MODELLING AND SIMULATION OF AMMONIA-WATER SEPARATION FOR APPLICATION IN ABSORPTION HEAT PUMP

BY

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DECLARATION

I, Adegboyega Adetokunboh Surajudeen OLAWALE, hereby declare that this thesis is composed by myself and that it is the authentic record of my own research work. It has never been submitted anywhere before for any degree. All quotations are shown by quotation marks and the literature cited are acknowledged by means of references.

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OCTOBER 1993

CERTIFICATION

This project report entitled **"Modelling and Simulation of Ammonia-Water Separation for Application in Absorption Heat Pump"** by Adegboyega Adetokunboh Surajudeen OLAWALE, meets the regulation governing the award of the degree of Master of Science in Chemical Engineering of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

Chairman, Supervisory Committee	Date
Member, Supervisory Committee	Date
External Examiner	Date
Head, Department of Chemical Engineering	Date
Dean, Postgraduate School	Date

DEDICATION

This work is dedicated to the glory and benevolence of the Almighty God, the Most Knowing and, to MAMA, the most precious of all.

ACKNOWLEDGMENT

I am very grateful to the Almighty God for seeing me through to the completion of this project.

My unquantifiable appreciation and gratitude is to my supervisor, Professor S.S. Adefila, of Chemical Engineering Department for his very able supervision and advice throughout the duration of this work.

I also wish to expreee my appreciation to, my wife and children for their support and, my elder brother for his undying interest in the project.

The cooperation and assistance of membere of staff of Chemical Engineering Department and friends are highly appreciated

I can never thank you all enough.

ABSTRACT

Theoretical thermodynamic simulations (analyses) were carried out on the "Extraction-System-Attached" (ESA) Ammonia-Water Absorption Heat Pump cycles which were developed with the aim of improving the thermodynamic performance achievable with the conventional cycle. Theoretical simulation of the liquid-liquid-equilibria (LLE) of amnion i a-water-3ol vent (ternary) systems using the tested semi-empirical model called UNIQUAC equation was the basis for determining whether or not the extracting solvents (of desirable physical properties) could form two-phase ternary systems with aqueous ammonia solution. The UNIQUAC binary parameters of ammonia-water mixtures and the binary mixtures of the selected solvents and water or ammonia, for use in the LLE simulation, were obtained from mutual solubility and infinite dilution coefficient data. Capacity and selectivity diagrams obtained from the data generated from LLE simulation were used for further confirmation of the suitability of the solvents for liquid-liquid-extraction process.

Five cycles were derived from the conventional absorption system by using the extraction or stripping separation process as substitute for the non-isothermal separation process used in the conventional ammonia-water absorption heat pump. Thermodynamic analysis models used for obtaining the irreversibilities and COP of the cycles were derived from system's parameters and working fluid properties such as concentration of strong (XST) and weak (XWK) aqueous ammonia solution, reflux or recirculation ratio (R), solvent-to-feed

ratio (SFR), enthalpy change. Simulation of these thermodynamic models for two ESA-ammonia-water absorption heat pump cycles (employing five different organic solvents in the extraction step of the system) and the conventional **ammonia-water absorption** heat pump cycle at two evaporator's temperatures indicated that better **thermodynamic performance,** in term of the COP (heating and cooling modes) and irreversibility, could be achieved by using liquid-liquid extraction process to recover **ammonia** from the strong aqua **ammonia formed** in the absorber during the pump's operation. The cycles employing nitrobenzene as the extract solvent, among the. **KSA** systems, gave the lowest irreversibilty and highest COP values.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOL/ABBREVIATION	DESCRIPTION	UNIT
ABSOR	Absorber	-
B	Availability	kJ
CAP	Capacity	-
conc	Concentration	-
CONDS	Condenser	-
COP	Coefficient of performance	dimensionless
COPC, COP_C	Coefficient of performance in the cooling mode	dimensionless
COPH, COP_H	Coefficient of performance in the heating mode	dimensionless
Cp	Specific enthalpy of a substance at constant pressure	kJ/kg.K
D	Distribution coefficient	dimensionless
dH	Infinitesimal enthalpy change of a system	kJ/kg
dP	Infinitesimal pressure change of a system	atm. bar
dQ	Infinitesimal heat energy change of a system	kJ/kg
dS	Infinitesimal entropy change of a system	kJ/kg.K
dT	Infinitesimal temperature change of a system	K, °C
ECONO	Economiser	-

E_{rr}	Energy due to mechanical friction, Irreversibility	kJ
EVAPR	Evaporator	-
Ex	Exergy	kJ
Ex_Q,Q	Heat exergy, Heat energy	kJ
extr	Extract	-
EXVA1	Expansion valve into absorber	-
EXVA2	Expansion valve into evaporator	-
frn	Fraction	-
g, g^E	Specific Gibbs free energy Excess Gibbs Free energy	kJ/kg
GENER	Generator	-
GHG	Green house gases	-
GNP	Gross national product	dimensionless
H	Enthalpy of a system	kJ/kg
h	Vertical height	m
HGE	High grade energy	-
I	Irreversibility	kJ/kg
L	Raffinate phase rate	kg/s
mol	Mole	dimensionless
MW	Molecular weight	dimensionless
NH3	Ammonia	-
P	Pressure of a system	atm, bar
R	Gas constant	cal/gmole
R	Reflux ratio	dimensionless
raff	Raffinate	-
RECTF	Rectifier	-
S	Entropy of a system	kJ/kG.K

sel	Selectivity	dimensionless
sf	Solvent mass fraction	dimensionless
sfr	Solvent to feed ratio	dimensionless
sol	Solubility	dimensionless
SOLV	Solvent	-
T,TEMPT	Temperature of a system	K, °C
T-IRR	Total irreversibility	kJ/kg
USA	United States of America	-
VAP	Vaporisation	-
VAPOR	Vaporiser	-
V_r	Molar volume	m^3
wt %	percentage by weight	-
W,Wa	Work (mechanical energy)	kJ, kJ/kg
XST	Concentration of ammonia in strong aqua ammonia	-
XWK	Concentration of ammonia in weak aqua ammonia	-

Subscript

SUBSCRIPT	DESCRIPTION
1	inlet stream, component 1
2	outlet stream, component 2
i	component i
in	inlet stream
irr	irreversibility
j	component j
med	medium
mix	mixture

o	ambient condition
out	outlet stream
tot	total

Superscript

SUPERSCRIPT	DESCRIPTION
E	Excess property
//, s//	Extract phase
/, s/	Raffinate phase
k	a constant

Greek notations

SYMBOL	DESCRIPTION	UNIT
α	Separation factor	dimensionless
γ	Activity coefficient	dimensionless
δ	Partial differential	-
Δ	Increment	-
θ'	Modified area fraction	dimensionless
θ	Area fraction	dimensionless
ρ	Density	kg/m3
τ	Binary interaction parameter	dimensionless
Φ	Segment fraction	dimensionless
Φ'	Modified segment fraction	dimensionless
Φ_A	Added energy to a system	kJ
Φ_m	Mass flow rate	kg/s
$\int$	Integral sign	-
J		
Σ	Summation sign	-

CHAPTER ONE

1. INTRODUCTION

1.1 Energy and Its Conservation

The rate of depletion of fossil fuels which are the major world energy sources is expected to keep rising with economic growth given the reported dwindling effort in energy conservation in the industrialised world after the crash of oil prices in the seventies [Anon., 1990a]. This anticipated increased pressure on these non-renewable energy sources could lead to a rise in energy cost. The pollution problems usually associated with their utilisation also pose a threat to their uses in future [Anon., 1990a; Scoullos, 1990; Anon., 1990].

It is therefore necessary that strategies that will reduce pressure on fossil fuels and, for that matter, energy sources in general, be pursued. Two of such strategies are:-

a. Reduction of waste in fuel consumption, i.e. conservation of energy.

b. Increased utilisation of the renewable energy sources, which are clean and free but have low utilitarian value, e.g. solar energy.

The former strategy could be achieved by either:

- decreasing economic activities requiring energy thereby reducing the amount of aggregate energy consumed in the economic system, or

- using the available energy more efficiently. This energy conservation strategy, unlike the former, does

not constrain economic growth and development. Moreover, it minimises pollution problems through the reduction of the fossil fuel that will be burnt in the first place. Thus this approach is preferred from two perspectives:

- **compatibility with economic growth**
- **minimization of environmental pollution**

With this approach energy conversion and/or consumption methods that produce as little reject (waste) heat as possible are employed in unit processes and/or operations. Furthermore reject heat is either recycled to extract from it all useful work or it (including those waste heat which otherwise are normally considered unavoidable) is upgraded to a more useful level.

Heat pump as the only device currently available for raising the temperature of waste heat to more useful level could be used for energy conservation. The device is also the basis for refrigeration and air-conditioning. It is thus worthwhile to examine possible means of reducing energy degradation accompanying its operations since this will boost the unique attractiveness of its applications.

