}{R.T} - D.(1-\epsilon).V.\rho \qquad (14)$$

$$a = \frac{.V}{R.T} \qquad (15)$$

$$c = -H_1.E \qquad (16)$$

The material balance in each reservoir B is calculated from the sum of each volume element that enters it.

$$R_{BH1} = \sum_{J=1}^{J=\tau_H} \frac{\epsilon . V . P_1(n,J)}{R.T} \tag{17}$$

$$R_{BHT} = \frac{V_{RH} . \pi_H}{R.T} \tag{18}$$

The final composition of component 1 in the reservoir B can be calculated as

$$Y_1 = \frac{R_{BH1}}{R_{BHT}} \tag{19}$$

and the partial pressure of component 1 in reservoir B is

$$P_1(B, \tau_H) = Y_1 . \pi_H \tag{20}$$

To simplify the calculations that follow in the next three quarter-cycle, two groups of constants are defined.

$$F = \frac{\epsilon . V}{R.T} \tag{21}$$

$$G = (1 - \epsilon).V.\rho \tag{22}$$

<u>Second quarter-cycle</u>:

The expansion of gases in reservoir B (Figure 4c) illustrates the distribution of the volume segments throughout the adsorber column before and after one time step of expansion. In order to simplify the calculations for the expansion operation, it is assumed that the expansion occurs in small instantaneous steps, and only a very small time lapse is necessary for the equilibrium of gas and solid phases. The total number of steps to complete the expansion to the low pressure π_L is calculated by Equation 10.

The initial conditions of each volume segment will be the same as the last conditions for the previous quarter-cycle. Therefore,

$$P_I(I,1) = P_I(I,\tau_H) \tag{23}$$

$$Q_I(I,1) = Q_I(I,\tau_H) \tag{24}$$

The volume of the gases in the reservoir B at any time J is,

$$V_{REJ} = V_{RH} + \epsilon.V.J \tag{25}$$

The total volume in reservoir B and the column, at any time step J, V_{TJ}, is

$$V_{TJ} = V_{AD} + V_{REJ} \tag{26}$$

The fraction of volume increase any given time FRCT is defined as:

$$FRCT = \frac{V_{TJ}}{V_{TJ} + V.\epsilon} \tag{27}$$

The actual volume moved from the column to the adsorber at each time step is,

$$V' = V_{AD}.(1 - FRCT) \tag{28}$$

The gas phase of each volume segment during the expansion step moves in such a way that a different amount of overlapping occurs throughout the column. This effect can be seen in Figure 4c. Two new factors are defined in order to simplify the material balance of any segment. These factors give the relative amount of component 1 in the gas phase of the two volume elements used in the material balance of the volume element after the time step. These volume-pressure factors are defined as follows:

$$F_1 = \frac{(\epsilon.V - V'.G_{11}).FRCT}{R.T} \qquad (29)$$

$$F_2 = \frac{V'.G_{11}.FRCT}{R.T} \qquad (30)$$

where F_1 and F_2 are constant for one time step, that is, V' must be calculated by Equations 26, 27 and 28, every time J moves one integer. The factor G_{11} is the volume proportionality factor as the calculations are carried from position n to 1, and is:

$$G_{11} = \frac{n - I}{n} \qquad (31)$$

The material and equilibrium balance is started in reservoir B after each time step and sequentially computed for each volume segment through the column to segment 1. The material balance for this expansion process has an additional term to account for the fraction of volume of the two segments involved in the composition of the new segment. A technic similar to the previous quarter-cycle is used to solve this expansion quarter-cycle.

It is worthwhile to mention here that, for the sake of continuity in the mathematical expressions, the reservoir A will correspond to position 0 and reservoir B to position n + 1. The general equation for the material balance of a volume element is:

$$F.P_1(n+1-I,J) + G.Q_1(n+1-I,J) = G.Q_1(n+1-I,J-1) + F_1.P_1(n+1-I,J-1) + F_2.P_1(n-I,J-1) \qquad (32)$$

The right hand of the equation can be calculated from the previous time step, and the Equation 32 is rewritten using a new constant for the J - 1 terms, H_2.

$$H_2 = F.P_1(n+1-I,J) + G.Q_1(n+1-I,J) \qquad (33)$$

Solving Equation 33 with the equilibrium relation, Equation 1, and rearranging the terms to fit the standard quadratic equation form,

$$a.(P_1(n+1-I,J))^2 + b.P_1(n+1-I,J) + c = 0 \qquad (34)$$

where,

$$a = F \qquad (35)$$

$$b = E.F + G.D - H_2 \qquad (36)$$

$$c = - E.H_2 \qquad (37)$$

After calculating $P_1(n+1-I,J)$ using the quadratic equation, the equilibrium adsorbate density can be calculated by Equation 1.

$$P_1(n-1-I,J) = \frac{-b + \sqrt{b^2 - 4.a.c}}{2.a} \qquad (38)$$

The material balance in reservoir B is obtained by adding the moles coming from the column to the initial number of moles in the reservoir. The total material in reservoir B is R_{BHT} with a component 1 concentration of $Y_1(B,\tau_H)$. The number of moles of component 1 is R_{BH1}, with a partial pressure of $P_1(B,\tau_H)$.

$$R_{BE1} = R_{BH1} - \sum_{J=1}^{J=\tau_E} \frac{V'.FRCT.P_1(n,J)}{R.T} \tag{39}$$

The final composition of 1 in reservoir B is,

$$Y_1(B,\tau_E) = \frac{R_{BE1}}{R_{BET}} \tag{40}$$

The total number of moles in reservoir B after the expansion quarter-cycle is completed, R_{BET}, is calculated from the ideal gas law, using the low pressure conditions.

$$R_{BET} = \frac{V_{RL}.\pi_L}{R.T} \tag{41}$$

The partial pressure of component 1 reservoir B is,

$$P_1(B,\tau_E) = Y_1(B,\tau_E).\pi_L \tag{42}$$

The initial conditions of the next quarter-cycle are the final conditions of this quarter-cycle, and the total pressure is the low pressure π_L.

Third quarter-cycle:

This quarter-cycle consists in moving the gas at constant low pressure, π_L, from reservoir B through the column to reservoir A.

The initial conditions are,

$$P_1(I,1) = P_1(I, \tau_E) \tag{43}$$

$$Q_1(I,1) = Q_1(I, \tau_E) \tag{44}$$

The time step change is represented in Figure 4d, and it is the reverse operation of the first stage, but a large number of time steps are required because of the large volume involved in this quarter-cycle.

The material balance of one volume segment is,

$$F.P_1(n+1-I,J) + G.Q_1(n+1-I,J) = F.P_1(n+2-I,J-1) + G.Q_1(n+1-I,J-1) \tag{45}$$

All the terms of the time step J - 1 are known and can be calculated as a constant H_3. Then the Equation 45 can be solved for $P_1(n+1-I,J)$ using the same approach as in the previous quarter-cycles. The quadratic equation constants are as follows:

$$a = F \tag{46}$$

$$b = E.F + G.D - H_3 \tag{47}$$

$$c = - E.H_3 \tag{48}$$

Substituting these constants in Equation 38, $P_1(n+1-I,J)$

is calculated and the corresponding equilibrium adsorbate density is calculated with Equation 1.

The material balance in reservoir A is calculated by adding each segment volume that enters the reservoir. The number of moles of component 1 at the end of this quarter-cycle is,

$$R_{AL1} = \sum_{J=1}^{J=\tau_L} F.P_1(1,J-1) \tag{49}$$

and the total number of moles is,

$$R_{ALT} = \sum_{J=1}^{J=\tau_L} F.\pi_L = \frac{V_{RL}.\pi_L}{R.T} \tag{50}$$

The final composition of component 1 in reservoir A can be calculated from the mole ratio,

$$Y_1(A,\tau_L) = \frac{R_{AL1}}{R_{ALT}} \tag{51}$$

and the partial pressure of component 1 in reservoir A is,

$$P_1(A,\tau_L) = Y_1(A,\tau_L).\pi_L \tag{52}$$

<u>Fourth quarter-cycle</u>:

The final quarter-cycle of the cycle consists of compressing the gases in reservoir A and into the column. Figure 4e represents one time step of this compression quarter-cycle. From this schematic representation the effect of the compression in the overlapping of volume segments from one time step to the other is clearly shown, as well as the similarity to the expansion process.

Using a procedure similar to the second quarter-cycle calculations, the material balance is solved taking into account the volume contraction that occurs in each time step. The piston of reservoir A moves to produce a volume change in the total system equal to a volume change in the total system equal to a volume segment, but the penetration of the gases in the column is only a fraction of that volume due to the compression effect of the other n segment volumes in the column.

The volume of reservoir A at any time J, V_{RAJ} is,

$$V_{RAJ} = V_{RL} - V.\epsilon.J \tag{53}$$

and the total volume of the system at any time J, V_{TJ} is the sum of the free volume of the column, V_{AD}, and the volume of reservoir A at the particular time, J.

$$V_{TJ} = V_{AD} + V_{RAJ} \tag{54}$$

The fraction of volume produced by the compression, FRCT, that is, the fraction of the original volume of one segment volume after one time step, is calculated as follows:

$$FRCT = \frac{V_{TJ} - V.\epsilon}{V_{TJ}} \tag{55}$$

The volume displaced in the column by the gases entering from reservoir A, V' is,

$$V' = V_{AD}.(1 - FRCT) \tag{56}$$

The partial pressure of component I in the reservoir increases as the total pressure in the system increases; therefore this pressure must be recalculated after each time step.

The initial conditions of pressure and concentration for this quarter-cycle are the final conditions for the previous quarter-cycle, both in the column and reservoir.

$$P_1(A,J) = P_1(A,1).\frac{(V_{RL} - V_{AD})}{V_{TJ}} \qquad (57)$$

where $P_I(A,J)$ is the partial pressure of component 1 in the reservoir A at any time J.

For any given segment through the column, the volume of gas moved into it after one time step comes partially from the previous volume element; the balance of the free volume in the segment remains from the gas volume before the time step change. This fraction G_4 is calculated for each position in the column.

$$G_4 = \frac{(n - I)}{(n - 1)} \qquad (58)$$

The calculations are started in segment volume I and are ended in segment volume n. This sequence of calculations is carried until the total high pressure is reached, that is τ_C times.

The material balance is similar to the second quarter-cycle.

$$F.P_1(I,J) + G.Q_1(I,J) = F_3.P_1(I,J-1) + F_4.P_1(I-1,J-1) + G.Q_1(I,J-1) \qquad (59)$$

The terms F_3 and F_4 define the fraction of that volume element that enters in the calculated volume element after one time step, and are defined as follows,

$$F_3 = \frac{(\epsilon.V - V'.G_4)}{R.T.FRCT} \tag{60}$$

$$F_4 = \frac{V'.G_4}{R.T.FRCT} \tag{61}$$

These two terms are divided by the term FRCT, to take into account the increase in pressure during the step change.

The conditions prior to the change (the terms in J-1) are known; therefore the right hand side of the equation can be calculated as a new constant H_4. The partial pressure of component 1 ($P_1(I,J)$) is calculated using the quadratic equation, as in all previous quarter-cycles, and the equilibrium relation, Equation 1. The terms for the quadratic equation are as follows,

$$a = F \tag{62}$$

$$b = G.D + E.F - H_4 \tag{63}$$

$$c = - E.H_4 \tag{64}$$

The equilibrium adsorbate density $Q_1(I,J)$ is now calculated from Equation 1. The number of moles of component 1 in reservoir A at the end of the compression quarter-cycle is calculated from the value of $P_1(A,J)$, Equation 57, at the end of the stage.

$$R_{AH1} = \frac{P_1(1, T_C).V_{RH}}{R.T} \tag{65}$$

This final quarter-cycle leaves the pistons in the position to start the new cycle, which will start with the first quarter-cycle described, moving the gases again from reservoir A through the adsorber to reservoir B.

In order to correct for axial mixing, and to maintain a constant pressure for all cycles, the partial pressure of component 1 is proportionally adjusted to hold the total pressure constant through the equipment.

$$\mathrm{PROP} = \frac{Y_1.(V_{AD} + V_{RH}).\pi_H/R.T}{\dfrac{V_{RH}.P_1(A,\ \tau_E)}{R.T} + \displaystyle\sum_{I=1}^{I=n} F.P_1(I,\tau_E)} \qquad (66)$$

This proportionality factor, PROP, is used to adjust all the pressure terms for the new cycle.

$$P_I(I,1) = \mathrm{PROP}.P_I(I,\ \tau_E) \qquad (67)$$

A Fortran IV computer program* has been designed to solve this mathematical model.

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* See Appendix 3.

SAMPLE CALCULATIONS

The system Propane-Argon will be used to illustrate the calculations of the equations presented in the mathematical model. The constants for the equilibrium relation, Equation 1, are taken from Jenczewski and Myers (7), for the system Propane-Argon on "Pittsburg BPL" activated carbon, 4x6 mesh, as adsorbent.

It is impossible to give here all the calculations necessary for one complete stage or cycle, but for the purpose of illustration, and to give an idea of the number of significant figures required to obtain the separation effect of the model, the initial position and time step are calculated, for each stage, and the final conditions assumed to permit the calculations of the next stage.

The units are presented in the first stage calculations to show the dimensional balance of the equations, but they are omitted in the other three stages, because they have similar dimensions.

The iteration process is always started from the reservoir that contains the gases and into the column, calculating each position step until the last volume segment is moved at the opposite end of the column, and this sequence of calculations is carried for each time step until the stage is completed.

The data used for the sample calculation is typical, and was used in the computer run number 8, so the complete results are summarized in the Results Summary Sheet 3.

The sample calculations are presented in two sections: the basic data given to solve the problem, and the calculations of the mathematical model as described in the previous chapter.

A.- Basic Data:

I.-Equilibrium Equation.

Constants D and E for Equation 1.

$D = 0.00934 - 0.00001376.T$

$E = 0.269.T - 67.55$

For $T = 290$ ºK

$D = 0.0053496$ gm mole of 1/gms of carbon

$E = 10.46$ cmHg

II.- Equipment Dimensions.

Z = Length of column = 78.5 cm

d = Diameter of Column = 2.54 cm

V_C = Total Volume of Column = 398.0 cc

V_{RH} = Volume of Reservoir at π_H = 76.0 cc

V_{RL} = Volume of Reservoir at π_L = 760.0 cc

III.- Adsorber Characteristics.

ϵ = Void Fraction = 0.762

ρ = Adsorber Density = 2.1 gm/cc

V_{AD} = Free Volume of the column, $\epsilon . V_C$ = 304.0 cc

IV.- Volume Segment.

n = Number of segments = 20

Z/n = Length of column segments = 3.925 cm

V = Volume of one segment, V_C/n = 19.9 cc

V.- Gas Phase Data.