1.2 Heat Pump System

In a typical heat pump, heat energy is picked up from one area of the system called the heat source and delivered at another area of the same system known as the heat sink. In the process the quality of the heat energy is upgraded such that the

low grade energy taken up at the heat source is available at the heat sink at a higher temperature as higher quality energy. The medium for the transfer and upgrading of the energy which is called **working fluid**, undergoes phase changes as it moves through the system in accordance with the prevailing thermodynamic conditions at different points in the system. During the process of "heat pumping" the heat source is cooled and the heat sink becomes hotter.

It was estimated that economical operation of heat pump could lead to the recovery of 1.06 X 10^5J of energy per year from USA industrial sector and that about 25% of waste heat was rejected as low temperature energy that might require upgrading by heat pumping in 1977 [Oleszewski, 1980]. Apart from upgrading heat for heating purposes, a heat pump is used for cooling (refrigeration and air-conditioning).

1.2.1 Types of heat pump

Different criteria are used in classifying heat pumps [Adefila,1983; von Cube and Steimle,1981]. Bugaje [1987] published a detailed classification of heat pumps. Vapour compression heat pump and vapour absorption heat pump are two of the most popular classes.

A vapour compression heat pump is made up of two heat exchangers (evaporator and condenser), compressor and expansion valve. The evaporator and condenser exchange heat energy with heat source and sink respectively and the compressor provides the high grade energy (HGE) and the means of maintaining the throttling effect in the system. In this system, the working

fluid flowing through the evaporator takes up the low grade energy from the environment and vaporises (or expands). Thereafter, the vapour (or gas) is lifted to a higher pressure by compression. The working fluid then condenses (or compresses) by releasing its latent heat of vaporisation before it is throttled to the lower pressure in the evaporator, and the cycle continues. A diagram of vapour compression heat pump is shown in Figure 1.1.

In the vapour absorption heat pump, a "thermodynamic pump" performs functions similar to that of the compressor in the vapour compression heat pump. The "thermodynamic pump" consists of the absorber, the liquid pump and the desorbing unit. This difference in the hardware architecture of the two systems is due to the fact that in a vapour absorption heat pump, liquid rather than vapour is lifted to the higher pressure. The absorption of the main working fluid by the absorbent takes place in the absorber; the resulting working fluid mixture formed by the main working fluid and the absorbent is then lifted to the higher pressure by liquid pump. The main working fluid is thereafter separated from the absorbent in the generator by the addition of heat energy. The desorbed main working fluid goes to the condenser and from here it goes through the same steps as in the vapour compression heat pump until it reaches the evaporator. Meanwhile, the absorbent, which is the working fluid mixture depleted of the main working fluid, is cooled and sent back to the absorber. The vapour of the main working fluid from the evaporator is transported into the absorber where it mixes with the absorbent to form the working fluid mixture, and the cycle

continues. A diagram of the conventional vapour absorption heat pump is shown in Figure 1.2.

In contrast to the vapour compression heat pump, there are two units of equipment exchanging energy with the heat (energy) sources and another two or three do the same with the heat sinks in the absorption heat pump. These are the evaporator, generator, absorber, rectifier and condenser. Mechanical energy, albeit relatively small, is supplied by the liquid pump.

Some of the common working fluid pairs used in the vapour absorption heat pump are ammonia-water, water-lithium bromide and ammonia-sodium thiocyanate. The first compound in the above-listed pairs are the main working fluids of the systems.

As it has been pointed out already heat pump is used in the cooling and/or heating modes. Infact the pump necessarily works in the two modes simultaneously and its ability to do so improves the economics of its application. In the heating mode, space heating, water heating and drying are some of its uses. In addition to upgrading the quality of reject heat, heat pump can also be used to improve the quality of low grade energy from primary sources such as solar energy. In whatever capacity heat pump is to be used its utilisation would only become more important if 'heat pumping' process is made more energy efficient.

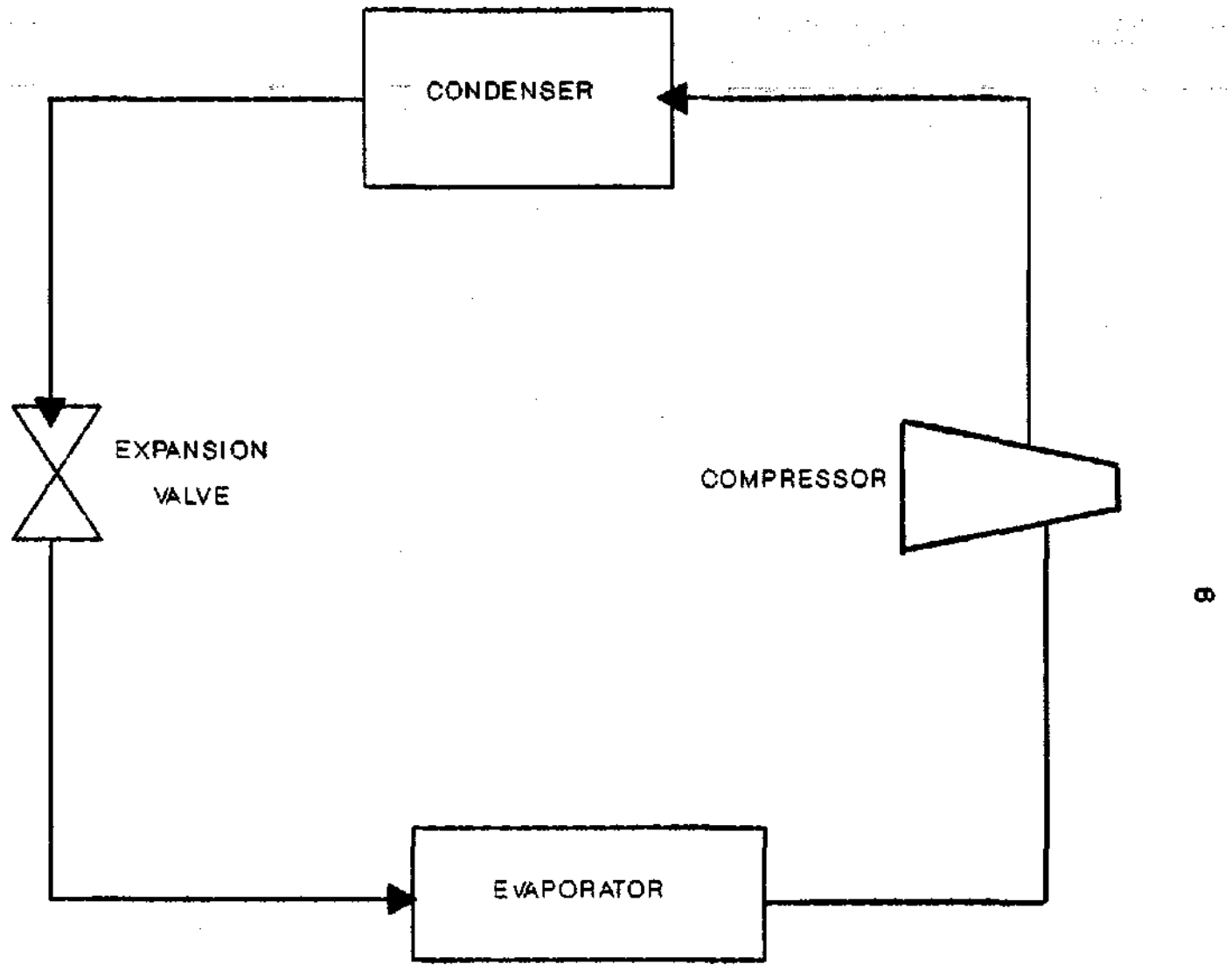


Figure 1.1: Cycle of Conventional Vapour Compression Heat Pump

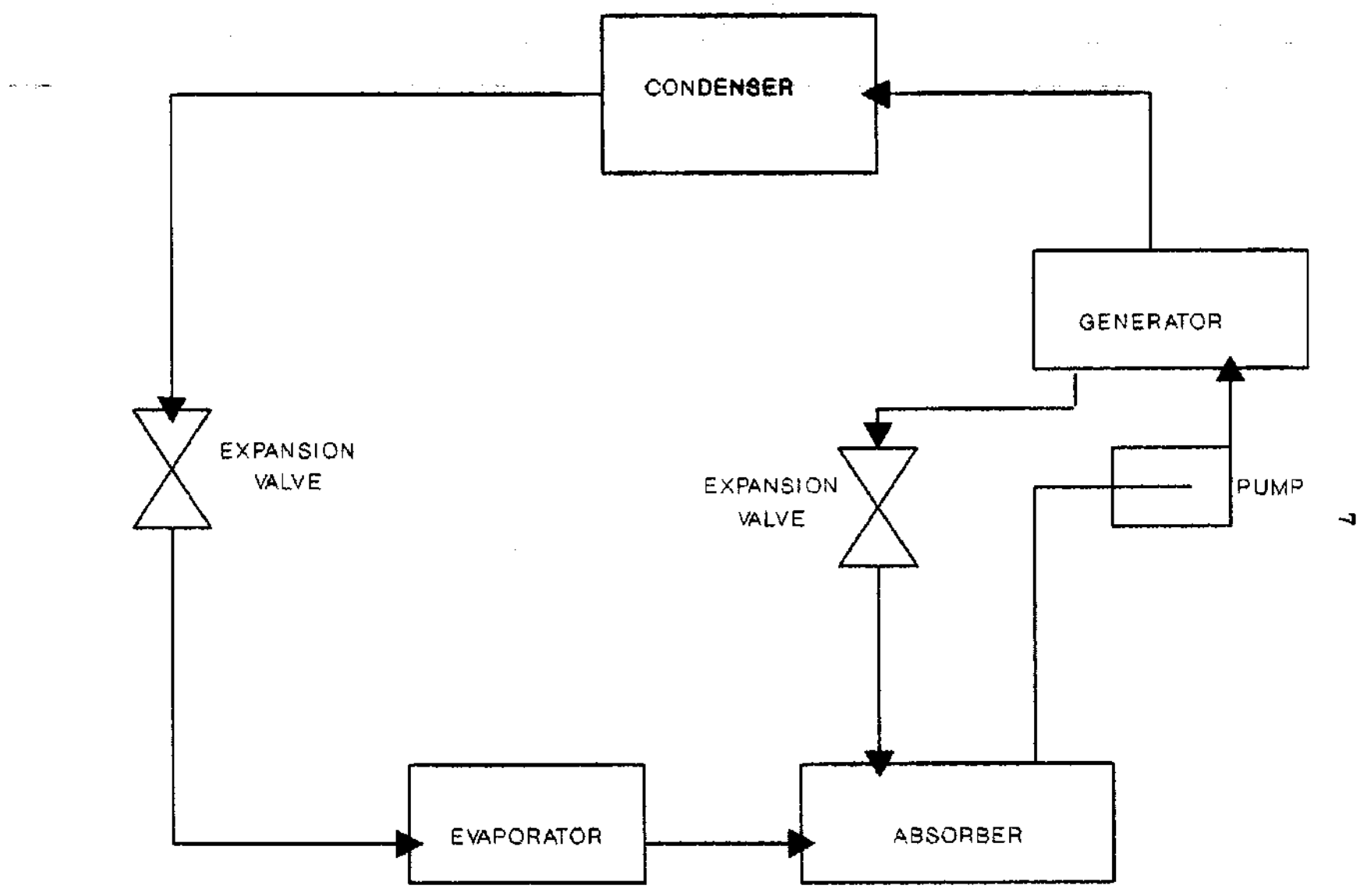


Figure 1.2: Conventional Vapour Absorption Heat Pump Cycle

1.2.2 Efficiency of heat pump

The coefficient of performance (COP) is a popular measure of the efficiency of a heat pump system . Its value depends on the type of, and the mode in which, the pump is operating. Generally, the vapour compression heat pumps have higher COP values than the vapour absorption heat pumps and the COP of a system is higher in the heating mode than in the cooling mode.

The efficiency of a heat pump is related to the level of irreversibilities in the system. The higher the level, the lower the efficiency and vice-versa. Irreversibility is caused by non-ideality in the hardware, the working fluid and the processes of the system. The non-ideality in the hardware is dictated by the technology gap in the fabrication of the equipment of interest; the wider this gap the more the hardware-related non-ideality. The non-ideality in the working fluid could be traced to the thermophysical and chemical properties of the fluid. Some of the irreversibilities usually encountered in the heat pump and heat engine cycles that are traceable to the non-ideality in the working fluid and/or the processes are those due to:

- large temperature difference during heat transfer between the working fluids and heat sources or sinks.
- unrestrained expansion of the fluid as in the throttling process
- friction experienced by the working fluid as a result of its thermophysical properties.

In addition, irreversibility could be introduced as a result of the inability of the working fluid to meet various thermophysical and kinetic requirements of an ideal working

fluid. Some of these properties have been listed by Adefila [1983] and Mansouri and Patel [1979].

1.2.3 Absorption heat pump

The effect of modification of a cycle of heat pump is obvious from the comparison of the values of the COP of vapour compression heat pump and vapour absorption heat pump. Though it has the lower COP, absorption heat pump is preferred to the vapour compression system in some applications because of its advantages, some of which are listed below.

- relatively low quantity of energy is required to lift liquid to the higher pressure compared to that required for the vapour of the same compound to be so lifted.
- the liquid pump is the only machine in the system and the only object with moving part. So its operation is simpler and it is cheaper to maintain.
- it can use relatively low grade energy as heat source.
- efficiency of the system is less sensitive to the operating temperature than the vapour compression system.

In absorption heat pump absorbent brings the working fluid into the liquid state at a fast rate so that:

- the working fluid vapour is continuously swept away from the evaporator to ensure that the required refrigeration load is maintained.

- the liquid solution resulting can be lifted to higher pressure using liquid pump in place of compressor used in vapour compression system; this ensures that less quantity of mechanical energy is used for lifting the working fluid to higher pressure.

Since absorption process is necessary in the vapour absorption heat pump there is the need for the desorption of the working fluid from the mixture of the working fluid and the absorbent because the mixture does not usually make a good working fluid. For instance, water on its own is an excellent working fluid in certain applications but in ammonia-water absorption heat pump it is necessary to separate ammonia from water after the absorption process because if water goes through the rest of the cycle with ammonia, the following undesirable phenomena would arise:

- blockage of the evaporator's pipes shall ensue and this can cause a reduction in the efficiency of the system and bursting of pipe.
- larger condenser unit would be required and this means higher cost.

Rectification is usually required to obtain pure main working fluid after vapour generation where the difference in the vapour pressure of the main working fluid and the absorbent is not large enough to prevent the vapour of the absorbent from being desorbed with the vapour of the main working fluid in the process of regeneration. A minimum difference of 200°C is expected between the normal boiling points of the absorbent and the working fluid to avoid rectification [Renz, 1978]. Thus in

the conventional ammonia-water absorption heat pump cycle, rectification process is included in the "thermodynamic pump" as shown in Figure 1.3.