Component 1 = Propane

Component 2 = Argon

R = Ideal Gas Constant = $6236.0 \ \frac{\text{cc.cmHg}}{\text{gm-mole.}^{\circ}\text{K}}$

π_H = Total High Pressure = 1000.0 cmHg

π_L = Total Low Pressure = 357 cmHg

P_1 = Initial Partial Pressure of Component 1 = 100 cmHg

Y_1 = Mole Fraction of Gas 1 = 0.1

Y_2 = Mole Fraction of Gas 2 = 0.9

VI.- Initial Adsorbate Density Throughout the Column.

$$Q_1 = \frac{D.P_1}{E + P_1}$$

$$Q_1 = \frac{(0.0053496 \text{ gm-mole/gm}).(100.0 \text{ cmHg})}{10.46 \text{ cmHg} + 100.0 \text{ cmHg}}$$

Q_1 = 0.00484302 gm-mole of 1/gm of carbon

VII.- Time Constants.

$$\tau_H = \frac{V_{RH}}{V.\epsilon} = \frac{76.0 \text{ cc}}{(19.9 \text{ cc}).(0.762)} = 5$$

$$\tau_L = \frac{V_{RL}}{V.\epsilon} = \frac{760.0 \text{ cc}}{(19.9 \text{ cc})(0.762)} = 50$$

$$\tau_C = \tau_E = \frac{V_{RL} - V_{RH}}{V.\epsilon} = \frac{(760.0 - 76.0) \text{ cc}}{(19.9 \text{ cc}).(0.762)} = 45$$

These time constants are calculated from Equations 8, 9 and 10.

VIII.- Equations 21 and 22 Constants.

$$F = \frac{\epsilon.V}{R.T} = \frac{(0.762).(19.9\text{cc})}{(6236.0 \ \frac{\text{cc.cmHg}}{\text{gm-mole.}^{\circ}\text{K}}).(290.0 \ ^{\circ}\text{K})} = 0.00000839 \ \frac{\text{gm-mole}}{\text{cmHg}}$$

$$G = (1. - \epsilon).V.\rho = (1. - 0.762).(19.9\text{cc}).(2.1 \ \frac{\text{gm of carbon}}{\text{cc}})$$

G = 9.94602 gm of carbon

B.- Mathematical Model Calculations:

I.- First Stage.

For Position $I = 1$

and Time $J = 1$

From Equation 11,

$$H_1 = F.P_1 + G.Q_1$$

$$H_1 = \left(0.00000839\ \frac{\text{gm-mole}}{\text{cmHg}}\right).(100.0\ \text{cmHg}) + (9.94602\text{gm}).\left(0.004843\frac{\text{gm-mole}}{\text{gm}}\right)$$

$$H_1 = 0.04900777\ \text{gm-mole}$$

The constants for Equation 13 are calculated from Equations 14, 15, and 16.

$$a = F = 0.00000839\ \text{gm-mole/cmHg}$$

$$-b = H_1 - F.E - D.G$$

$$F.E = (0.00000839\ \text{gm-mole/cmHg}).(10.46\ \text{cmHg}) = 0.000087759\text{gm-mole}$$

$$D.G = (0.0053496\ \text{gm-mole/gm}).(9.94602\ \text{gm}) = 0.05320723\ \text{gm-mole}$$

$$-b = 0.04900777 - 0.000087759 - 0.05320723$$

$$b = 0.00419946\ \text{gm-mole}$$

$$c = -H_1.E = -(0.04900777\ \text{gm-mole}).(10.46\ \text{cmHg})$$

$$c = -0.51262127\ \text{gm-mole.cmHg}$$

$$P_1(1,1) = \frac{-b + \sqrt{b^2 - 4.a.c}}{2a}$$

$$b^2 = (0.00419946\ \text{gm-mole})^2 = 0.00001764\ \text{gm-mole}^2$$

$$4.a.c = 4.\left(0.00000839\ \frac{\text{gm-mole}}{\text{cmHg}}\right).(-0.51262127\ \text{gm-mole.cmHg})$$

$$4.a.c = 0.00001720\ \text{gm-mole}^2$$

$$b^2 - 4.a.c = (0.00001764\ \text{gm-mole}^2) + (0.00001720\ \text{gm -mole}^2)$$

$$P_1(1,1) = \frac{-(0.00419946\ \text{gm-mole}) + (0.00003484\ \text{gm-mole})^{1/2}}{2.\left(0.00000839\ \frac{\text{gm-mole}}{\text{cmHg}}\right)}$$

$$P_1(1,1) = 101.4946364\ \text{cmHg}$$

From Equation 1,

$$Q_1(1,1) = \frac{D.P_1(1,1)}{E + P_1(1,1)}$$

$$D.P_1(1,1) = (0.0053496 \text{ gm-mole/gm}).(101.4946364 \text{ cmHg})$$
$$= 0.54350 \ \frac{\text{gm-mole.cmHg}}{\text{gm}}$$

$$E - P_1(1,1) = 10.46 \text{ cmHg} + 101.4946364 \text{ cmHg}$$
$$= 111.9546364 \text{ cmHg}$$

$$Q_1(1,1) = \frac{(0.54350 \text{ gm-mole.cmHg/gm})}{(111.9546364 \text{ cmHg})} = 0.00485200 \text{ gm-mole/gm}$$

For the initial cycle, the first stage, moving gases from reservoir A to reservoir B does not change the initial composition or equilibrium concentration in the column. This is because the concentration is constant throughout the system, as set by the initial conditions.

After calculating $P_1(I,1)$ and $Q_1(I,1)$ for I = 1 to I = 20, the calculation is repeated for J = 2, and $P_1(I,2)$ and $Q_1(I,2)$ are calculated in the same sequence, repeating this calculation cycle until $J = \tau_H = 5$.

The number of moles in the reservoir B, when $J = \tau_H = 5$, is calculated from Equations 17 and 18.

$$R_{BH1} = \tau_H.F.P_1(n,J)$$

$$R_{BH1} = 5.(0.00000839 \text{ gm-mole/cmHg}).(100.0 \text{ cmHg}) = 0.004195 \text{ gm-mole}$$

$$R_{BHT} = \frac{V_{RH}.\pi_H}{R.T} = \frac{(76.0 \text{ cc}).(1000.0 \text{ cmHg})}{(6236.0 \ \frac{\text{cc.cmHg}}{\text{gm-mole.°K}}).(290 \text{ °K})}$$

$$R_{BHT} = 0.04202517 \text{ gm-mole}$$

$$Y_1 = \frac{R_{BH1}}{R_{BHT}} = \frac{(0.004195 \text{ gm-mole})}{(0.04202517 \text{ gm-mole})} = 0.0999 = 0.1 \text{ approx.}$$

$$P_1(B,\tau_H) = (0.1).(1000.0 \text{ cmHg}) = 100.0 \text{ cmHg}$$

II.-Second Stage.

From Equations 23 and 24 the initial conditions of this stage are defined.

$$P_1(I,1) = P_1(I,\tau_H) = 100.0 \text{ cmHg}$$

$$Q_1(I,1) = Q_1(I,\tau_H) = 0.00484302 \text{ gm-mole/gm}$$

To calculate the volume fraction, FRCT, Equations 25, 26, 27 and 28 are solved.

For J = 1 and I = 1

$$V_{REJ} = V_{RH} + \epsilon.V.J = 76.0 \text{ cc} + (0.762).(19.9 \text{ cc}).1$$

$$V_{REJ} = 91.1638 \text{ cc}$$

$$V_{TJ} = V_{AD} + V_{REJ} = 304.0\text{cc} + 91.1638\text{cc} = 395.1638 \text{ cc}$$

$$\text{FRCT} = \frac{V_{TJ}}{V_{TJ} + V.\epsilon} = \frac{395.1638}{395.1638 + (19.9).(0.762)}$$

$$\text{FRCT} = 0.96304465$$

$$V' = V_{AD}.(1 - \text{FRCT}) = (304.0).(1.0 - 0.96304465)$$

$$V' = 11.23442635 \text{ cc}$$

The two volume constants F_1 and F_2 are calculated by Equations 29 and 30.

$$G_{11} = \frac{n - I}{n} = \frac{20 - 1}{20} = 0.95$$

$$F_1 = \frac{(G.V - V'.G_{11}).FRCT}{R.T}$$

$$F_1 = \frac{((0.762).(19.9) - (11.23442635).(0.95)).(0.96304465)}{(6236.0).(290.0)}$$

$$F_1 = \frac{(4.49109497).(0.96304465)}{(1{,}808{,}440)} = 0.00000239 \text{ gm-mole/cmHg}$$

$$F_2 = \frac{V'.G_{11}.FRCT}{R.T}$$

$$F_2 = \frac{(11.23442635).(0.95).(0.96304465)}{(6236.0).(290.0)}$$

$$F_2 = 0.00000568 \text{ gm-mole/cmHg}$$

From Equation 32,

$$H_2 = G.Q_1(20,0) + F_1.P_1(20,0) + F_2.P_1(19,0)$$

$$G.Q_1(20,0) = (9.94602).(0.00484302) = 0.0481687738 \text{ gm-mole}$$

$$F_1.P_1(20,0) = (0.00000239).(100.0) = 0.000239 \text{ gm-mole}$$

$$F_2.P_1(19,0) = (0.00000568).(100.0) = 0.000568 \text{ gm-mole}$$

$$H_2 = 0.04897577 \text{ gm-mole}$$

To solve Equation 38, the constants are calculated from Equations 35,36, and 37.

$$a = F = 0.00000839 \text{ gm-mole/cmHg}$$

$$b = (E.F + G.D) - H_2$$

$$b = (0.000087759 + 0.05320723) - 0.04897577 = 0.00423146 \text{ gm-mole}$$

$$c = -E.H_2 = -(10.46).(0.04897577) = -0.51228655 \text{ gm-mole.cmHg}$$

$$P_1(20,1) = \frac{-b + (b^2 - 4.a.c)^{1/2}}{2.a}$$

$$b^2 = (0.00423146)^2 = 0.00001790 \text{ gm-mole}^2$$

$$4.a.c = 4.(0.00000839).(-0.51228655) = -0.00001792 \text{ gm-mole}^2$$

$$(b^2 - 4.a.c)^{1/2} = (0.00001790 + 0.00001792)^{1/2}$$

$$= 0.00592368 \text{ gm-mole}$$

$$P_1(20,1) = \frac{-0.00423146 + 0.0059268}{2.(0.00000839)} = 100.8475141 \text{ cmHg}$$

From the equilibrium relation Equation 1 the adsorbate density is calculated.

$$Q_1(20,1) = \frac{D.P_1(20,1)}{E + P_1(20,1)}$$

$$Q_1(20,1) = \frac{(0.0053496).(100.8475141)}{10.46 + 100.8475141}$$

$$Q_1(20,1) = 0.0048485 \text{ gm-mole/gm}$$

The material balance of reservoir B for component 1 is calculated every time step by Equations 39 and 40.

$$R_{BE1} = R_{BH1} + \frac{V'.FRCT.P_1(n,J)}{R.T}$$

$$\frac{V'.FRCT.P_1(20,1)}{R.T} = \frac{(11.23442635).(0.96304465).(100.0)}{(6236.0).(290)}$$

$$= 0.00059824 \text{ gm-mole}$$

$$R_{BE1} = 0.04195 + 0.00059824 = 0.04254824 \text{ gm-mole}$$

An approximation for $J = \tau_E$ is made to continue the calculations.

$$R_{BE1} = Y_I . R_{BLT} = Y_1 . \frac{V_{RL} \cdot \pi_L}{R.T}$$

$$R_{BE1} = \frac{(0.1).(760.0).(357.0)}{(6236.0).(290)} = 0.01500299 \text{ gm-mole}$$

$$R_{BET} = R_{BLT} = 0.1500299 \text{ gm-mole}$$

$$Y_1(B,45) = \frac{R_{BE1}}{R_{BET}} = \frac{0.01500299}{0.1500299} = 0.1$$

$$P_1(B,45) = Y_1(B,45).\pi_L = (0.1).(357.0) = 35.7 \text{ cmHg}$$

$$Q_1(1,45) = \frac{D.P_1(1,45)}{E + P_1(20,45)}$$

$$= \frac{(0.0053496).(35.7)}{10.46 + 35.7} = 0.00413736 \text{ gm-mole/gm}$$

III.- Third Stage.

The initial conditions of this stage are the final conditions of stage two. The numbers used for the sample calculation are similar in magnitude **to** the actual numbers but **assume that no** separation has **occurred,** to keep the calculations as simple as possible.

$$P_1(I,1) = P_1(I,\tau_E)$$

$$Q_1(I,1) = Q_1(I,\tau_E)$$

For I = 1 and J = 1

$$P_1(1,1) = P_1(1,45) = 35.7 \text{ cmHg}$$

$$Q_1(1,1) = Q_1(1,45) = 0.00413736 \text{ gm-mole/gm}$$

From Equation 45, H_3 is calculated for I = 1 and J = 1.

$$
\begin{aligned}
H_3 &= F.P_1(21,0) + G.Q_1(20,0) \\
&= (0.00000839).(35.7) + (9.94602).(0.00413736) \\
&= 0.00029952 + 0.04115030 = 0.04144982 \text{ gm-mole}
\end{aligned}
$$

To solve for $P_1(n + 1 - I, J)$ the quadratic equation constants are calculated.

$$a = F = 0.00000839 \text{ gm-mole/cmHg}$$

$$b = (E.F + G.D) - H_3$$

$$b = 0.05320723 - 0.041444982 = 0.01175741 \text{ gm-mole}$$

$$c = -E.H_3 = -(10.46).(0.041444982) = -0.43356512 \text{ gm-mole.cmHg}$$

$$P_1(20,1) = \frac{-b + (b^2 - 4.a.c)^{1/2}}{2.a}$$

$$b^2 = (0.0117541)^2 = 0.00013824 \text{ gm-mole}^2$$

$$4.a.c = -4.(0.00000839).(0.43356512) = -0.00001455 \text{ gm-mole}^2$$

$$
\begin{aligned}
(b^2 - 4.a.c)^{1/2} &= (0.00013824 + 0.00001455)^{1/2} \\
&= 0.01236069
\end{aligned}
$$

$$P_1(20,1) = \frac{-0.01175741 + 0.01236069}{0.00001678} = 35.95240285 \text{ cmHg}$$

The adsorbate density can be calculated from Equation 1 again.

$$
\begin{aligned}
Q_1(20,1) &= \frac{D.P_1(20,1)}{E + P_1(20,1)} \\
&= \frac{(0.0053496).(35.9524)}{10.46 + 35.9524} = 0.00414396
\end{aligned}
$$

The total number of moles of component 1 in reservoir A is calculated by Equations 49 and 50, but for the sake of illustrating the problem, it is enough to make the following approximation.

$$R_{AL1} = \tau_L.F.P_1(1,J-1)$$

$$R_{AL1} = (50).(0.00000839).(35.7) = 0.01497615 \text{ gm-mole}$$

$$R_{ALT} = \frac{V_{RL}.\pi_L}{R.T} = 0.1500299 \text{ gm-mole}$$

$$Y_1(A,50) = \frac{R_{AL1}}{R_{ALT}} = \frac{0.01500299}{0.1500299} = 0.1$$

$$P_1(A,50) = Y_1(A,50).\pi_L = (0.1).(357.0) = 35.7 \text{ cmHg}$$

It should be mentioned again that the figures presented in this sample calculation are only intended to give the relative size of the numbers, but do not represent the actual figures as calculated by the computer which takes into account every position and time step of the calculation.