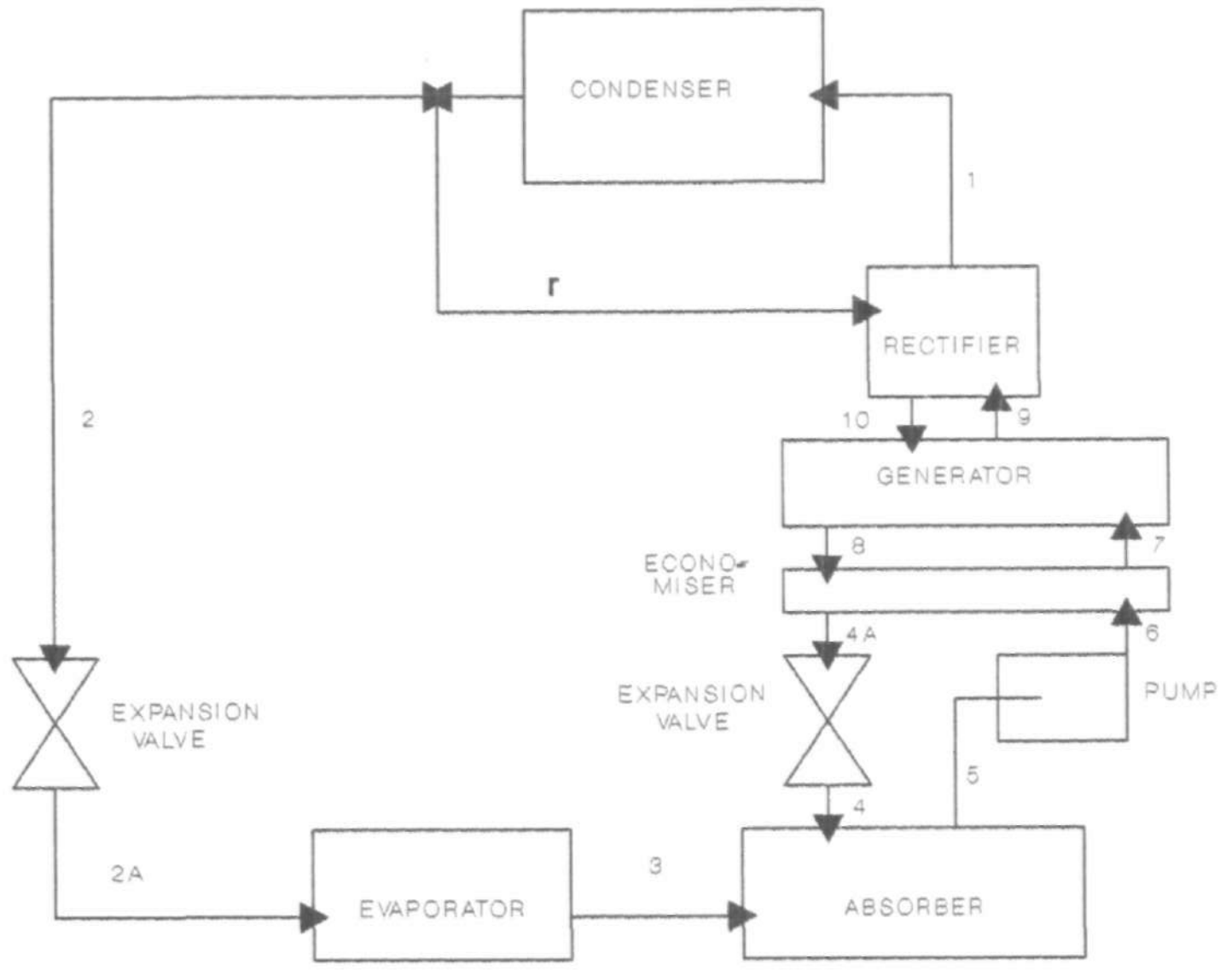


Figure 1.3: Conventional Ammonia-Water Absorption Heat Pump

1.3 Research Objectives

1.3.1 Problem definition

The maximum obtainable COP for vapour absorption heat pumps have been reported to be 1.80 and 0.80 for heating and cooling modes respectively [Kanoche,1982; Landauro-Paredes et al, 1983].

Mumah [1990] has established that thermodynamic pump is the greatest source of irreversibility in ammonia-water vapour absorption heat pump. Absorption process is an indispensable part of this heat pump system and the fast rate of mixing and high capacity of the absorbent for the working fluid desired in the process makes it inevitably an exothermic process.

In the conventional absorption heat pump the vehicular fluid (absorbent), having carried out its primary function of liquifying the working fluid, is still pumped to the higher pressure only to be throttled back to the lower pressure after it is separated from the working fluid. Before this vehicular fluid is throttled to the lower pressure, it consumes, as part of the working fluid mixture, substantial part of the HGE supplied to the system in the vapour generation stage. Yet it has to be cooled after it has been separated from the main working fluid. This then means that the part of the HGE so expended is not available to enrich the quality of the low grade heat energy taken up at the heat source by the working fluid. Thus the work and, heat transfer and the associated energy dissipation, occurring in the course of:

- transportation of the vehicular fluid from and to the absorber, and

- separation of the working fluid from the vehicular fluid

could be avoided or reduced if the two fluids were separated before pumping to higher pressure takes place.

Irreversibility also occure in the process of heating for separation , and cooling thereafter, of the absorbing fluid, as a result of heat transfer across large temperature gradient involved in the separation and cooling steps. The irreversibility due to the heating and cooling of the absorbent should be avoidable if absorbent can be recovered isothermally before the fluid is pumped to the higher pressure.

On the basis of this qualitative analysis it is expected that focusing on the processes of the thermodynamic pump would be a fruitful effort in reducing or eliminating some of the irreversibilities accompanying processes in the thermodynamic pump so that higher COP can be obtained in the system.

1.3.2 Objectives

The main objective of this work is to carry out a theoretical modification of the post-absorption processes in the "thermodynamic pump" of the conventional ammonia-water absorption heat pump such that the coefficient of performance of the system is increased by incorporating liquid-liquid extraction unit in the system. It is expected that the HGE consumed by the vehicular fluid and the consequent degradation of this high quality energy could be reduced or eliminated if process(es) that engender(s) the consumption of this HGE by the vehicular fluid could be modified or eliminated.

Cheng and Shih [1987] stated that COP values higher than the usually obtained figures could result if liquid-liquid extraction process is used to remove water from water-lithium bromide mixture in the water-lithium bromide absorption heat pump. Apart from the advantage of replacing the non-isothermal separation process of the conventional vapour absorption heat pump system with isothermal or nearly-isothermal process, a reduction in the water content of the aqueous ammonia solution prior to pumping should reduce the irreversibilities associated with **pumping**, **heating**, **cooling** and **throttling** the absorbent component of agua ammonia. In addition, less HGE would be needed if further purification, by non-isothermal means, of the resulting ammonia is needed since the amount of water in the impure ammonia would have been reduced drastically. The irreversibility involved is also expected to be reduced substantially.

It will be a big boost if this envisaged higher efficiency results in cost saving. To achieve the major objective stated above it is necessary to:

(a) examine all the possible extraction configurations (schemes) to determine if they can be realised in practice.

(b) identify potentially useful solvent and carry out the computer simulation to obtain the conjugate phase compositions of the ternary systems formed by such solvents and the aqueous ammonia mixture, so as to determine:

- **if the ternary mixtures separate into two layers**
- **if the capacity and selectivity of the solvents are appropriate**

(c) develop possible alternative thermodynamic cycles based on the result of (a) above and:

- carry out the thermodynamic analysis of the resulting ammonia-water absorption systems and calculate their COPs.
- determine, if possible, the optimal COP for each cycle.

The achievement of the objective of this work is of technological and economic significance. The increased efficiency anticipated would give greater impetus to the use of heat pumps as this may reduce the operating cost of the system.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Problems of Energy

The per capita energy consumption of the world was put at an average of 1.6gJ in 1985 [Anon., 1990]. North America was responsible for the highest value of about 7.8gJ while Africa and Asia-Oceania jointly accounted for the least value of about 0.3gJ.

While the price hike of petroleum oil in 1973 forced the industrialised countries to pay attention to the need to cut energy loss by reducing wastage and increase efficiency since the early seventies, it is only in the last seven years or so that the world started paying serious attention to the environmental pollution consequences of the consumption of energy from sources such as fossil fuels. These fuels give off green house gases (GHG) which increase the temperature of the surface of the earth [Anon. 1990a]. The GHG include carbon dioxide (CO_2), dinitrous oxide (N_2O), methane (CH_4), chlorofluorocarbons (CFCs), etc.

The threat of earth warming demands that consumption of fossil fuels be reduced in order to reduce the emission of GHG into the atmosphere. Yokobori [1990] has shown through Equation 2.1 below that a change in GHG emission is a function of three factors namely, economic growth (GNP), change in energy intensity of the economy and change in GHG intensity of the energy.

GHG emission = Energy/GNP x GHG/energy x GNP 2.1

It is obvious, from the equation, that to keep economic activity going with little or no GHG emission, " ... **a great improvement in energy/economy intensity (i.e. energy conservation) or GHG/energy intensity (i.e. a shift away from carbon intensive energy sources) or both will be required**" [Yokobori, 1990]. The second option constrains the use of fossil fuel as energy sources. However from Table 2.1 below, it can be seen that the world would still have to depend on fossil fuels for some time to come.

It is known that by adopting energy conservation strategy which include energy efficiency improvement, faster benefit is produced at less cost than other options like installing new energy conversion plants; it also minimises negative effects on the environment [Scoullos, 1990].

SOURCES OF ENERGY	CONSUMPTION, %
OIL	33
COAL	26
NATURAL GAS	17
RENEWABLE ENERGIES	14
HYDRO AND OTHERS	6
NUCLEAR	4

Table 2.1: Global Distribution of Energy Use in 1986
[Anon., 1990]

2.2 Strategies for Reducing or Eliminating Irreversibilities

Improved energy efficiency usually leads to savings in cost. An impressive case concerning refrigerator has been reported by Scoullos [1990] in which he stated

> **"... by spending US$240 million to improve the energy efficiency of three million refrigerators, US$360 million saving was obtained ...."**

This savings was achieved in addition to the prevention of CO_2 emission that would have occurred if coal-fired power plant was used to fill the energy gap that might have existed in the absence of the energy efficiency improvement scheme.

The first step in tackling the problem of irreversibilities in a system is to identify their sources. The first and second law analyses of the system will reveal the sources of the irreversibilities. The techno-economic themes put forward by Linnhoff [1979] and which are discussed in Chapter 5 can then be used to identify the avoidable irreversibilities and help determine the right steps to remove them if it is economically expedient to do so. Some of these themes are listed below:

(a) Thermodynamic potential is not the same as cost.

(b) Replacement is not equivalent to alteration.

(c) Minimum driving force.

(d) Network interaction.

(e) Choice of sources and sink.

Irreversibilities originating from the processes could be tackled by modifying the processes. In absorption heat pump cycle this category of irreversibility offers perhaps the greatest scope for reduction of energy loss in the system.

Strategies employed in reducing or eliminating energy loss originating from the process operations could be classified as **energy recovery** or **reductive process dissipation.**

(a) **Energy recovery:** This involves :

- energy recycling and
- insulation of process equipment, pipes, etc.

In energy recycling, waste heat from a process is used in another process either within the same system or in another system within the same plant. An example is the utilisation of saturated water vapour (steam) from the dryer to preheat boiler water in a pulp and paper industry. Techniques like cascading and co-generation are commonly used in energy recycling [Gunn, 1980]. Heat exchangers are used to transfer heat from the source to the sink where the quality of such heat is high enough to be useful in the sink. Optimal synthesis of the heat exchanger network is necessary in order to have as much energy conservation (and improved energy efficiency) as possible using energy recycling method. Linnhoff [1979] and Nishida et al [1981] have reviewed works on synthesis of heat exchanger network. Linnhoff [1983], Flower and Linnhoff [1978, 1983], Townsend and Linnhoff [1983] and Umeda et al [1978] used the concepts of energy target and network pinch for optimal synthesis of heat exchanger network. The essence of this approach is to match certain "hot" streams with certain "cold" streams such that the temperature potentials resulting from such matchings ensures the least energy loss possible during heat transfer.

Insulation of equipment is normally done to prevent heat loss to the environment through the surfaces of the process equipment, pipes and fittings.

(b) **Reductive process dissipation:**

Process that have intrinsic irreversibility could either be modified or replaced to reduce or eliminate irrevereibility arising from the process. Equilibrium processes are more energy efficient than non-equilibrium (rate) processes, if other factors remain constant, because the steps of the former processes could be reversed while the steps of rate processes are not reversible. Also an isothermal process is more energy efficient than a non-isothermal process because heat transfer across temperature gradient in non-isothermal process results in energy dissipation whereas there is no heat transfer in isothermal process.

Outside the realm of **energy recycling**, attempts at reducing irreversibility accompanying non-isothermal processes in heat pump systems have been directed at reducing the temperature gradient accompanying such processes. Of recent Mumah [1990] averred that irreversibility accompanying absorption and rectification processes in ammonia-water absorption heat pump are reduced by using split units, instead of a single unit, of absorber and rectifier. With the probable exception of the work by Cheng and Shih [1987] little or no attention appears to have been paid to the possibility of reducing irreversibility in absorption heat pump by elimination of some of the non-isothermal processes of this system.

Cheng and Shih [1987] attempted to show that it might be possible to increase the COP of water-lithium bromide absorption heat pump system by extracting water from the dilute aqueous lithium bromide solution using the **isothermal** liquid-liquid extraction process. Mumah [1990] also attempted using this approach for ammonia-water absorption heat pump.

This present work is an effort, in part, to follow this trail in order to identify alternative separation process(es) that can lead to higher COP in ammonia-water absorption heat pump than obtainable in the conventional system.

2.3 Semi-empirical Models

Models that can predict phase splitting in non-ionic system include van Laar equation, Margule equations, non-random-two-liquid (NRTL) model, local effective mole fraction (LEMF) model, modified Wilson equation, Universal Quasichemical (UNIQUAC) model and Universal Quasichemical Function Activity Coefficient (UNIFAC) model [Prausnitz et al, 1975, 1978, 1980; Fredeslund et al, 1977; Mukhopadhyay and Pathak 1986; Mukhopadhyay and Dongaonkar, 1983; Reid et al, 1977; Marina and Tassios,1973; Renon and Prausnitz, 1968]. A more detailed list of the applicable models have been compiled by Simonethy et al [1982].

These semi-empirical models are used to correlate the activity coefficients of the components of non-ionic mixture in the two phases with the mole fraction of the components present in the phases. At least two adjustable parameters per pair of components of the mixture obtained from the reduction of some binary experimental data of the components are usually required

by the models to correlate or predict liquid -liquid equilibria of a mixture. Some of these experimental data include [Prausnitz et al, 1978, 1980]:

(1) vapour liquid equilibrium data.

(2) mutual solubility data

(3) infinite dilution coefficient data

(4) azeotropic data

Except the modified Wilson equation [Negata et al, 1975] other equations or models listed above have been used extensively to correlate the liquid-liquid equilibria of non-ionic multi-component mixture. The degree of accuracy of the phase equilibrium data obtained from these models or equations depend on many factors. These include:

(1) The adequacy of the model in describing the phase equilibrium of the mixture.

(2) The number of parameters used per pair of the components of the mixture. The higher this number, the better the accuracy of correlation.

(3) The type of mixture being correlated. Only very few can correlate, with fairly good accuracy, the activity coefficient of mixture involving polar compounds.

(4) The miscibility gap between the raffinate solvent and extract solvent.

Both van Laar and Margule equations are polynomial models [Rowlinson, 1959; Hála et al.,1967]. Most of the other models developed in the last three decades have better correlation ability for liquid phase equilibria than these polynomial equations. NRTL model [Renon and Prausnitz, 1968] uses three

binary parameters to correlate vapour-liquid and liquid-liquid equilibria; the third parameter usually has fixed values for different sets of compounds. LEMF [Marina and Tassios, 1975] is a modified form of NRTL; the main point of departure from NRTL is in the procedure used in obtaining the value of the third parameter. These models when used for mixtures of non-polar fluid give results whose accuracy are comparable to the UNIQUAC model. However, UNIQUAC model has been found to be better at correlating the liquid-liquid equilibrium of mixture containing polar compounds than any of the phase equilibria correlating equations or models we know of [Prausnitz et al 1975, 1978, 1980].

If two adjustable binary parameters are used in the model, only binary experimental data are needed to predict or correlate the conjugate phase composition of multi-component system. Because of the greater non-ideality in the liquid, accuracy of the models in predicting liquid-liquid equilibria is less than for vapour-liquid equilibria. Type I system (liquid-liquid system) is more difficult to predict or correlate correctly, especially where vapour-liquid-equilibrium data are used for binary parameter estimation. Greater accuracy is usually achieved with UNIQUAC model if the binary parameters obtained from vapour-liquid equilibrium data are fixed with limited ternary data. This is true especially for type I system [Prausnitz et al, 1978, 1980].

2.4 Thermodynamic Analysis

A lot of work has already been done to generate design data for heat pump. Mumah [1987,1990] and Adefila et al [1988] generated thermodynamic property data for the whole range of conditions usually encountered in practice for ammonia-water mixture using the Chebyshev polynomials procedure. Grover et al [1988] presented data depicting interrelationship between the operating temperatures, concentration (and flow ratios), Carnot COP and other COPs for water-lithium bromide absorption system for cooling. Adefila et al [1987] produced graphic illustrations of the interrelationships between almost all the parameters affecting the performance of ammonia-water absorption heat pump system.

Thermodynamic analysis has always been carried out on heat pump systems as a means of gauging their performances. Some of the recent ones include R22 (tetraethylene glycol)-dimethylether (DMETEG) absorption system [Phuong et al, 1988] and lithium bromide-water absorption system [Cheng et al, 1988; Adefila, 1983].

CHAPTER THREE

3. DEVELOPMENT OF THERMODYNAMIC CYCLES

3.1 Introduction

Like in other systems, any attempt to reduce the irreversibility in the conventional ammonia-water heat pump will affect the process flowsheet of the system. Two of the techno-economic themes enunciated by Linnhoff [1979] support this assertion. One of these themes states **"Network interaction often cause drastic changes in the overall state of the process following change in one operation"** and the second one says **"Replacement and alteration of equipment are not equivalent"**. For instance, since isothermal processes such as liquid-liquid extraction operation could be carried out at relatively low temperature there would be reduced heat load on the economizer and in the weak solution (vehicular fluid) returning to the absorber, and consequently on the absorber, if extraction separation process is used in place of the non-isothermal separation process used in the conventional absorption system. The heat losses would follow the same trend. The same thing may happen if any of the processes of the system is **altered** in any way. **Changing** or **altering** separation process or any other process in the conventional ammonia-water heat pump will lead to alterations in the flowsheet configuration of the system.

A great deal of irreversibility is introduced into the absorption heat pump system in the process of absorbing and regenerating the main working fluid due to heat transfer across

large temperature gradient and input of HGE involved in these processes. The susceptibility of the processes in "thermodynamic pump" of this system to irreversibility is due largely to their non-isothermal nature. Possibilities for reduction of irreversibility should exist if the accompanying non-isothermal separation processes can be carried out isothermally. Other possible means of reducing irreversibility in the thermodynamic pump is a reduction of the quantity of material being circulated through the liquid pump and throttling valve within the unit.

Attempts to decrease the level of irreversibility in the conventional ammonia-water absorption heat pump by reducing the amount of HGE used for desorbing ammonia from the aqua ammonia requires that the separation process and possibly other associated process(es) be changed or altered. Consequently the flowsheet of the cycle of the conventional system would be altered. Various alternative cycles developed as a consequence of this alteration are discussed later in this chapter.