IV.- Fourth Stage.

To calculate the volumes from each segment, Equations 53, 54, and 55, and 56 are solved.

For I = 1 and J = 1

$$V_{RAJ} = V_{RL} - V.\epsilon.J$$

$$V_{RAJ} = 760.0 - (19.9).(0.762).(1) = 744.8362 \text{ cc}$$

$$V_{TJ} = V_{AD} + V_{RAJ} = 304.0 + 744.8362 = 1048.8362 \text{ cc}$$

$$FRCT = \frac{V_{TJ} - V.}{V_{TJ}} = \frac{1048.8362 - (19.9).(0.762)}{1048.8362}$$

$$FRCT = 0.98554217$$

$$V' = V_{AD}.(1.0 - FRCT) = (304.0).(0.01445783) = 4.395181 \text{ cc}$$

The pressure of component 1 in reservoir A, as compression progress, is calculated as follows,

$$P_1(A,J) = P_1(A,1).\frac{(V_{RL} + V_{AD})}{V_{TJ}}$$

$$P_1(A,J) = \frac{(35.7).(760.0 + 304.0)}{1048.8363} = 36.21613783 \text{ cmHg}$$

$$G_4 = \frac{n - I}{n - 1} = \frac{20 - 1}{20 - I} = 1.0$$

From Equations 59, 60, and 61 the factor H_4 can be calculated.

$$F_3 = \frac{(\epsilon.V - V'.G_4)}{R.T.FRCT}$$

$$= \frac{(0.762).(19.9) - (4.39518121).(1.0)}{(6236.0).(290.0).(0.98554217)} = 0.00000604 \ \frac{\text{gm-mole}}{\text{cmHg}}$$

$$F_4 = \frac{V'.G_4}{R.T.FRCT}$$

$$F_4 = \frac{(4.39518121).(1.0)}{(6236.0).(290.0).(0.98554217)} = 0.00000247 \ \frac{\text{gm-mole}}{\text{cmHg}}$$

$$H_4 = F_3.P_1(I,J-1) + F_4.P_1(I-1,J-1) + G.Q_1(I,J-1)$$

$$F_3.P_1(1,0) = (0.00000604).(35.7) = 0.00021563 \text{ gm-mole}$$

$$F_4.P_1(0,0) = (0.00000247).(35.7) = 0.00008818 \text{ gm-mole}$$

$$G.Q_1(1,0) = (9.94602).(0.00414396) = 0.04121591 \text{ gm-mole}$$

$$H_4 = 0.00021563 + 0.00008818 + 0.04121591 = 0.04151972 \text{ gm-mole}$$

The constants from the quadratic equation are solved from Equations 62, 63, and 64.

$$a = F = 0.00000839 \text{ gm-mole/cmHg}$$

$$b = G.D + E.F - H_4$$

$$b = 0.05320723 \div 0.04151972 = 0.01168751 \text{ gm-mole}$$

$$c = -E.H_4 = -(10.46).(0.04151972) = -0.43429627 \text{ gm-mole.cmHg}$$

$$P_1(I,J) = \frac{-b + (b^2 - 4.a.c)^{1/2}}{2.a}$$

$$(b^2-4.a.c)^{1/2} = ((0.01168751)^2 - 4.(0.00000839).(-0.43429627))^{1/2}$$

$$= 0.01229532$$

$$P_1(1,1) = \frac{-0.01168751 + 0.01229532}{0.00001678} = 36.2225039 \text{ cmHg}$$

$$Q_1(1,1) = \frac{D.P_1(1,1)}{E + P_1(1,1)}$$

$$= \frac{(0.0053496).(36.2225039)}{10.46 + 36.2225039} = 0.00415093 \text{ gm-mole}$$

$$R_{AH1} = \frac{P_1(1, \tau_C).V_{RH}}{R.T}$$

Since it was assumed that the concentration of component 1 is very small, and the total pressure is not affected by the change in component 1 partial pressure, at the end of each cycle a proportionallity factor is calculated and used to adjust the partial pressure of component 1 throughout the system before the next cycle starts.

$$\text{PROP} = \frac{\text{Moles of component 1 that should be in the gas phase}}{\text{Actual moles of component 1 in gas phase}}$$

The equation to calculate this factor is Equation 66.

RESULTS AND DISCUSSION

The mathematical model previously described for the batch isothermal pressure changing parametric pump was solved for eighteen different data combinations, with the help of a computer. The same column and packing parameters, similar to Jenczewski and Myers (7), were used for all sets of data.

The data for each computer run is listed in Appendix 1, and a summary of the results are tabulated in Appendix 2. The computer calculation time was limited to 10 minutes per run, and each run was calculated for as many cycles as possible within this time limit. Single precision (24 bits) numbers were used for all runs except 13 and 15, where double precision (48 bits) was used. For the dilute gas mixtures, where very small differences are calculated in the material balance, the precision of the calculations is very important, but in the other hand the greater the precision, the less number of cycles the computer was able to calculate in the time available.

Figure 11 shows the importance of the computer precision for low partial pressures on the separation results obtained. Curves 1 and 1.a are calculated from the same set of data, for a dilute concentration of propane, $Y_1 = 0.01$. The separation results, P_{1A}/P_{1B}, is the same up to the first cycle for both curves, but as the cycles progress, curve 1 continues an upward trend, while curve 1.a becomes flat. The reason for this difference in behavior is that the curve 1 was calculated with double precision, while the curve 1.a was calculated with single precision. Due to this computer limitation the separation results reported with single precision calculations are reliable only for the first ten cycles. From the two double precision runs it can be predicted that the separation curves will continue to go up as the number of cycles increases.

To illustrate the distribution of propane partial pressure throughout the column, Figure 6 shows a family of curves for cycles 1 to 5, at the high total pressure. From this figure **it is** evident that the reservoir A, where the compression occurs, gains in propane as the reservoir B, where expansion occurs, is depleted from it. **The same effect is shown in Figure 9 after** 30 cycles, for the same initial conditions.

In Figure 7 the separation results of five different sets of data versus the number of cycles are **plotted.** Curves 1 and 3 at a lower temperature (310 ºK) give a greater separation than curves 2 and 4 at a higher temperature (373 ºK) , all other parameters equal. The lower initial partial pressure of propane gives a lower separation factor, but the **behavior** of this curves beyond ten cycles is difficult to predict due to the previously **explained** computer limitations. Curve 6 was taken from reference (7), and it shows the predicted separation for the temperature changing parametric pump, for the same system Propane-Argon on carbon. Curve 5 has the same parameters as curve 2 except it has a lower penetration, V_{RI}/V_{AD}. The rate of separation is smaller for the lower penetration factor.

Comparing the results of the batch temperature changing model (7) with the pressure changing model for a similar parametric pump, for the same fraction change of absolute temperature and pressure, the temperature changing model predicts three times more separation than the pressure changing model* with similar propane partial pressure.

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*See Figure 7.

Figure 8 shows the concentration of propane, Y_1, at each reservoir against the number of cycles. The curves with positive slope represent the increase in concentration of propane in reservoir A, and the negative **sloped** curves the concentration in reservoir B.

The distance the plug flow front travels from the reservoir into the column is **referred** as the penetration of the gas phase. The maximum penetration occurs when the low pressure (largest volume) reservoir is moved into the column. Figure 9 shows the partial pressure distribution of propane after 30 cycles of the computer run 5, which has a maximum penetration, V_{RL}/V_{RH}, of 0.79. In this figure, a change in slope occurs at the position in the column, where the maximum penetration reaches.

The effect of the volume ratio of the reservoirs at the two different pressures, V_{RL}/V_{RH}, and the maximum penetration are shown in Figure 10. The deeper the penetration in the column, and the larger the ratio of V_{RL}/V_{RH}, the faster the separation, P_{1A}/P_{1B}, that is obtained.* The effect of the maximum penetration appears to be more significant than the relative size of the reservoirs on the rate of separation, but the effect of **these parameters** beyond ten cycles is difficult to predict.

The runs with lower partial pressure of propane appear to give better rate of separation than the higher ones. As **may be seen** in figure 11, curve 1 shows an upward trend, which anticipates greater separation ratios than the curves in Figure 7 and 10. Run 15 and run 8 are identical except for the initial concentration of propane, Y_1, which is 10 times lower in run 15, and

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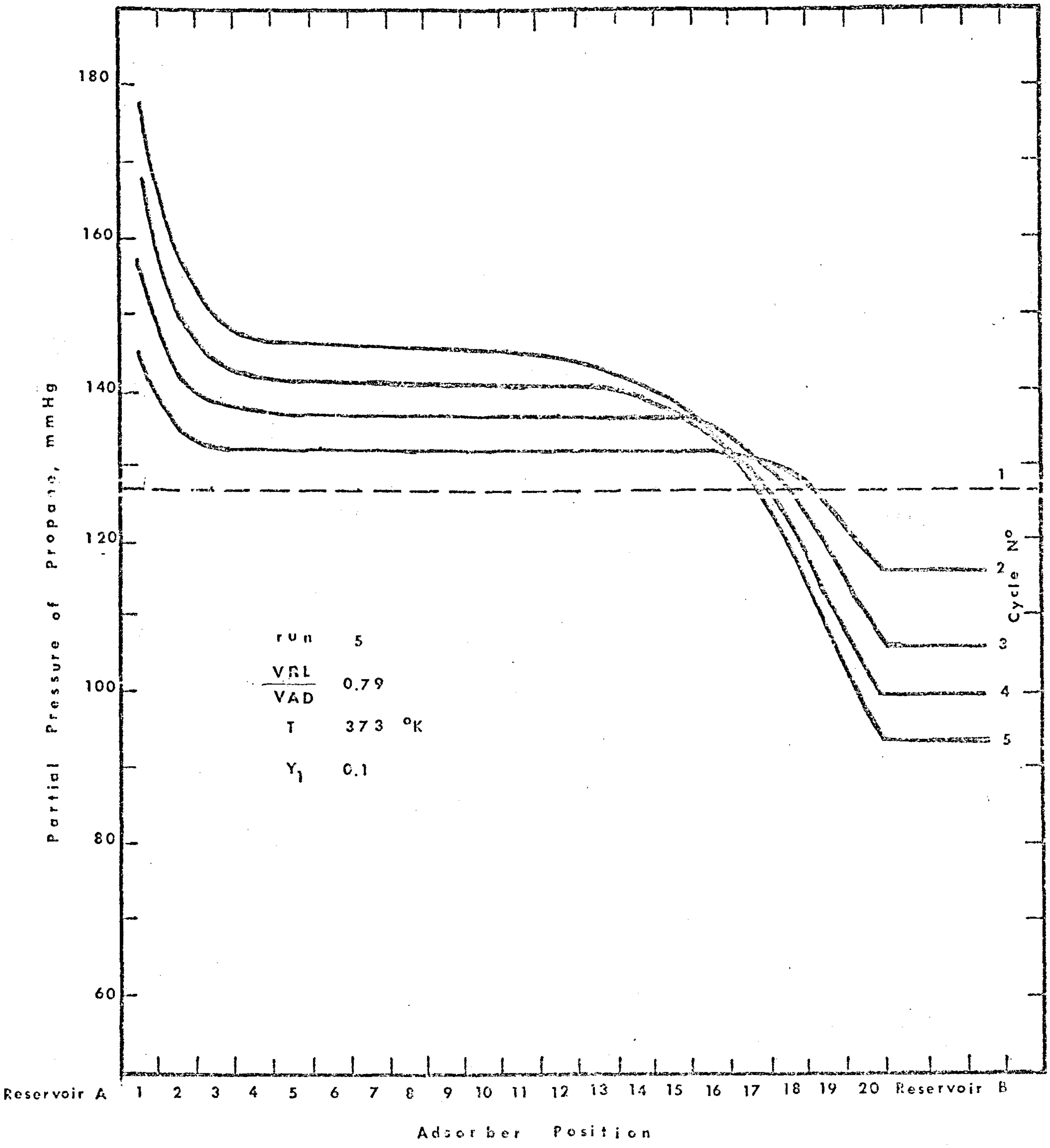
* See Figure 5.