The flowsheet of the cycle developed in this work have extraction process unit, and in one case, stripping process unit, included. The units are placed in the flowsheet with the aim of reducing the amount of HGE used by the processes in the "thermodynamic pump" as well as the accompanying irreversibility.

3.2 Separation Processes

Liquid-liquid extraction, stripping and adsorption processes appear attractive for the modification of the non-isothermal separation processes employed in the conventional ammonia-water absorption heat pump because each of them fulfils, at least in

part, the following criteria [Pratt, 1967; Perry and Green, 1984]:

- **ability to separate homogenous liquid mixture**
- **being semi-equilibrium process which ensures that degradation of energy for driving the processes is less compared to that of non-equilibrium processes.**
- **possibility of being carried out isothermally or nearly isothermally**

Since in each of these three processes mass separating agents are used in place of the heat (energy) employed in the separation processes of the conventional system, secondary separations are required to recover the solute from the separating agent or vice-versa. As a result:

- more capital and operating cost may have to be expended
- non-isothermal processes may be involved

Adsorption process would appear less attractive on the basis of the second consequences mentioned above; the secondary separation process is either non-isothermal (thermal regeneration) or "tertiary" separation would be required if wet regeneration is employed. Moreover the process itself is at best carried out nearly-isothermally. Of the other two processes, only liquid-liquid extraction process is carried out almost always isothermally; *and it is for this reason that extraction process* is being used to achieve the objective of this work.

The concept of solubility parameter, selectivity and capacity and, consolute solution temperature (CST) were used to select solvents for extraction separation process (more detailed

discussions can be found in Appendix F). Organic solvents would generally select ammonia from its agueous solution while inorganic solvents (electrolytes) would select water from the same solution.

3.3 Thermodynamic Cycles

Since the absorber and the condenser operate at about the same temperature it should be remembered, in developing heat pump cycles incorporating extraction process that what takes place in the "thermodynamic pump" is just the desorption, possibly at a higher pressure; thus no temperature change is required of the working fluid while moving between absorption and condensation which are otherwise consecutive processes. The implication of this is that *desorbing* by any isothermal or nearly isothermal process such as liquid extraction and stripping will be thermodynamically consistent with the operation of the system.

The attractiveness of liquid-liquid extraction process in this project is due to its isothermal nature which ensures no energy loss due to heat transfer. Even where it becomes necessary to distil off impurities from the solute obtained after extraction less heat and irreversibility should be involved [Scheibel, 1965].

The first and foremost consideration for the utilisation of any of the two extraction schemes discussed below is its technological feasibility. The selectivity and capacity of the solvent for the designated solute must be adequate enough to ensure its extraction, purity of the solute in the raffinate or extract phase and easy separation of the extract; the selectivity

should also be such as to limit the number of stages needed to achieve subsequent separation.

The type of solvents selected for the separation of aqueous ammonia solution by liquid-liquid extraction separation process depends on which of the two constituents of the solution is desired to be passed into the extracting solvent phase. As already noted ammonia is generally selected by organic solvents while the ionic solvents select water preferentially from the mixture of these two compounds. Based on the component of aqueous ammonia solution passed into the extracting solvent in the course of separating the constituents of the solution by liquid-liquid extraction, two schemes are possible. These are discussed below.

(a) **Water-extracted scheme:**

In this scheme the water component of the aqueous ammonia solution is passed into the extracting solvent, leaving ammonia in the raffinate phase. The problems associated with this scheme are outlined below:

- Organic solvent for this scheme must be rare considering the fact that the intermolecular forces of organic solvent is more similar to that of ammonia than it is to water. Indeed organic solvent would select ammonia in preference to water [Nicholls, 1979; Lagowski, 1967]. While there are probably some organic solvents that meet the requirements of this scheme as shown on the triangular co-ordinates in Figures 3.1a and 3.1b, the search for such solvent(s)

require vast number of binary solubility data involving ammonia, water and the solvents as well as the consolute solution temperature (CST) data, all of which are not easy to come by. Ionic solvents would select water preferentially but they suffer from the handicap of higher heat capacity and heat of vaporisation.

- Recovery of solvent having higher specific heat and heat of vaporisation might increase heat consumption. This is not desirable since the aim of liquid-liquid extraction process is to reduce irreversibility in the system.
- The separation may not be effected at lower pressure as pure ammonia in the raffinate phase may be in gaseous state under the conditions in the absorber.

Considering these problems, it is doubtful if the water extracted-scheme whose hypothetical binodal curve is given in Figure 3.1a is technically favourable or even feasible.

The "appropriate" variant of this scheme (see Figure 3.1b) proposed by Mumah [1990] appears impossible considering that, from the diagram, the solvent is expected to render ammonia and water immiscible and at the same time be miscible with these two compounds. Such solvent must be rare if we consider the factors affecting selectivity and capacity of one compound for another as listed by Hansen and Beerbower [1971] and Shinoda [1978].

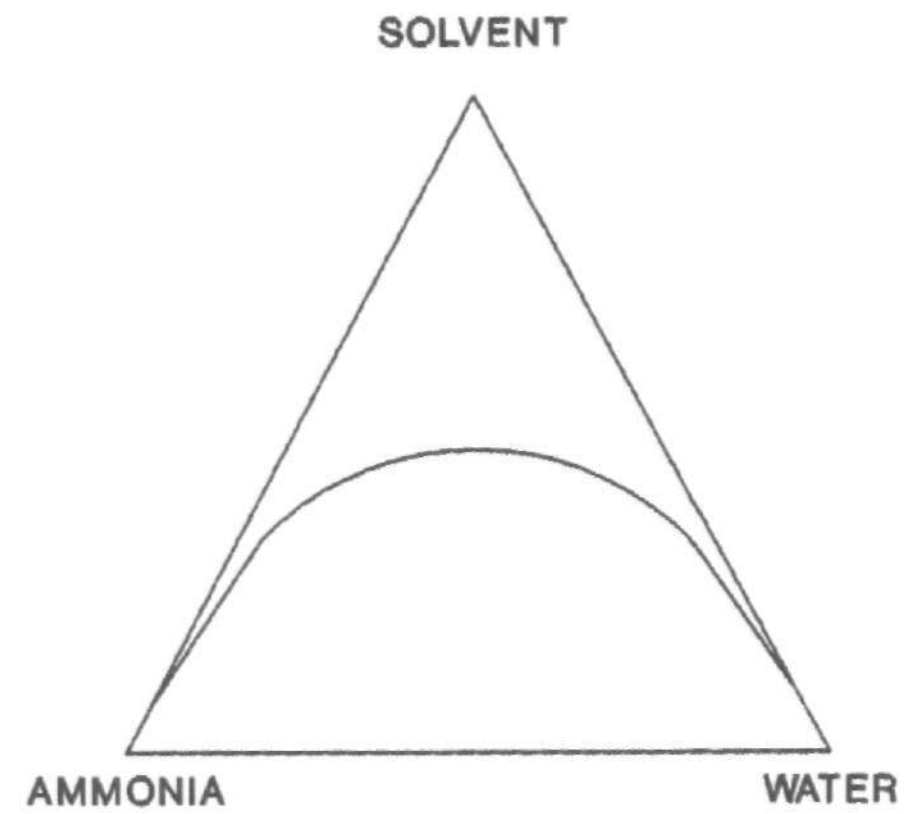


Figure 3.1a: "Appropriate" Binodal Curve for Water-Extracted Scheme [Mumah, 1990]

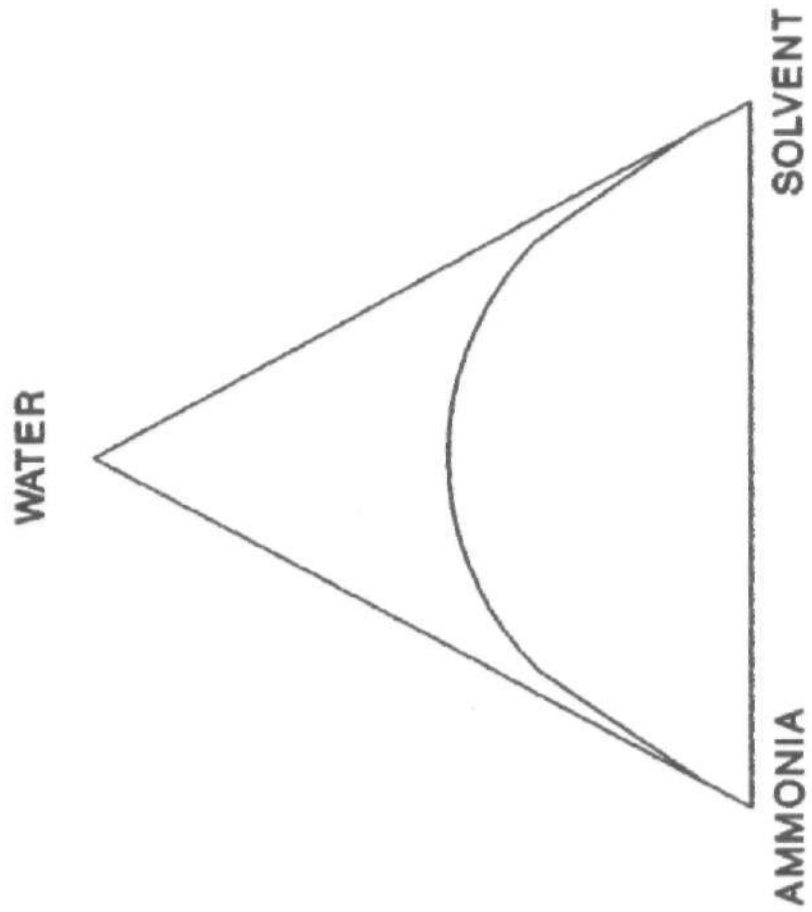


Figure 3.1b: Hypothetical Binodal Curve for Water-Extracted Scheme

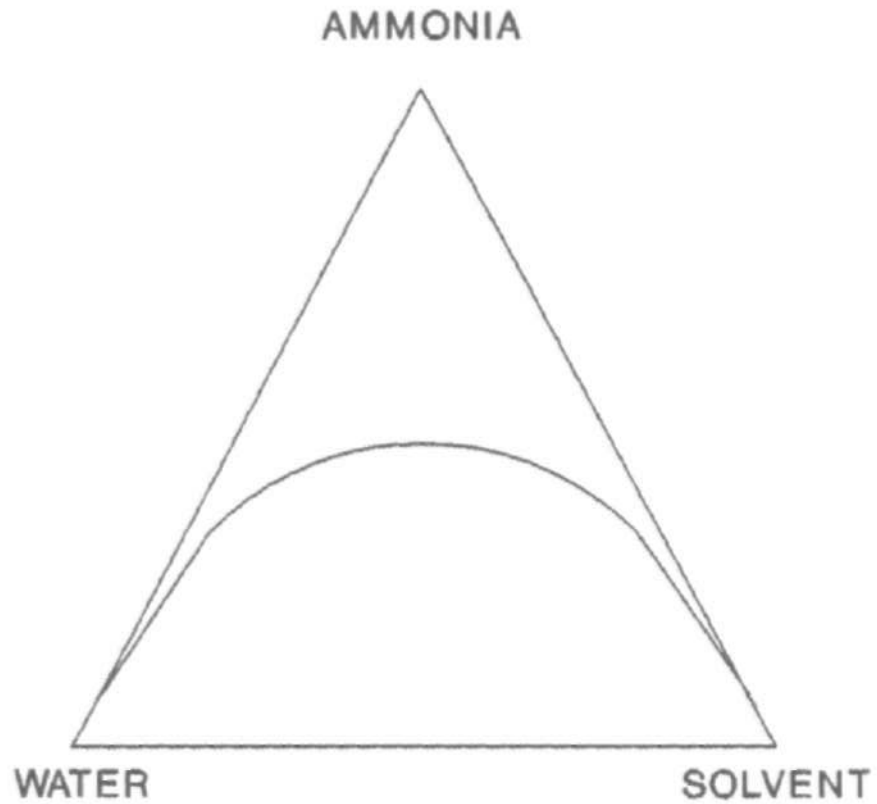


Figure 3.2: Appropriate Binodal Curve for Ammonia-Extracted Scheme

(b) **Ammonia-extracted scheme:**

Ammonia is passed into the extract phase to leave water in the raffinate phase. Organic solvents having favourable specific heat capacity and heat of vaporisation can be found that select ammonia in preference to water. High purity extract (and ammonia) could be obtained by refluxing the extract phase to the corner of the binodal curve [Somekh, 1966]. The solvent can be recovered completely from the extract to leave pure ammonia by adjusting the system's pressure if the difference between the boiling points of ammonia and the solvent is more than 200°C, otherwise rectification becomes necessary. By making use of the solvents with lower specific heat and heat of vaporisation than water and with the small quantity of water impurity that may be present in the extract phase, saving in heat energy is ensured even where secondary separation processes such as evaporation and/or distillation is needed to purify ammonia after the extract solvent has been recovered.

This scheme appears technically favourable and feasible. The appropriate binodal curve is shown in Figure 3.2. The appropriate binodal curve specifies non-miscibility between water and the solvent as indicated by the presence of full miscibility gap. However, some miscibility could be tolerated in practice. Thus in selecting solvents for this scheme, very low miscibility between water and the solvent is a critical consideration. As type I system is preferred in this work, ammonia must be totally miscible with the solvent (i.e under the process condition the consolute solution temperature of the ammonia-solvent mixture must be lower than the temperature at which the separation will

occur in the system). Type I system is selected to limit the size of the extraction column that may be required for the separation.

Four thermodynamic cycles of the modified system (called extract-step-attached (ESA) ammonia-water absorption heat pump or 'derived' system) have been suggested based on this scheme. In two of the cycles the extracted ammonia is used as the main working fluid as in the conventional absorption system while the other two cycles used the pure or purified extract phase fluid as the main working fluid of the absorption system. These cycles and that derived from stripping process are described below.

3.3.1 Feasible thermodynamic cycle

These cycles, as stated before, are modified forms of the conventional ammonia-water absorption heat pump cycle. The modification involves the working fluid used, the process employed and the hardware of the system.

a) **Cycle One:**

The strong agua ammonia from the absorber is mixed with the extracting solvent in the extractor thereby ensuring that ammonia passes into the extract phase leaving water in the raffinate phase. The resulting raffinate which should be relatively pure water is sent back, as the vehicular fluid, to the absorber. The extract phase made up of ammonia and the solvent is pumped to the higher pressure where secondary separation is carried out to recover solvent and ammonia. The fairly pure solvent is sent back to the extraction column and the pure ammonia obtained by refluxing is split into the reflux and condensate stream after it has passed through the condenser. The reflux stream is sent

to the extraction column and the condensate stream is throttled into the evaporator where it picks up heat and vaporises. The ammonia vapour is thereafter absorbed by the weak solution that might contain a little solvent and the resulting strong solution is pumped to the extraction column where it mixes with the solvent. The mixture separates into the raffinate and extract phase and the cycle continues. The schematic diagram of this cycle is shown in Figures 3.3a.

The solvents for this scheme must meet the following conditions to be useful.

- The boiling point must be above 167°C at atmospheric pressure to reduce the heat input for secondary separation, otherwise secondary separation would involve rectification.
- The specific heat capacity should be far lower than that of water.
- The capacity for ammonia should be moderate and capacity for water should be very low or nil.
- The selectivity for ammonia must be as high as the desired capacity for the same compound would allow.
- The solvent should not form azeotrope with ammonia.

Where the normal boiling point of the solvent is not above 167°C there is the need for rectification of the vapour from the vaporiser to obtain pure ammonia. Figure 3.3b represents this case.

b) **Cycle Two:**

This cycle is different from cycle one in only one respect: the extraction takes place at the higher pressure instead of the

lower pressure in cycle one. Other processes follow the same pattern as in cycle one.

The solvents used in the cycle are required to meet the same set of conditions as those of cycle one. The diagram of cycle two is presented in figure 3.4a. The flow-sheet of this cycle when the normal boiling point of the solvent is not higher than 167°C is presented in Figure 3.5b.

c) **Cycle Three:**

Like in cycles One and Two, ammonia is passed into the extract layer. However, the extract, rather than being separated into its constituents, goes through the remaining processes of the cycle as the main working fluid, while the raffinate goes back to the absorber. The extract is thus the working fluid mixture in this case. In addition the absorption of ammonia component of the mixed vapour by and, the mixing of the working fluid with, water (absorbent) take place in the absorber. Thus the heat effects in the absorber include heat of condensation of ammonia and the solvent as well as the heat of absorption of ammonia in water.

The "extract" working fluid resulting from the mixing (and separation into phases) in the absorber is pumped to a higher pressure, vaporised if need be before condensation process takes place. The condensed "extract" working fluid is then throttled into the evaporator. The vapour of the working fluid mixture is sucked into the absorber where it mixes with the absorbent and thereafter separated into the extract and raffinate phases. The

extract which thereafter constitute the working fluid is pumped to a higher pressure and the cycle continues.

d) **Cycle Four:**

This cycle has a great deal of similarity with cycle three. In this case, the extract working fluid is passed straight to the evaporator through the liquid pump and throttling device after it is purified. The vapour of the mixed working fluid from the evaporator is sucked in by the absorbent and mixes with it in the absorber to effect separation. The 'extract' working fluid obtained from the separation is pumped to a higher pressure and the cycle continues. The condenser is omitted in this case and so this cycle can be used in the cooling mode only. The schematic diagrams of cycles three and four are shown respectively in Figures 3.5 and 3.6.