FIGURE 6

FINAL PARTIAL PRESSURE OF PROPANE IN THE HIGH PRESSURE STAGE THROUGH THE ADSORBER



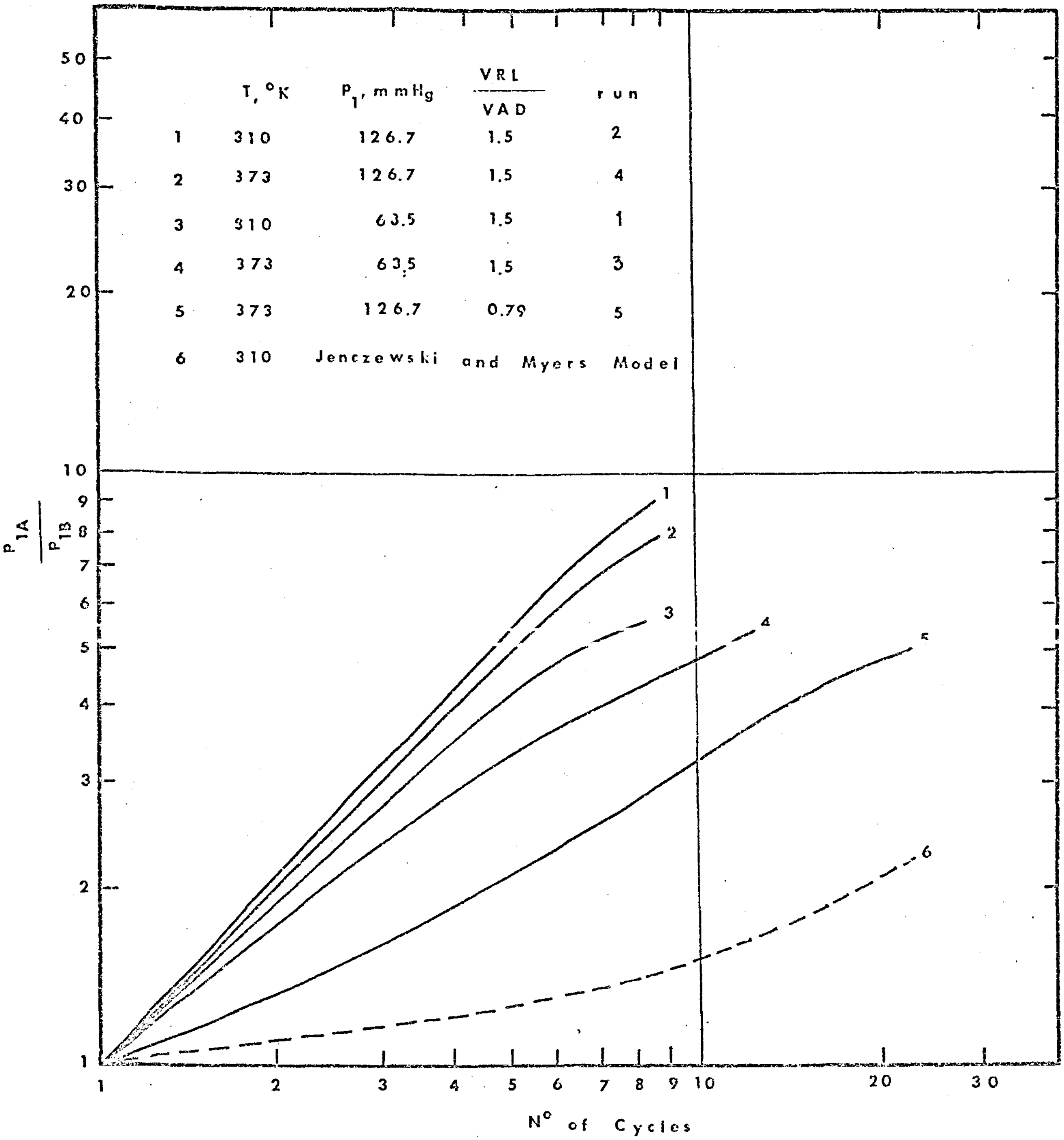


FIG. 7

PROPANE SEPARATION VS. NUMBER OF CYCLES

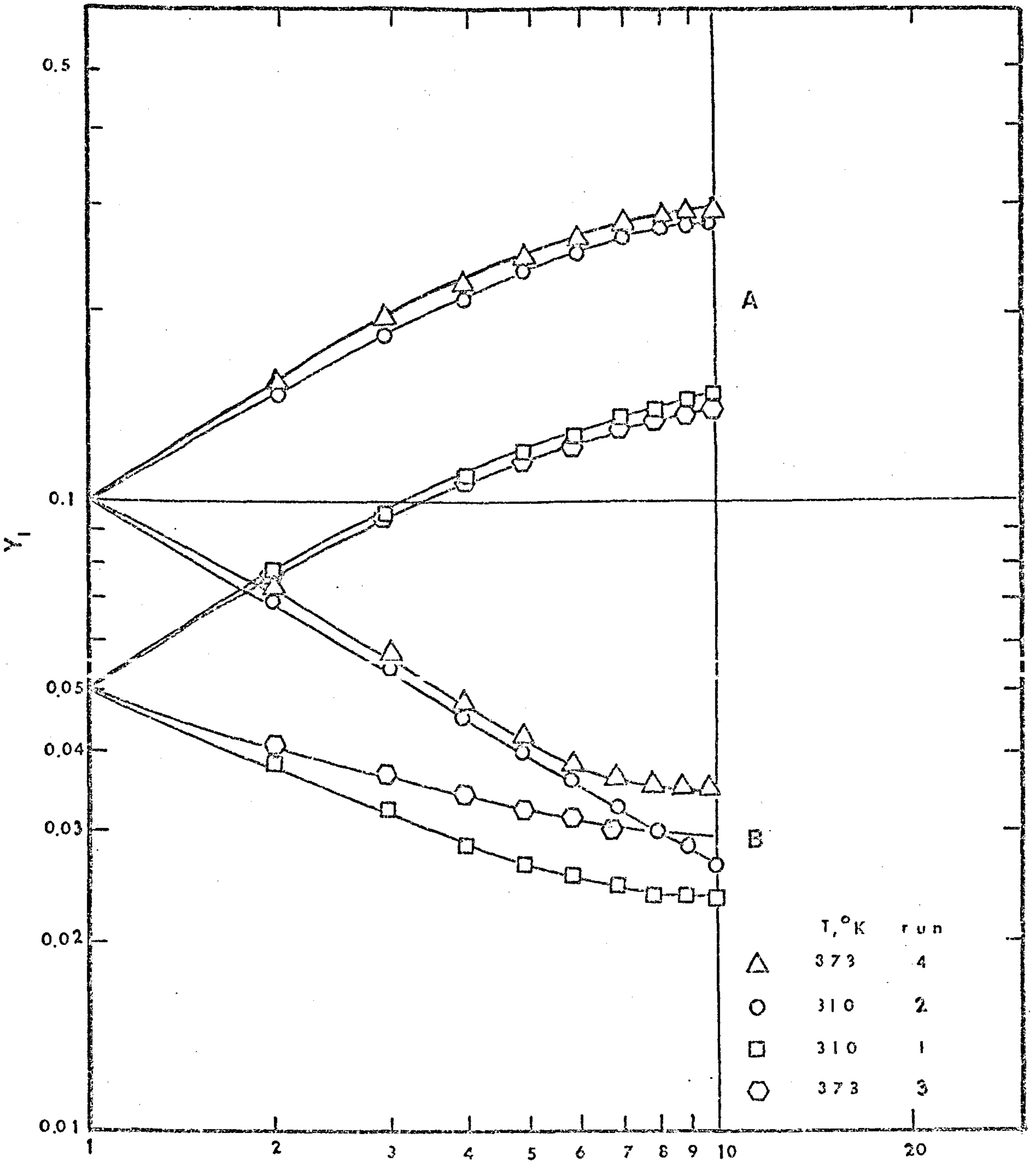


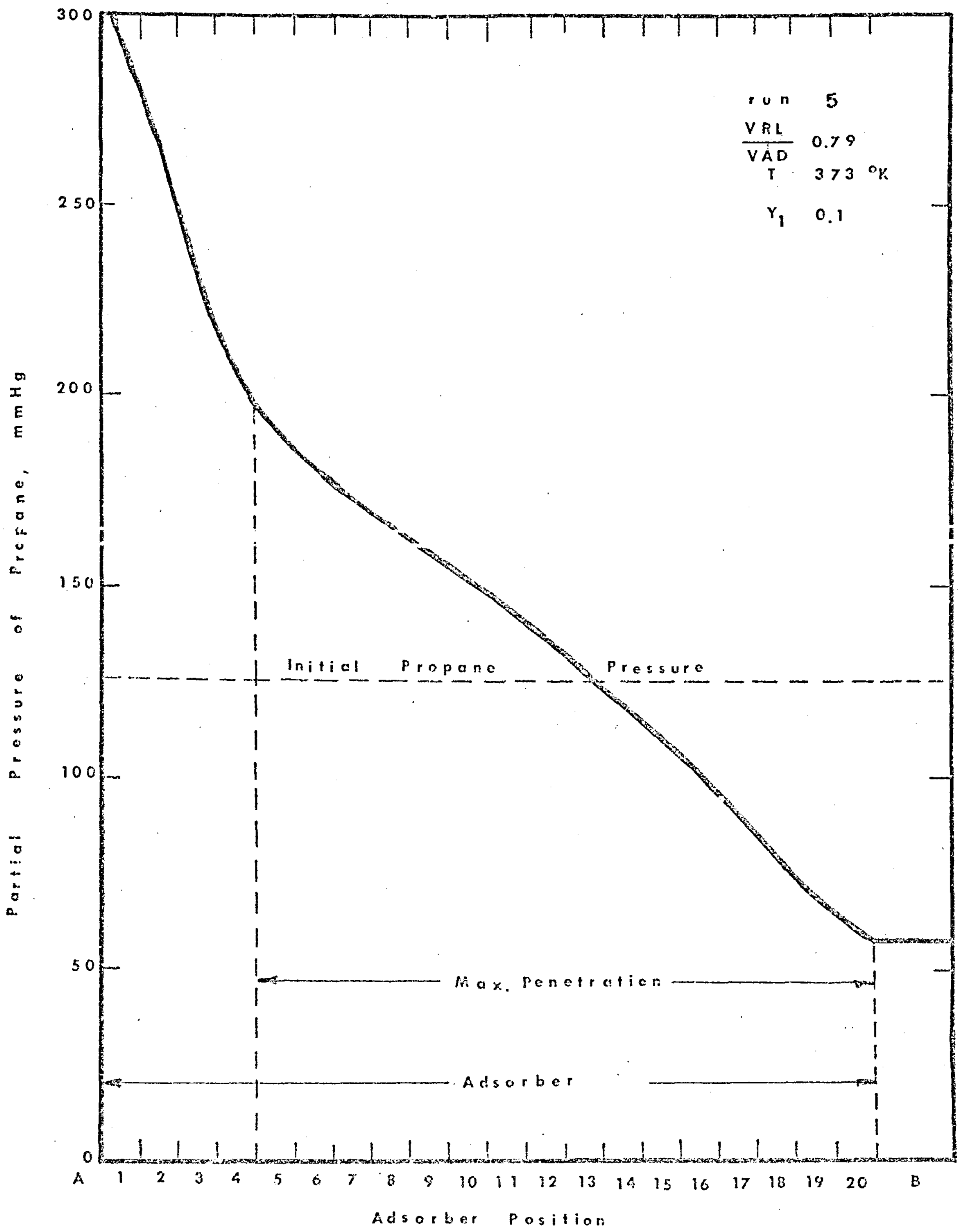
FIG. 8

MOLE FRACTION OF PROPANE AT EACH RESERVOIR

VS. NUMBER OF CYCLES

FIGURE 9

PARTIAL PRESSURE OF PROPANE IN THE HIGH PRESSURE STAGE OF THE 30th CYCLE



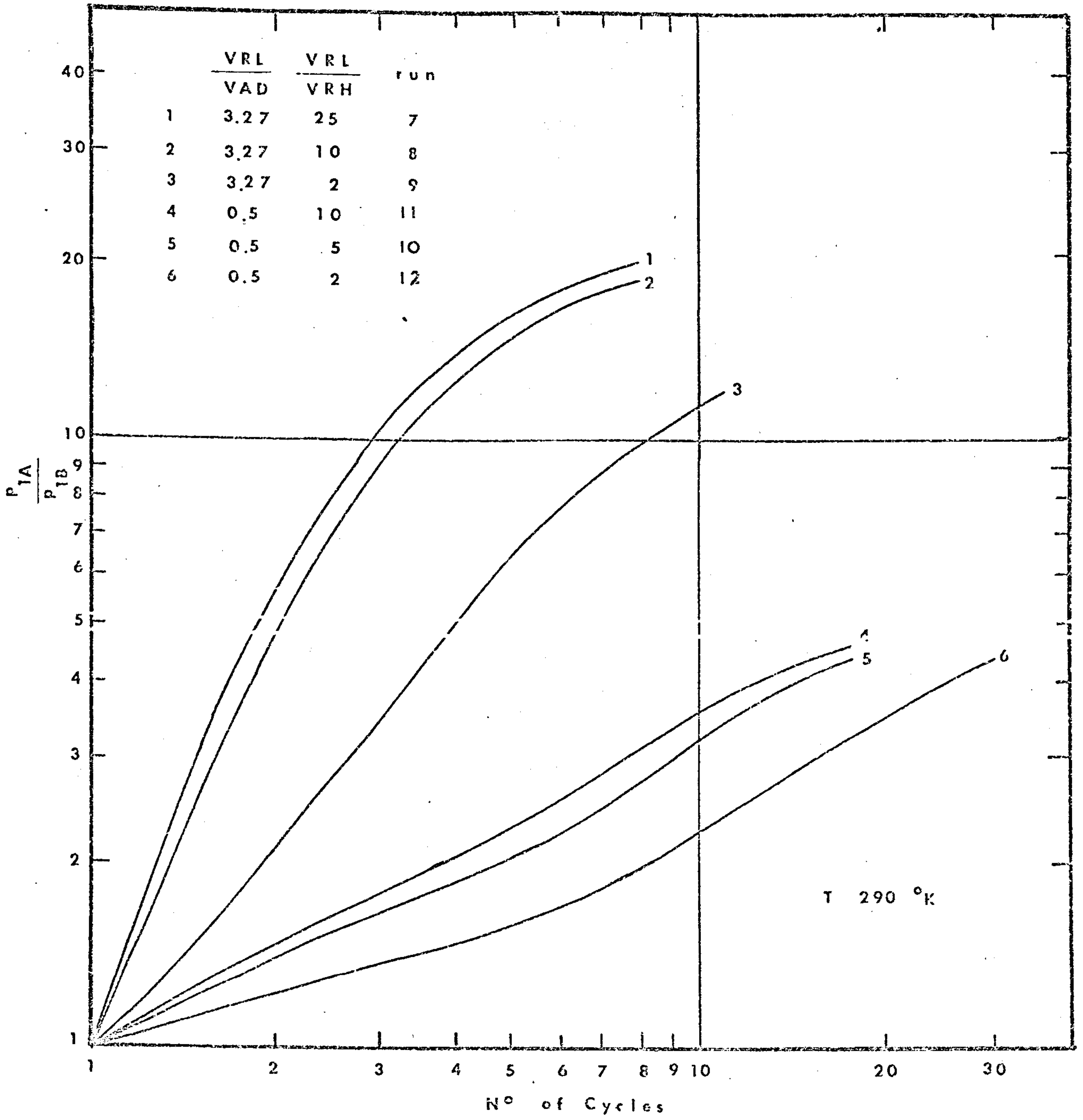


FIG. 10

SEPARATION VS. PENETRATION AND RESERVOIR RATIO the fact that run 8 was calculated with single precision while run 15 was done with double precision. The effect of the dilution (lower partial pressure of propane) and the calculation precision are very significant in the slope of the separation curves.

Figure 12 shows the concentration of propane, Y_1, in both reservoirs for each cycle, for two reservoirs size variations, with the low propane concentration. This figure shows similar curves as Figure 8. The rate of depletion of propane from reservoir B appears to increase as the number of cycles increases in Figure 12, while in Figure 8 the curves tend to reduce the rate concentration changes as the number of cycles increase.

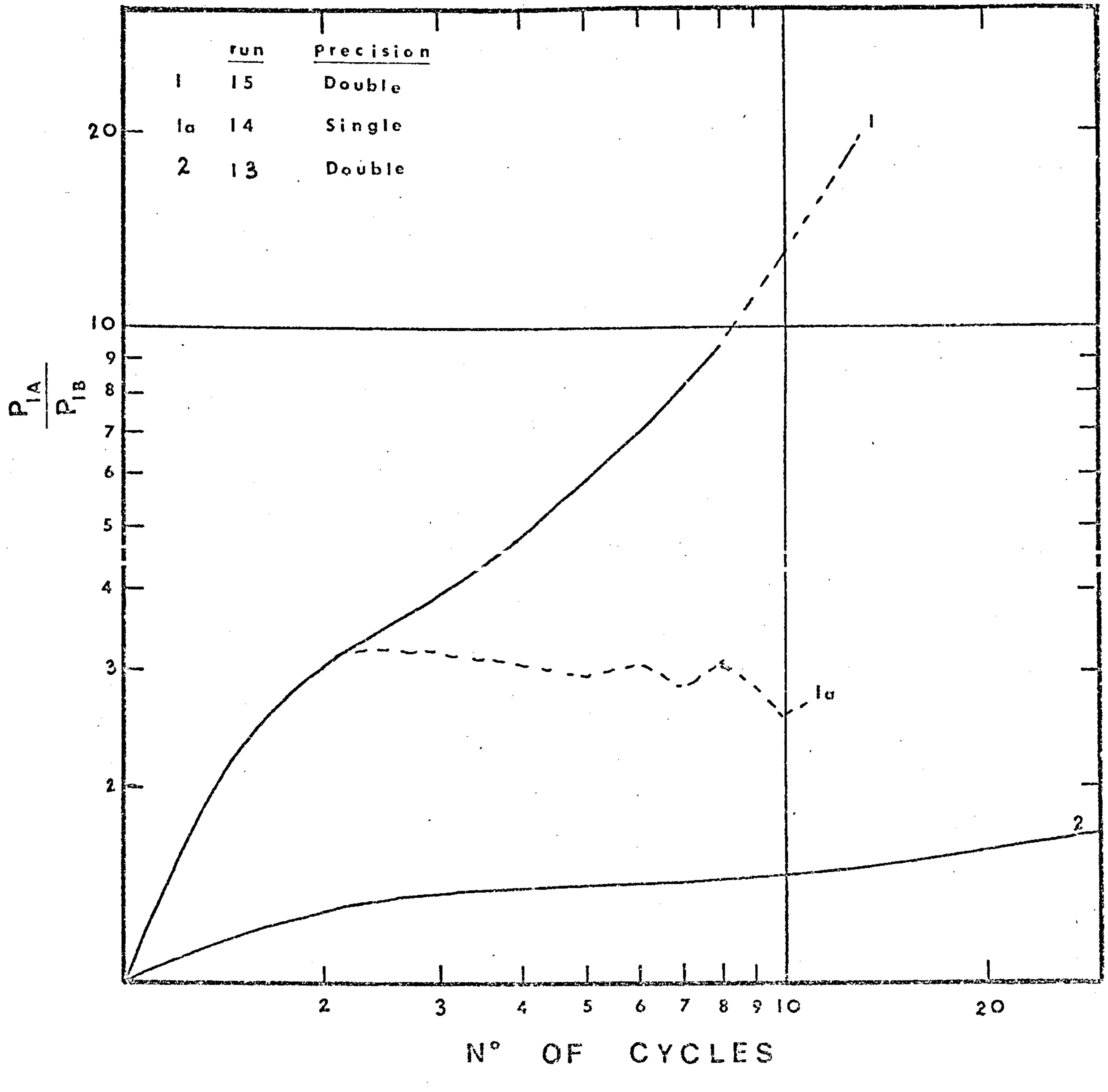


FIG. 11

COMPUTER PRECISION VS. SEPARATION

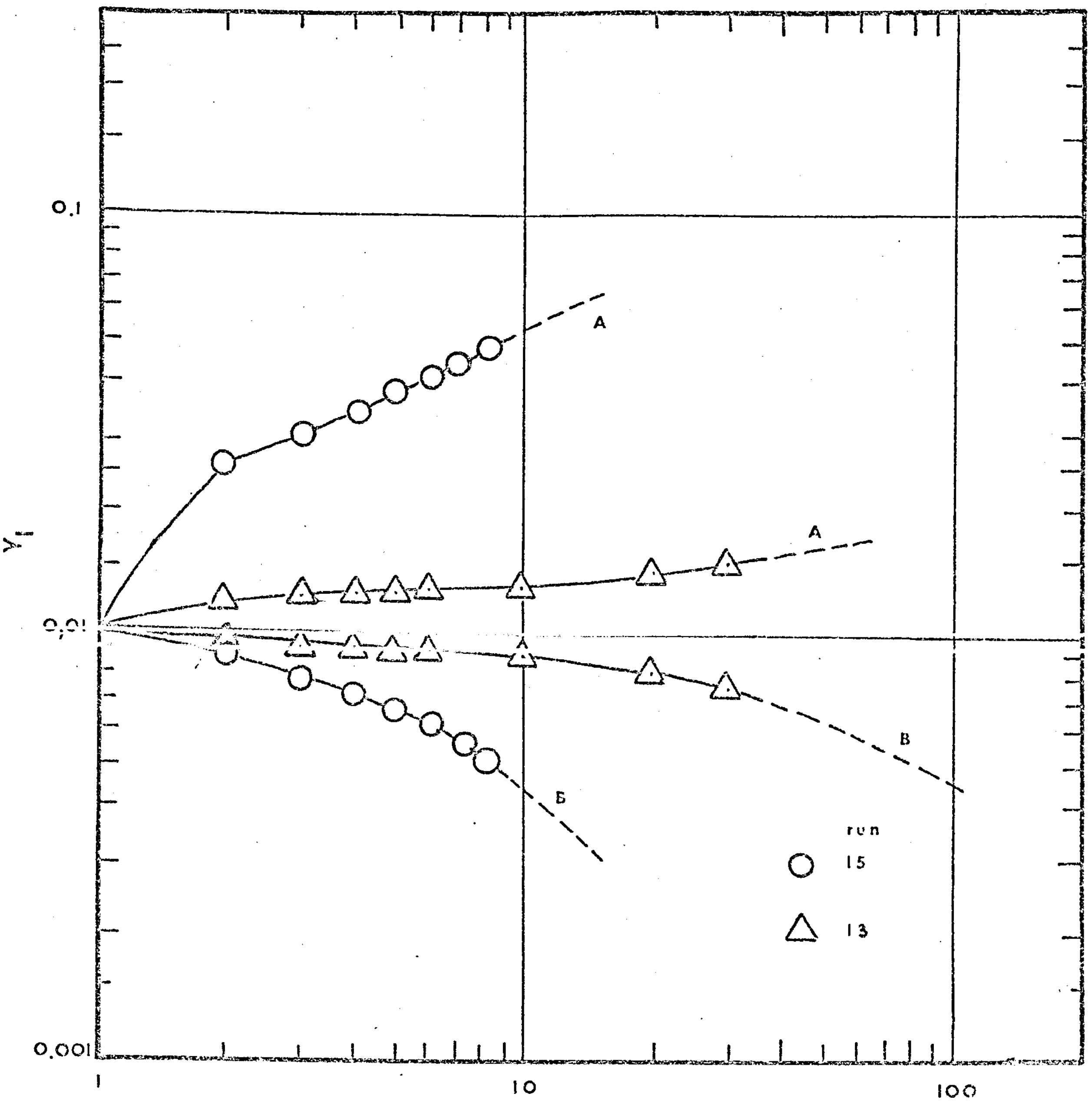


FIG. 12

MOLE CONC. OF PROPANE VS. NUMBER OF CYCLES.

NOTATION

A = Reservoir A.

a = Quadratic equation constant.

B = Reservoir B.

b = Quadratic equation constant.

c = Quadratic equation constant.

D = Adsorption equilibrium equation temperature dependent constant, gm-mole/gm.

d = Inside diameter of column, cm.

E = Adsorption equilibrium equation temperature dependent constant, cmHg.

F = Volume element mole-pressure factor, gm-mole/cmHg.

F_1, F_2 = Fraction of volume element mole-pressure factor used in the expansion stage, gm-mole/cmHg.

F_3, F_4 = Fraction of volume element mole-pressure factor used in the expansion stage, gm-mole/cmHg.

FRCT = Fraction of volume change in any given time step, dimensionless. (see Equation 27).

G = Adsorber weight of volume element, gm.

G_{11} = Position distribution factor in the expansion stage, dimensionless.

H_1 = Moles of component 1 in first stage material balance of a volume element, gm-mole.

H_2 = Moles of component 1 in the second stage material balance of a volume element, gm-mole.

H_3 = Moles of component 1 in the third stage material balance of a volume element, gm-mole.

H_4 = Moles of component 1 in the fourth stage material balance of a volume element, gm-mole.

I = Position element, dimensionless.

J = Time element, dimensionless.

K_1 = Adsorption equilibrium constant as $P_1 \rightarrow 0$, $\frac{\text{gm-mole}}{\text{gm.cmHg}}$.

K_2 = Adsorption equilibrium constant as $P_1 \rightarrow \infty$, $\frac{\text{gm-mole}}{\text{gm}}$.

n = Number of column volume elements, dimensionless.

n_T = Total number of moles, gm-mole.

PROP = Correction factor, dimensionless.

P_1 = Partial pressure of component 1, cmHg.

P_2 = Partial pressure of component 2, cmHg.

$P_1(I,J)$ = Partial pressure of component I at position I in the column and time J, cmHg.

Q_1 = Adsorbate density of component 1, gm-mole/gm.

$Q_1(I,J)$ = Adsorbate density of component 1 at position I in the column and time J, gm-mole/gm.

R = Ideal gas constant, 6236.0 $\frac{\text{cc.cmHg}}{\text{gm-mole.}^\circ\text{K}}$.

R_{ACI} = Number of moles of component I in reservoir A during compression stage, gm-mole.

R_{ACT} = Total number of moles in reservoir A during compression stage, gm-mole.

R_{AH1} = Number of moles of component 1 in reservoir A during the high pressure stage, gm-mole.

R_{AHT} = Total number of moles in reservoir A during the high pressure stage, gm-mole.

R_{AL1} = Number of moles of component 1 in reservoir A during the low pressure stage, gm-mole.

R_{ALT} = Total number of moles in reservoir A during the low pressure stage, gm-mole.

R_{BE1} = Number of moles of component 1 in reservoir B during the expansion stage, gm-mole.

R_{BET} = Total number of moles in reservoir B during the expansion stage, gm-mole.

R_{BH1} = Number of moles of component 1 in reservoir B during the high pressure stage, gm-mole.

R_{BHT} = Total number of moles in reservoir B during the high pressure stage, gm-mole.

R_{BL1} = Number of moles of component 1 in reservoir B during the low pressure stage, gm-mole.

R_{BLT} = Total number of moles in reservoir B during the low pressure stage, gm-mole.

T = Absolute temperature, ºK.

V = Volume of one column element, cc.

V' = Volume element adjusted for one step pressure change, cc.

V_A = Volume of reservoir A, cc.

V_B = Volume of reservoir B, cc.

V_{AD} = Free volume of column, cc.

V_C = Total volume of column, cc.

V_{REJ} = Volume of gases in reservoir B at any time J, cc.

V_{RAJ} = Volume of gases in reservoir A at any time J, cc.

V_{RH} = Maximum volume of reservoirs at high pressure, cc.

V_{RL} = Maximum volume of reservoirs at low pressure, cc.

V_T = Total free volume of column plus reservoirs, cc.

V_{TJ} = Total free volume of the system at any time J, cc.

Y_1 = Molar concentration, of component 1 in the gas phase, dimensionless.

Y_2 = Molar concentration of component 2 in the gas phase, dimensionless.

Greek Letters

ϵ = Void fraction in packing, dimensionless.
π_H = Total high pressure, cmHg.
π_L = Total low pressure, cmHg.
τ_H = Number of time steps for the high pressure stage, dimensionless.
τ_E = Number of time steps for the expansion stage, dimensionless.
τ_L = Number of time steps for the low pressure stage, dimensionless.
τ_C = Number of time steps for the compression stage, dimensionless.
= Specific density of the adsorber, gm/cc.

Subscripts

AD = Adsorber column
C = Compression stage (except for V_C).
E = Expansion stage.
H = High pressure.
L = Low pressure.
R = Reservoir.
T = Total.

APPENDIX 1

DATA SHEETS

DATA SHEET 1

Variable	Unit	Computer Run 1	2	3
P_H	cmHg	1267.0	1267.0	1267.0
P_L	cmHg	761.0	761.0	761.0
T	ºK	310.5	310.5	373.0
V_{RH}	cc	154.0	154.0	154.0
V_{RL}	cc	462.0	462.0	462.0
P_{HIII}	cmHg	163.35	126.75	163.35
Y_1	-	0.05	0.15	0.05
Y_2	-	0.95	0.95	0.95
JTAUH	-	11	11	11
JTAUE	-	21	21	21
JTAUC	-	21	21	21
JTAUL	-	31	31	31
V_{RL}/V_{AD}	-	1.5	1.5	1.5
V_{RL}/V_{RH}	-	3.0	3.0	3.0

DATA SHEET 2

Variable	Unit	Computer Run		
		4	5	6
P_H	cmHg	1267.0	1267.0	1000.0
P_L	cmHg	761.0	984.0	356.58
T	ºK	373.0	373.0	290.0
V_{RH}	cc	154.0	121.0	159.2
V_{RL}	cc	462.0	243.2	995.0
P_{H111}	cmHg	126.7	126.7	100.0
Y_1	–	0.1	0.1	0.1
Y_2	–	0.9	0.9	0.9
JTAUH	–	11	9	9
JTAUE	–	21	9	43
JTAUC	–	21	9	43
JTAUL	–	31	17	51
V_{RL}/V_{AD}	–	1.5	0.79	3.0
V_{RL}/V_{RH}	–	3.0	2.0	6.2

DATA SHEET 3

Variable	Unit	Computer Run		
		7	8	9
P_H	cmHg	1000.0	1000.0	1000.0
P_L	cmHg	323.0	357.0	642.0
T	°K	290.0	290.0	290.0
V_{RH}	cc	30.4	76.0	380.0
V_{RL}	cc	760.0	760.0	760.0
P_{H111}	cmHg	100.0	100.0	100.0
Y_1	-	0.1	0.1	0.1
Y_2	-	0.9	0.9	0.9
JTAUH	-	3	6	26
JTAUE	-	49	46	26
JTAUC	-	49	46	26
JTAUL	-	51	51	51
V_{RL}/V_{AD}	-	3.27	3.27	3.27
V_{RL}/V_{RH}	-	25.0	10.0	2.0

DATA SHEET 4

Variable	Unit	Computer Run		
		10	11	12
P_H	cmHg	1000.0	1000.0	1000.0
P_L	cmHg	731.0	698.0	830.0
T	ºK	290.0	290.0	290.0
V_{RH}	cc	30.4	15.4	76.0
V_{RL}	cc	154.0	154.0	154.0
P_{HIII}	cmHg	100.0	100.0	100.0
Y_1	-	0.1	0.1	0.1
Y_2	-	0.9	0.9	0.9
JTAUH	-	3	2	6
JTAUE	-	9	10	6
JTAUC	-	9	10	6
JTAUL	-	11	11	11
V_{RL}/V_{AD}	-	0.5	0.5	0.5
V_{RL}/V_{RH}	-	5.0	10.0	2.0

DATA SHEET 5

Variable	Unit	Computer Run 13	14	15
P_H	cmHg	1000.0	1000.0	1000.0
P_L	cmHg	731.0	357.0	357.0
T	ºK	290.0	290.0	290.0
V_{RH}	cc	30.4	76.0	76.0
V_{RL}	cc	154.0	760.0	760.0
P_{H111}	cmHg	10.0	10.0	10.0
Y_1	-	0.01	0.01	0.01
Y_2	-	0.99	0.99	0.99
JTAUH	-	3	6	6
JTAUE	-	9	46	46
JTAUC	-	9	46	46
JTAUL	-	11	51	51
V_{RL}/V_{AD}	-	0.5	3.27	3.27
V_{RL}/V_{RH}	-	5.0	10.0	10.0

DATA SHEET 6

Variable	Unit	Computer Run		
		16	17	18
P_H	cmHg	1000.0	1000.0	1000.0
P_L	cmHg	323.0	323.0	467.1
T	ºK	350.0	400.0	290.0
V_{RH}	cc	30.4	30.4	760.0
V_{RL}	cc	760.0	760.0	1520.0
P_{HI11}	cmHg	100.0	100.0	100.0
Y_1	-	0.1	0.1	0.1
Y_2	-	0.9	0.9	0.9
JTAUH	-	3	3	51
JTAUE	-	49	49	51
JTAUC	-	49	49	51
JTAUL	-	51	51	101
V_{RL}/V_{AD}	-	3.27	3.27	5.0
V_{RL}/V_{RH}	-	25.0	25.0	2.0

APPENDIX 2

RESULTS SUMMARY SHEETS

RESULTS SUMMARY SHEET 1

Computer Run

	1		2		3	
Reservoir	A	B	A	B	A	B
Total moles	0.183	0.101	0.183	0.101	0.151	0.024
Cycle	Concentration of Propane in each reservoir, Y_1					
0	0.05	0.05	0.10	0.10	0.05	0.05
1	0.0792	0.0376	0.150	0.0683	0.0795	0.0405
2	0.0967	0.0327	0.185	0.0545	0.095	0.037
3	0.1091	0.0287	0.213	0.0455	0.107	0.034
4	0.1200	0.0267	0.234	0.0386	0.115	0.033
5	0.1273	0.0257	0.247	0.0346	0.123	0.032
6	0.1338	0.0248	0.255	0.0317	0.130	0.031
7	0.1395	0.0238	0.257	0.0308	0.135	0.030
8	0.1442	0.0238	0.263	0.0288	0.139	0.0286
9	0.1510	0.0238	0.264	0.0279	0.143	0.0286
10	0.1530	0.0238	0.265	0.0299	0.148	0.0286

RESULTS SUMMARY SHEET 2

Computer Run

	4		5		6	
Reservoir	A	B	A	B	A	B
Cycle	Concentration of Propane in each reservoir, Y_1					
0	0.10	0.10	0.10	0.10	0.10	0.10
1	0.1545	0.0714	0.108	0.10	0.129	0.034
2	0.1920	0.0584	0.118	0.093	0.172	0.022
3	0.219	0.0487	0.125	0.088	0.194	0.017
4	0.242	0.0429	0.131	0.083	0.200	0.016
5	0.261	0.0383	0.137	0.077	0.201	0.015
6	0.275	0.0369	0.143	0.074	0.202	0.015
7	0.284	0.0358	0.148	0.070	-	-
8	0.291	0.0358	0.152	0.068	-	-
9	0.294	0.0358	0.158	0.065	-	-
10	0.295	0.0345	0.164	0.063	-	-

RESULTS SUMMARY SHEET 3

	Computer Run					
	7		8		9	
Reservoir	A	B	A	B	A	B
Cycle	Concentration of Propane in each reservoir, Y_1					
0	0.100	0.100	0.100	0.100	0.100	0.100
I	0.258	0.049	0.232	0.051	0.142	0.071
2	0.303	0.031	0.287	0.033	0.187	0.055
3	0.327	0.023	0.313	0.024	0.227	0.045
4	0.334	0.020	0.319	0.021	0.251	0.038
5	0.336	0.019	0.322	0.019	0.265	0.032
6	0.337	0.018	0.323	0.018	0.272	0.030
7	-	-	-	-	0.276	0.028
8	-	-	-	-	0.279	0.026

RESULTS SUMMARY SHEET 4

	Computer Run					
	10		11		12	
Reservoir	A	B	A	B	A	B
Cycle	Concentration of Propane in each reservoir, Y_1					
0	0.100	0.100	0.100	0.100	0.100	0.100
1	0.122	0.084	0.127	0.082	0.110	0.089
2	0.123	0.075	0.127	0.072	0.114	0.083
3	0.126	0.068	0.127	0.065	0.116	0.078
4	0.129	0.063	0.130	0.059	0.118	0.074
5	0.132	0.058	0.134	0.054	0.121	0.071
6	0.136	0.055	0.138	0.051	0.124	0.068
7	0.140	0.052	0.143	0.048	0.127	0.065
8	0.145	0.049	0.149	0.045	0.130	0.063
9	0.151	0.047	0.154	0.044	0.133	0.061
10	0.156	0.046	0.160	0.042	0.136	0.059
20	0.178	0.041	0.179	0.039	0.161	0.051
30	0.180	0.040	0.180	0.038	0.170	0.048

RESULTS SUMMARY SHEET 5

Reservoir	Computer Run					
	13		14		15	
	A	B	A	B	A	B
Cycle	Concentration of Propane in each reservoir, Y_1.					
0	0.01	0.01	0.01	0.01	0.01	0.01
1	0.0128	0.0098	0.0255	0.0085	0.0266	0.0087
2	0.0129	0.0097	0.0255	0.0082	0.0306	0.0079
3	0.0130	0.0096	0.0261	0.0085	0.0344	0.0072
4	0.0131	0.0095	0.0249	0.0085	0.0380	0.0066
5	0.0132	0.0094	0.0239	0.0078	0.0415	0.0061
6	0.0133	0.0093	0.0240	0.0085	0.0447	0.0057
7	0.0134	0.0092	0.0240	0.0078	0.0476	0.0053
8	0.0135	0.0091	0.0248	0.0085	–	–
9	0.0136	0.0090	0.0247	0.0095	–	–
10	0.0137	0.0089	0.0236	0.0087	–	–
20	0.0143	0.0082	–	–	–	–
30	0.0149	0.0076	–	–	–	–

RESULTS SUMMARY SHEET 6

Concentration of Propane in each reservoir, Y_1

Reservoir Cycle	Computer Run 16 A	16 B	17 A	17 B	18 A	18 B
0	0.10	0.10	0.10	0.10	0.10	0.10
1	0.275	0.053	0.279	0.054	0.155	0.063
2	0.333	0.035	0.340	0.035	0.216	0.047
3	0.364	0.026	0.375	0.026	0.252	0.034
4	0.390	0.021	–	–	0.271	0.027
5	0.403	0.019	–	–	0.282	0.026
6	0.409	0.017	–	–	0.284	0.025

APPENDIX 3

COMPUTER PROGRAM

COMPUTER PROGRAM

The solution of the equations for the pressure changing parametric pump, as described in the sample calculation, requires the use of small volume segments to approximate the actual behavior of the system, and very high precision in the calculations, so the small differences in the material balances that produce the separation, are not smaller than the size of numbers used.

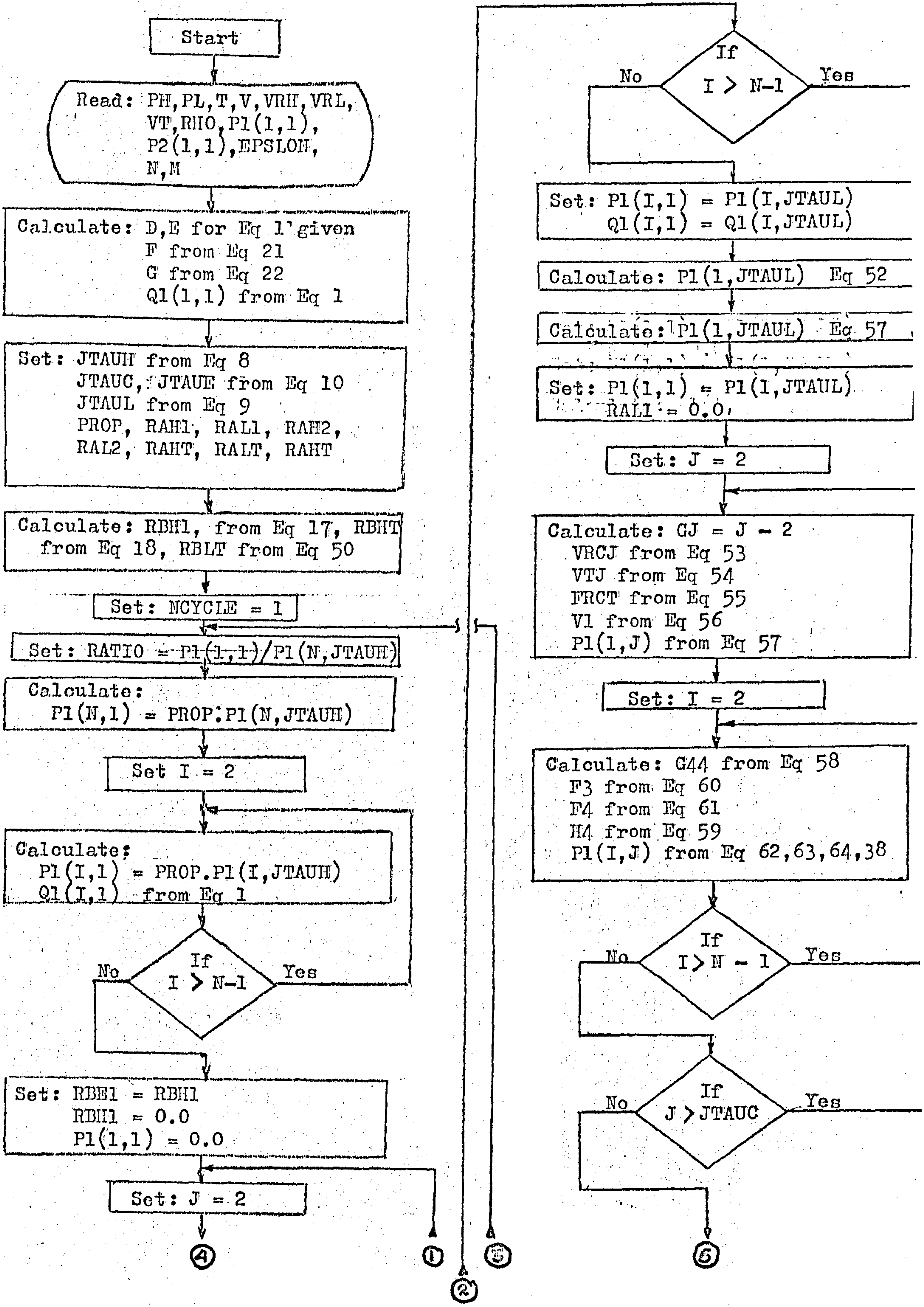
The use of a computer to carry this task is ideal, since both high precision and large number of calculations are possible. A Fortran IV computer program was written, and used to calculate 18 different sets of data. A computer program flow sheet is included to facilitate the understanding of the calculation sequence.

The parameters fed into the computer and used for all calculations made, are: V, VT, RHO, EPSLON, N, M, R, CYTIME, and VAD. The additional data used in the calculation of each computer run are: PH, PL, T, VRH, VRL, PH111, Y1,Y2, JTAUH, JTAUC, JTAUE, and JTAUL.

The data used for each computer run are summarized in the data sheets, and typical printouts of the results are also included. A list of Fortran statements printed by the computer shows a simplified version of the computer statements shown in the flow sheet, to give enough core storage capacity for double precision calculation. The difference is that for the flow sheet there is a different pressure and adsorbate density variable for each stage in the cycle, whereas in the Fortran statement list the same variable is used for all stages. This reduces the number of arrays necessary from eight to two, permitting larger arrays.

This program was run in a G. E. computer at E. I. duPont research facilities in Parlin, New Jersey.

COMPUTER PROGRAM FLOW SHEET



COMPUTER VARIABLES LIST

$TEMP	BSS	8	Temperature
PH	BSS	1	High Pressure.
PL	BSS	1	Low Pressure.
T	BSS	1	Temperature.
V	BSS	1	Volume element.
VRH	BSS	1	Reservoir volume at high pressure.
VRL	BSS	1	Reservoir volume at low pressure.
VT	BSS	1	Total volume of column.
RHO	BSS	1	Adsorbent specific density.
PH111	BSS	1	Initial partial press. of 1.
EPSLON	BSS	1	Void fraction.
N	BSS	1	Number of volume elements.
M	BSS	1	Number of cycles.
R	BSS	1	Ideal gas constant.
CYTIME	BSS	1	Time of one cycle.
VAD	BSS	1	Free volume of column.
Y1	BSS	1	Component 1 conc. in gas.
Y2	BSS	1	Component 2 conc. in gas.
JTAUH	BSS	1	High pressure stage time period.
JTAUC	BSS	1	Compression stage time period.
JTAUE	BSS	1	Expansion stage time period.
JTAUL	BSS	1	Low pressure stage time period.
D	BSS	1	Adsorption equilibrium constant.
E	BSS	1	Adsorption equilibrium constant.
F	BSS	1	Mole-pressure factor.
G	BSS	1	Volume element adsorbent weight.
I	BSS	1	Column position.
PROP	BSS	1	Correction factor.
RAH1	BSS	1	Moles of 1 at reservoir A and PH.
RAL1	BSS	1	Moles of 1 at reservoir A and PL.
RAH2	BSS	1	Moles of 2 at reservoir A and PH.
RAL2	BSS	1	Moles of 2 at reservoir A and PL.
RAHT	BSS	1	Total moles at reservoir A and PH.
RBH1	BSS	1	Moles of 1 at reservoir B and PH.
RBH2	BSS	1	Moles of 2 at reservoir B and PH.
RBHT	BSS	1	Total moles at reservoir B and PH.
RBLT	BSS	1	Total moles at reservoir B and PL.
RALT	BSS	1	Total moles at reservoir A and PL.
NCYCLE	BSS	1	Number of cycles (same as M)
RATIO	BSS	1	Press. of 1 in A/Press. of 1 in B.
SEPARA	BSS	1	Press. of 1 in A/Initial press. of 1.
SEPARB	BSS	1	Press. of 1 in B/Initial press. of 1.
RBE1	BSS	1	Moles of 1 in B at expansion.
J	BSS	1	Time element.
GJ	BSS	1	Time element (floating point).
VREJ	BSS	1	Reservoir volume for expansion time J.
VTJ	BSS	1	Total system volume for time J.
FRCT	BSS	1	Volume fraction.

```
 V1       BSS 1     Free volume of one element.
 G11      BSS 1     Volume distribution factor for exp.
 F1       BSS 1     Partial mole-pressure factor.
 F2       BSS 1     Partial mole-pressure factor.
 H2       BSS 1     Expansion material balance const.
 H3       BSS 1     Low press. material balance const.
 VRCJ     BSS 1     Reservoir volume for comp. time  J.
 G44      BSS 1     Volume distribution factor for comp.
 F3       BSS 1     Partial mole-pressure factor.
 F4       BSS 1     Partial mole-pressure factor.
 H4       BSS 1     Compression mat'l balance const.
 H1       BSS 1     High press. mat'l balance const.
 G50      BSS 1     Moles of I in column gas phase.
 G51      BSS 1     Moles of I in reservoir.
 G52      BSS 1     Moles of I in system gas phase.
 G53      BSS 1     Initial moles of I in gas phase.
 P1       BSS 2244   Partial pressure of I.
 Q1       BSS 2244   Adsorbate density of I.
 XXXEXP   LIB

 SQRTF    LIB


 *

 *PROGRAM END.     0 FORTRAN ERRORS
        END

                   0 ASSEMBLY ERRORS.
            013774 PROGRAM OCTAL SIZE.
            000542 EQL TABLE OCTAL SIZE.
```

Computer Program Statements - Fortran IV.

```
    IDN 000000                                                          1

                                                                        1
   ISOTHERMAL PRESSURE PARAMETRIC PUMP LOPEZ-CHEN                       7
   DIMENSION P1(22,52)                                                  7
    DIMENSION Q1(22,52)                                                 7
   PRINT 802                                                            7
2  FORMAT(1H1,$  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.$)      7
   READ 700,PH,PL,T,V,VRH,VRL,VT,RHO,PH111,     EPSLON,N,M,             7
  1R,CYTIME,VAD,Y1,Y2,JTAUH,JTAUC,JTAUE,JTAUL                           7
0  FORMAT(7F8.3,3F8.4/2I4,3F8.3,2F8.6,4I4)                              7
    P1(1,1) = PH111                                                     7
   PRINT 800                                                            7
0  FORMAT(1H0,$ P HIGH  P LOW    TEMP      VOL     VRH       VRL    $,  7
  1$PRESS1     VOID     N     M$)                                       7
   PRINT 801,PH,PL,T,V,VRH,VRL, P1(1,1),EPSLON,N,M                      7
1  FORMAT(1H,8F8.3,2I4)                                                 7
   D = 0.00934 - 0.00001376*T                                           7
   E = 0.269*T - 67.55                                                  7
   F = EPSLON*V/(R*T)                                                   7
   G = (1 - EPSLON)*V*RHO                                               7
    Q1(1,1) = D* P1(1,1)/(E+  P1(1,1))                                  7
    P1(N,1) =   P1(1,1)                                                 7
   DO 101  I = 2, N                                                     7
    P1(I,JTAUH) = P1(1,1)                                               7
1   Q1(I,JTAUH) =   Q1(1,1)                                             7
   PROP = 1.                                                            7
   RAH1 = 0.0                                                           7
   RAL1 = 0.0                                                           7
   RAH2 = 0.0                                                           7
   RAL2 = 0.0                                                           7
   RAHT = 0.0                                                           7
   RBH1 = VRH* P1(N,1)/(R*T)                                            7
   RBH2 = VRH*(PH- P1(N,1))/(R*T)                                       7
   RBHT = VRH*PH/(R*T)                                                  7
   RBLT = VRL*PL/(R*T)                                                  7
   RALT = RBLT                                                          7
   RAHT = RBHT                                                          7
   PRINT 850                                                            7
50 FORMAT(1H0,$ CYCLE   PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA $           7
  1$    SEPARB$)                                                        7
   DO 900  NCYCLE = 1,M                                                 7
   RATIO =  P1(1,1)/ P1(N,JTAUH)                                        7
   SEPARA = P1(1,1)/PH111                                               7
   SEPARB = P1(N,1)/PH111                                               7
   PRINT 851,NCYCLE, P1(1,1), P1(N,JTAUH),RATIO,                        7
  1SEPARA,SEPARB                                                        7
51 FORMAT(1H,2X,I3,2X,F8.4,1X,F8.5,2X,F8.4,2X,F8.5,2X,F8.5)             7
    P1(N,1) = PROP* P1(N,JTAUH)                                         7
   DO  102  I=2,N-1                                                     7
    P1(I,1) = PROP* P1(I,JTAUH)                                         7
02  Q1(I,1) = D* P1(I,1)/(E+ P1(I,1))                                   7
   RBE1 = RBH1                                                          7
   RBH1 = 0.0                                                           7
    P1(1,1) = 0.0                                                       7
```

```
      DO 201  J= 2,JTAUE
      GJ =J-2
      VREJ = VRH +V*GJ*EPSLON
      VTJ = VAD + VREJ
      FRCT = VTJ/(VTJ + V*EPSLON)
      V1 = VAD*(1. -FRCT)
       P1(1,J) = 0.0
      DO  200  I =1,N-2
      G11 = (N-2-I)/(N-2)
      F1 =((EPSLON*V - V1*G11)/(R*T)   )*FRCT
      F2 =(V1*G11*FRCT/(R*T)   )*FRCT
      H2 =F1* P1(N-I,J-1)+G* Q1(N-I,J-1)+F2* P1(N-1-I,J-1)
       P1(N-I,J) =(H2-E*F-G*D+ SQRTF((E*F +G*D -H2)**2 + 4.*F*E*
     1H2))/(2.*F)
200    Q1(N-I,J)  = D* P1(N-I,J)/(E+ P1(N-I,J))
201   RBE1 = RBE1 +( P1(N-1,J-1)*V1/(R*T) )*FRCT
       P1(N,1) = RBE1*PL/RBLT
      RBE1 = 0.0
       P1(1,1) =  P1(1,1)*PL/PH
      DO 202  I= 2,N-1
       P1(I,1)  =  P1(I,JTAUE)
202    Q1(I,1) =  Q1(I,JTAUE)
      DO 301  J=2,JTAUL
       P1(N,J) =  P1(N,1)
      DO 300  I= 2,N-1
      H3 = F* P1(N+2-I,J-1) + G* Q1(N+1-I,J-1)
       P1(N+1-I,J) = (H3-E*F -G*D + SQRTF((E*F+G*D -H3)**2 +4.*
     1F*E*H3))/(2.*F)
300    Q1(N+1-I,J) = D* P1(N+1-I,J)/(E +  P1(N+1-I,J))
301   RAL1 = RAL1 + F* P1(2,J-1)
       P1(1,JTAUL) = RAL1*PL/RALT
       P1(1,1) =  P1(1,JTAUL)
      RAL1 = 0.0
      DO 302  I=2,N-1
       P1(I,1)  =  P1(I,JTAUL)
302    Q1(I,1) =  Q1(I,JTAUL)
       P1(1,JTAUC) =  P1(1,JTAUL)*PH/PL
      DO 400  J=2,JTAUC
      GJ =J-2
      VRCJ = VRL  - V*GJ* EPSLON
      VTJ = VAD + VRCJ
      FRCT = (VTJ - V*EPSLON)/VTJ
      V1 = VAD*(1. -FRCT)
       P1(1,J) =  P1(1,1)*(VRL+ VAD)/VTJ
      DO 400  I= 2,N-1
      G44 = (N-I)/(N-2)
      F3 = (EPSLON*V - V1*G44)/(R*T*FRCT)
      F4 = V1*G44/(R*T*FRCT)
      H4 = G* Q1(I,J-1) +F3* P1(I,J-1)+F4* P1(I-1,J-1)
       P1(I,J) =(H4-E*F-G*D+SQRTF((E*F+G*D-H4)**2+4. *F*E*H4))/(2.*F)
400    Q1(I,J) = D* P1(I,J)/(E+ P1(I,J)     )
      RAH1 =  P1(1,JTAUC)*VRH/(R*T)
       P1(1,1) =  P1(1,JTAUC)
      DO 402  I=2,N-1
       P1(I,1) =  P1(I,JTAUC)
402    Q1(I,1) =  Q1(I,JTAUC)
      DO 501  J=2,JTAUH
       P1(1,J) =  P1(1,1)
```

```
        DO 500  I=2,N-1                                                          7
        H1 = F* P1(I-1,J-1) + G* Q1(I,J-1)                                       7
         P1(I,J)=(H1-E*F-G*D+SQRTF((E*F+G*D-H1)**2+4.*F*E*H1))/(2.*F)            7
 00      Q1(I,J) = D* P1(I,J)/(E+ P1(I,J) )                                      7
 01     RBH1 = RBH1 +F* P1(N-1,J-1)                                              7
        RAH1 =0.0                                                                7
         P1(N,JTAUH) = RBH1*R*T/VRH                                              7
        G50 = 0.                                                                 7
        DO 600 I= 2,N-1                                                          7
 00     G50 = G50 + EPSLON*V* P1(I,JTAUH)/(T*R)                                  7
        G51 = VRH* P1(N,JTAUH)/(R*T)                                             7
        G52 = G50 + G51                                                          7
        G53 = Y1*(VAD + VRH)*pH/(R*T)                                            7
 00     PROP = G53/G52                                                           7
        STOP                                                                     7
        END                                                                      7

*                                                                                1

*PROGRAM END.    0 FORTRAN ERRORS                                                1
          END                                                                    1
```

Computer Runs Results.

Run 9

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

 P HIGH    P LOW     TEMP      VOL      VRH       VRL      PRESS1
,1000.000 642.000 290.000  19.900  380.000  760.000  100.000

 CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB  SEPARA     SEPARB
,      1  100.0000 L*******     1.0000   1.00000    1.00000
,      2  142.1322 71.30525     1.9933   1.42132    0.66641
,      3  187.8313 55.25533     3.3993   1.87831    0.50205
,      4  227.3269 44.87349     5.0660   2.27327    0.39292
,      5  251.8531 37.71663     6.6775   2.51853    0.31789
,      6  265.0338 32.88312     8.0599   2.65034    0.26722
,      7  272.2565 29.70025     9.1668   2.72256    0.23380
,      8  276.4821 27.61050    10.0137   2.76482    0.21197
,      9  279.1133 26.22139    10.6445   2.79113    0.19764
TIME ABORT
```

Run 6

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

 P HIGH    P LOW     TEMP      VOL      VRH       VRL      PRESS1
,1000.000 356.580 290.000  19.900  159.200  995.000  100.000

 CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB  SEPARA     SEPARB
,      1  100.0000 L*******     1.0000   1.00000    1.00000
,      2  129.4864 34.10910     3.7962   1.29486    0.40075
,      3  172.3944 22.85917     7.5416   1.72394    0.21952
,      4  194.6274 17.98514    10.8216   1.94627    0.14483
,      5  200.3320 16.01974    12.5053   2.00332    0.11801
,      6  201.9506 15.20781    13.2794   2.01951    0.10770
,      7  202.6664 14.83780    13.6588   2.02666    0.10323
TIME ABORT
```

[illegible]

Run 7

```
    PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

   P HIGH   P LOW     TEMP      VOL     VRH      VRL      PRESS1
 ,1000.000 323.080 290.000  19.900  30.400  760.000 100.000

   CYCLE    PH1(1,1)PH1(N,TAUH)  RATIO1AB  SEPARA      SEPARB
 ,      1   100.0000 L*******     1.0000    1.00000     1.00000
 ,      2   258.2977 49.51625     5.2164    2.58298     0.45033
 ,      3   303.8741 31.09699     9.7718    3.03874     0.25317
 ,      4   327.7365 23.69279    13.8328    3.27736     0.17133
 ,      5   333.8507 20.49858    16.2865    3.33851     0.13905
 ,      6   335.5181 19.01941    17.6408    3.35518     0.12507
 ,      7   336.7631 18.22455    18.4785    3.36763     0.11789
 TIME ABORT
```

Run 8

```
    PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

   P HIGH   P LOW     TEMP      VOL     VRH      VRL      PRESS1
 ,1000.000 357.000 290.000  19.900  76.040  760.000 100.000

   CYCLE    PH1(1,1)PH1(N,TAUH)  RATIO1AB  SEPARA      SEPARB
 ,      1   100.0000 L*******     1.0000    1.00000     1.00000
 ,      2   232.2492 51.38469     4.5198    2.32249     0.46906
 ,      3   287.7551 32.96479     8.7292    2.87755     0.27294
 ,      4   313.4165 24.74475    12.6660    3.13417     0.18164
 ,      5   319.9782 21.01410    15.2268    3.19978     0.14324
 ,      6   321.6307 19.26862    16.6919    3.21631     0.12639
 ,      7   322.7490 18.34440    17.5939    3.22749     0.11791
 TIME ABORT
```

Run 12

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

  P HIGH   P LOW     TEMP       VOL     VRH      VRL      PRESS1
 ,1000.000 830.000 290.000  19.900  76.400 154.000 100.000

  CYCLE     PH1(1,1)PH1(N,TAUH)  RATIO1AB SEPARA      SEPARB
 ,     1   100.0000 L*******      1.0000   1.00000     1.00000
 ,     2   110.4501 89.25956      1.2374   1.10450     0.83211
 ,     3   113.6524 83.24935      1.3652   1.13652     0.76103
 ,     4   116.2365 78.45693      1.4815   1.16236     0.71157
 ,     5   118.7102 74.41550      1.5952   1.18710     0.67101
 ,     6   121.2463 70.94356      1.7091   1.21246     0.63658
 ,     7   123.9068 67.92931      1.8241   1.23907     0.60693
 ,     8   126.7217 65.29508      1.9408   1.26722     0.58117
 ,     9   129.7076 62.98398      2.0594   1.29708     0.55867
 ,    10   132.8656 60.95281      2.1798   1.32866     0.53896
 ,    11   136.1738 59.16771      2.3015   1.36174     0.52167
 ,    12   139.5822 57.60125      2.4232   1.39582     0.50652
 ,    13   143.0165 56.23026      2.5434   1.43017     0.49327
 ,    14   146.3899 55.03438      2.6600   1.46390     0.48171
 ,    15   149.6177 53.99506      2.7710   1.49618     0.47166
 ,    16   152.6306 53.09507      2.8747   1.52631     0.46295
 ,    17   155.3808 52.31828      2.9699   1.55381     0.45542
 ,    18   157.8437 51.64968      3.0560   1.57844     0.44894
 ,    19   160.0144 51.07544      3.1329   1.60014     0.44338
 ,    20   161.9031 50.58297      3.2007   1.61903     0.43860
 ,    21   163.5302 50.16096      3.2601   1.63530     0.43451
 ,    22   164.9212 49.79941      3.3117   1.64921     0.43100
 ,    23   166.1039 49.48955      3.3563   1.66104     0.42800
 ,    24   167.1059 49.22379      3.3948   1.67106     0.42542
 ,    25   167.9529 48.99559      3.4279   1.67953     0.42322
 ,    26   168.6684 48.79938      3.4564   1.68668     0.42132
 ,    27   169.2729 48.63040      3.4808   1.69273     0.41969
 ,    28   169.7842 48.48465      3.5018   1.69784     0.41828
 ,    29   170.2175 48.35871      3.5199   1.70217     0.41706
 ,    30   170.5855 48.24973      3.5355   1.70586     0.41602
 ,    31   170.8990 48.15526      3.5489   1.70899     0.41511
 ,    32   171.1667 48.07325      3.5605   1.71167     0.41432
 ,    33   171.3961 48.00198      3.5706   1.71396     0.41363
 ,    34   171.5932 47.93995      3.5793   1.71593     0.41304
 ,    35   171.7629 47.88592      3.5869   1.71763     0.41252
 TIME ABORT
```

Run 10

```
   PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

  P HIGH   P LOW     TEMP       VOL      VRH      VRL      PRESS1
 ,1000.000 731.000 290.000   19.900   30.400 154.000 100.00

  CYCLE     PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA       SEPARB
 ,      1   100.0000 L*******    1.0000   1.00000    1.00000
 ,      2   122.4532 84.58315    1.4477   1.22453    0.76223
 ,      3   123.8581 75.48917    1.6407   1.23858    0.66909
 ,      4   125.8635 68.40763    1.8399   1.25864    0.59888
 ,      5   128.6192 62.81319    2.0476   1.28619    0.54388
 ,      6   132.0003 58.32553    2.2632   1.32000    0.50022
 ,      7   135.9391 54.68857    2.4857   1.35939    0.46521
 ,      8   140.4158 51.72494    2.7147   1.40416    0.43694
 ,      9   145.4009 49.30968    2.9487   1.45401    0.41408
 ,     10   150.7604 47.35272    3.1838   1.50760    0.39566
 ,     11   156.1965 45.78470    3.4115   1.56196    0.38095
 ,     12   161.3146 44.54592    3.6213   1.61315    0.36935
 ,     13   165.7802 43.58043    3.8040   1.65780    0.36031
 ,     14   169.4271 42.83541    3.9553   1.69427    0.35334
 ,     15   172.2583 42.26322    4.0758   1.72258    0.34799
 ,     16   174.3812 41.82340    4.1695   1.74381    0.34388
 ,     17   175.9408 41.48343    4.2412   1.75941    0.34072
 ,     18   177.0774 41.21825    4.2961   1.77077    0.33825
 ,     19   177.9074 41.00917    4.3382   1.77907    0.33632
 ,     20   178.5198 40.84248    4.3709   1.78520    0.33478
 ,     21   178.9789 40.70821    4.3966   1.78979    0.33354
 ,     22   179.3300 40.59911    4.4171   1.79330    0.33254
 ,     23   179.6041 40.50986    4.4336   1.79604    0.33172
 ,     24   179.8223 40.43648    4.4470   1.79822    0.33105
 ,     25   179.9990 40.37594    4.4581   1.79999    0.33050
 ,     26   180.1439 40.32592    4.4672   1.80144    0.33004
 ,     27   180.2640 40.28454    4.4748   1.80264    0.32966
 ,     28   180.3639 40.25032    4.4811   1.80364    0.32935
 ,     29   180.4474 40.22204    4.4863   1.80447    0.32909
 ,     30   180.5171 40.19868    4.4906   1.80517    0.32888
 ,     31   180.5753 40.17942    4.4942   1.80575    0.32870
 ,     32   180.6238 40.16355    4.4972   1.80624    0.32855
 ,     33   180.6641 40.15049    4.4997   1.80664    0.32844
 ,     34   180.6975 40.13975    4.5017   1.80697    0.32834
 ,     35   180.7251 40.13093    4.5034   1.80725    0.32826
TIME ABORT
```

Run 11

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  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF, ADSORP.

  P HIGH   P LOW      TEMP      VOL     VRH      VRL     PRESS1
,1000.000 698.000 290.000  19.900  15.400 154.000 100.000

  CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA      SEPARB
 ,     1  100.0000 L*******     1.0000   1.00000    1.00000
 ,     2  127.1351 82.19193     1.5468   1.27135    0.74619
 ,     3  126.5411 72.18813     1.7529   1.26541    0.64454
 ,     4  127.7763 64.56638     1.9790   1.27776    0.56820
 ,     5  130.3605 58.72016     2.2200   1.30360    0.51015
 ,     6  133.8809 54.15576     2.4721   1.33881    0.46541
 ,     7  138.1603 50.54910     2.7332   1.38160    0.43051
 ,     8  143.1403 47.68350     3.0019   1.43140    0.40310
 ,     9  148.7480 45.41241     3.2755   1.48748    0.38159
 ,    10  154.7216 43.63337     3.5459   1.54722    0.36485
 ,    11  160.5527 42.26632     3.7986   1.60553    0.35204
 ,    12  165.6873 41.23798     4.0178   1.65687    0.34244
 ,    13  169.7961 40.47715     4.1949   1.69796    0.33534
 ,    14  172.8490 39.91842     4.3301   1.72849    0.33015
 ,    15  175.0090 39.50702     4.4298   1.75009    0.32633
 ,    16  176.4987 39.20080     4.5024   1.76499    0.32349
 ,    17  177.5204 38.96919     4.5554   1.77520    0.32135
 ,    18  178.2284 38.79092     4.5946   1.78228    0.31971
 ,    19  178.7301 38.65144     4.6242   1.78730    0.31843
 ,    20  179.0965 38.54083     4.6469   1.79097    0.31742
 ,    21  179.3728 38.45221     4.6648   1.79373    0.31660
 ,    22  179.5873 38.38074     4.6791   1.79587    0.31595
 ,    23  179.7579 38.32288     4.6906   1.79758    0.31542
 ,    24  179.8959 38.27595     4.7000   1.79896    0.31499
 ,    25  180.0088 38.23788     4.7076   1.80009    0.31465
 ,    26  180.1016 38.20704     4.7138   1.80102    0.31436
 ,    27  180.1780 38.18208     4.7189   1.80178    0.31414
 ,    28  180.2408 38.16194     4.7231   1.80241    0.31395
 ,    29  180.2923 38.14570     4.7264   1.80292    0.31380
 ,    30  180.3342 38.13264     4.7291   1.80334    0.31368
 ,    31  180.3683 38.12215     4.7313   1.80368    0.31359
 ,    32  180.3958 38.11373     4.7331   1.80396    0.31351
 ,    33  180.4180 38.10698     4.7345   1.80418    0.31345
TIME ABORT
```

Run 13

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF, ADSORP.

  P HIGH   P LOW     TEMP       VOL      VRH       VRL      PRESS1     VOID
 ,1000.000 731.180 290.000  19.900  30.400 154.000  10.000   0.762

  CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA     SEPARB
 ,     1   10.0000 10.00000     1.0000   1.00000   1.00000
 ,     2   12.7928  9.84115     1.2999   1.27928   0.77325
 ,     3   12.9309  9.74758     1.3266   1.29309   0.76460
 ,     4   13.0352  9.63500     1.3529   1.30352   0.75605
 ,     5   13.1357  9.52619     1.3789   1.31357   0.74737
 ,     6   13.2327  9.42093     1.4046   1.32327   0.73898
 ,     7   13.3265  9.31900     1.4300   1.33265   0.73086
 ,     8   13.4171  9.22020     1.4552   1.34171   0.72300
 ,     9   13.5047  9.12435     1.4801   1.35047   0.71537
 ,    10   13.5896  9.03126     1.5047   1.35896   0.70797
 ,    11   13.6717  8.94079     1.5291   1.36717   0.70078
 ,    12   13.7513  8.85279     1.5533   1.37513   0.69379
 ,    13   13.8285  8.76713     1.5773   1.38285   0.68698
 ,    14   13.9034  8.68369     1.6011   1.39034   0.68036
 ,    15   13.9761  8.60235     1.6247   1.39761   0.67391
 ,    16   14.0468  8.52302     1.6481   1.40468   0.66762
 ,    17   14.1155  8.44559     1.6713   1.41155   0.66148
 ,    18   14.1823  8.36998     1.6944   1.41823   0.65549
 ,    19   14.2473  8.29610     1.7174   1.42473   0.64964
 ,    20   14.3107  8.22389     1.7401   1.43107   0.64392
 ,    21   14.3725  8.15325     1.7628   1.43725   0.63833
 ,    22   14.4328  8.08414     1.7853   1.44328   0.63286
 ,    23   14.4916  8.01649     1.8077   1.44916   0.62751
 ,    24   14.5491  7.95023     1.8300   1.45491   0.62227
 ,    25   14.6052  7.88532     1.8522   1.46052   0.61713
 ,    26   14.6602  7.82169     1.8743   1.46602   0.61210
 ,    27   14.7139  7.75932     1.8963   1.47139   0.60717
 ,    28   14.7666  7.69814     1.9182   1.47666   0.60234
 ,    29   14.8182  7.63812     1.9400   1.48182   0.59760
 ,    30   14.8688  7.57921     1.9618   1.48688   0.59295
 ,    31   14.9185  7.52138     1.9835   1.49185   0.58838
 ,    32   14.9672  7.46459     2.0051   1.49672   0.58390
 ,    33   15.0151  7.40881     2.0267   1.50151   0.57950
 ,    34   15.0622  7.35401     2.0482   1.50622   0.57517
 ,    35   15.1085  7.30015     2.0696   1.51085   0.57092
 ,    36   15.1541  7.24721     2.0910   1.51541   0.56675
TIME ABORT
```

Run 14

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

   P HIGH   P LOW    TEMP      VOL      VRH      VRL      PRESS1
 ;1000.000 357.078 290.000  19.900  76.000 760.000  10.000

   CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA     SEPARB
 ,      1   10.0000 10.00000    1.0000   1.00000    1.00000
 ,      2   25.5510  8.48389    3.0117   2.55508    0.48554
 ,      3   25.5061  8.15479    3.1277   2.55060    0.44078
 ,      4   26.0522  8.47534    3.0739   2.60522    0.45796
 ,      5   24.9307  8.49536    2.9346   2.49304    0.45771
 ,      6   23.8923  7.84570    3.0453   2.38922    0.46846
 ,      7   23.9746  8.46960    2.8307   2.39746    0.45276
 ,      8   24.0127  7.84570    3.0606   2.40125    0.46822
 ,      9   24.8862  8.46960    2.9383   2.48862    0.45281
 ,     10   24.6763  9.53625    2.5876   2.46762    0.47163
 ,     11   23.6392  8.86975    2.6651   2.36389    0.51232
 TIME ABORT

         POST MORTEM
```

Run 15

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

   P HIGH   P LOW    TEMP      VOL      VRH      VRL      PRESS1
 ,1000.000 357.080 290.000  19.900  76.000 760.000  10.000

   CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA     SEPARB
 ,      1   10.0000 10.00000    1.0000   1.00000    1.00000
 ,      2   26.5819  8.71388    3.0505   2.65819    0.49495
 ,      3   30.5792  7.92951    3.8564   3.05792    0.44270
 ,      4   34.4137  7.24571    4.7495   3.44137    0.40106
 ,      5   38.0702  6.65632    5.7194   3.80702    0.36574
 ,      6   41.5018  6.14368    6.7552   4.15018    0.33551
 ,      7   44.6797  5.69433    7.8463   4.46797    0.30935
 ,      8   47.5935  5.29779    8.9837   4.75935    0.28652
 TIME ABORT
```

Run 16

```
   PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

 P HIGH   P LOW     TEMP      VOL      VRH      VRL      PRESS1
,1000.000 323.080 350.000  19.900  30.400 760.000 100.000

 CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA     SEPARB
 ,     1   100.0000 L*******    1.0000   1.00000    1.00000
 ,     2   275.8863 53.32964    5.1732   2.75886    0.46445
 ,     3   333.1647 35.24834    9.4519   3.33165    0.27036
 ,     4   364.9237 26.29546   13.8778   3.64924    0.18277
 ,     5   389.8689 21.45365   18.1726   3.89869    0.14067
 ,     6   403.8406 18.66582   21.6353   4.03841    0.11829
 ,     7   409.5178 17.03444   24.0406   4.09518    0.10580
TIME ABORT
```

Run 17

```
   PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

 P HIGH   P LOW     TEMP      VOL      VRH      VRL      PRESS1
,1000.000 323.080 400.000  19.900  30.400 760.000 100.000

 CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA     SEPARB
 ,     1   100.0000 L*******    1.0000   1.00000    1.00000
 ,     2   279.3605 54.37076    5.1381   2.79361    0.46716
 ,     3   340.7871 35.99343    9.4680   3.40787    0.27604
 ,     4   375.6010 26.35385   14.2522   3.75601    0.18552

000000000000000
```

Run 18

```
  PROPANE-ARGON ISOTHERMAL PRESSURE DIFF. ADSORP.

 P HIGH   P LOW      TEMP        VOL      VRH        VRL       PRESS1
,1000.000 467.180 290.000   19.900 760.0001520.000 100.000

 CYCLE    PH1(1,1)PH1(N,TAUH) RATIO1AB SEPARA      SEPARB
,      1  100.0000 L*******     1.0000   1.00000     1.00000
,      2  155.6406 63.47656     2.4519   1.55640     0.60167
,      3  216.5000 46.75391     4.6306   2.16498     0.40281
,      4  252.6426 34.28662     7.3685   2.52640     0.30010
,      5  271.9258 27.27808     9.9686   2.71924     0.22321
,      6  282.0586 26.31689    10.7178   2.82056     0.17822
,      7  284.4453 25.43115    11.1848   2.84445     0.16922
TIME ABORT
```

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