The solvents for this scheme must have the following properties:

- Appropriate thermodynamic and physical properties required of a good working fluid in heat pump system. Some of such properties include high latent heat of vaporisation, lower freezing point than the evaporator's ambient temperature, high molar density, low specific heat capacity, etc.,
- The solvent capacity for ammonia should be high and that for water should be very low or nil.
- The selectivity of the solvent for ammonia must be very high as pure extract is highly desirable.
- Freezing point should be low enough to prevent solidification in the evaporator.

- The boiling point need not be high but solvent should be liquid under the condition existing in the absorber and condenser.
- Solvent that form azeotrope with ammonia is preferable as this ensures that the mixed working fluid behaves as a pure substance.

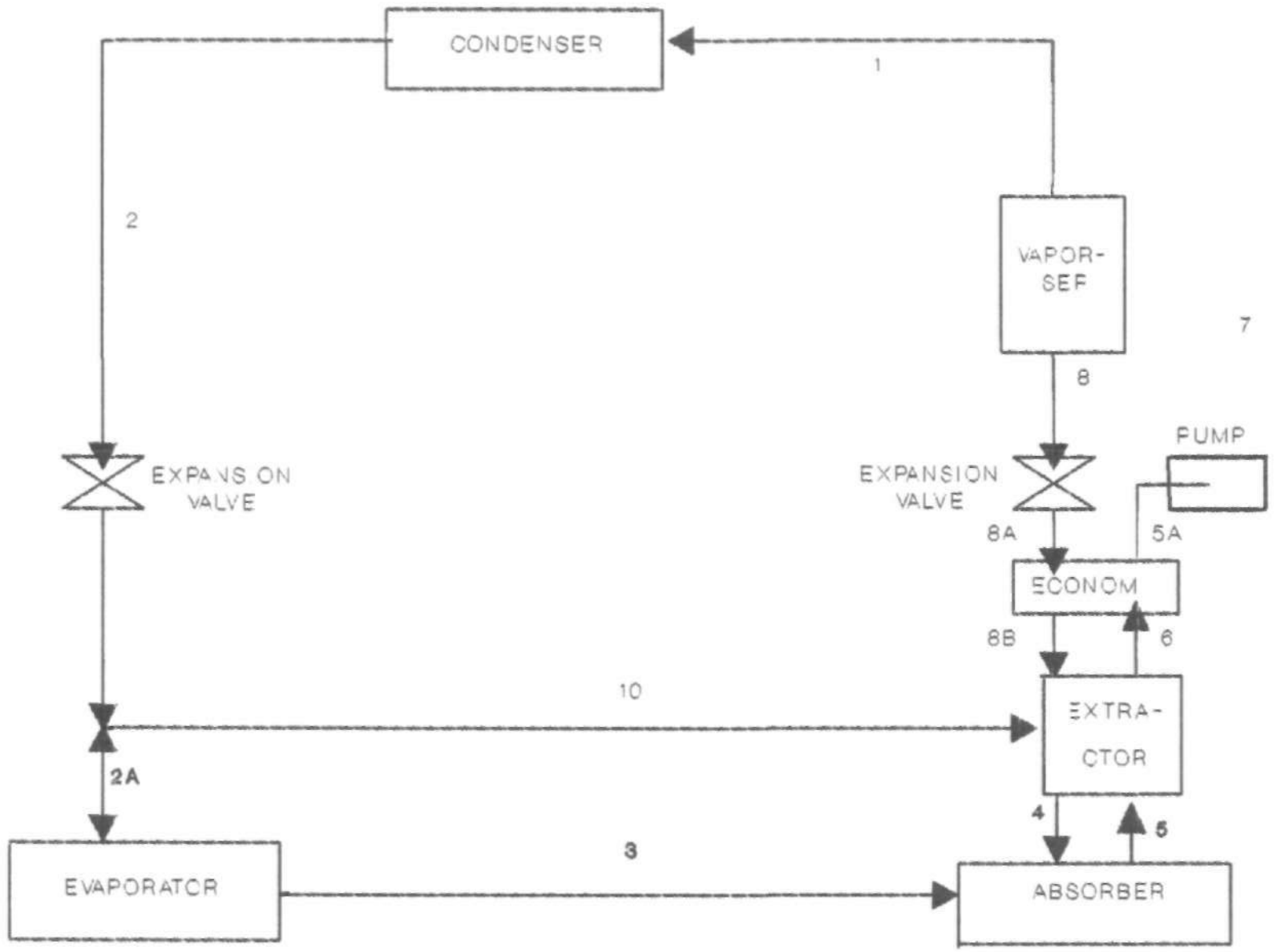


Fig 3.3a: Extraction-System-Attached Absorption Heat Pump Cycle One without Rectification

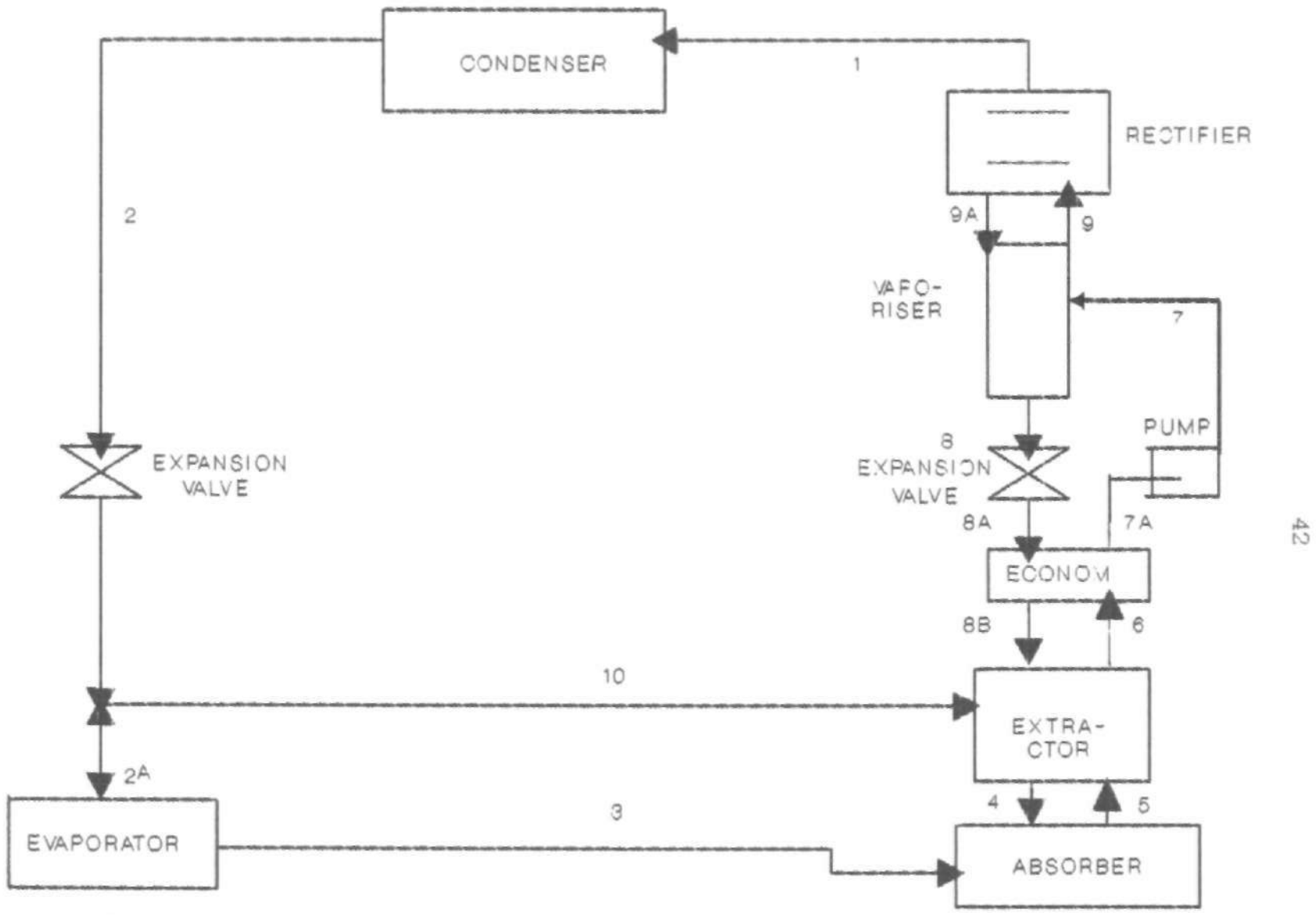


Fig 3.3b: Extraction-System-Attached Absorption Heat Pump Cycle One With Rectification

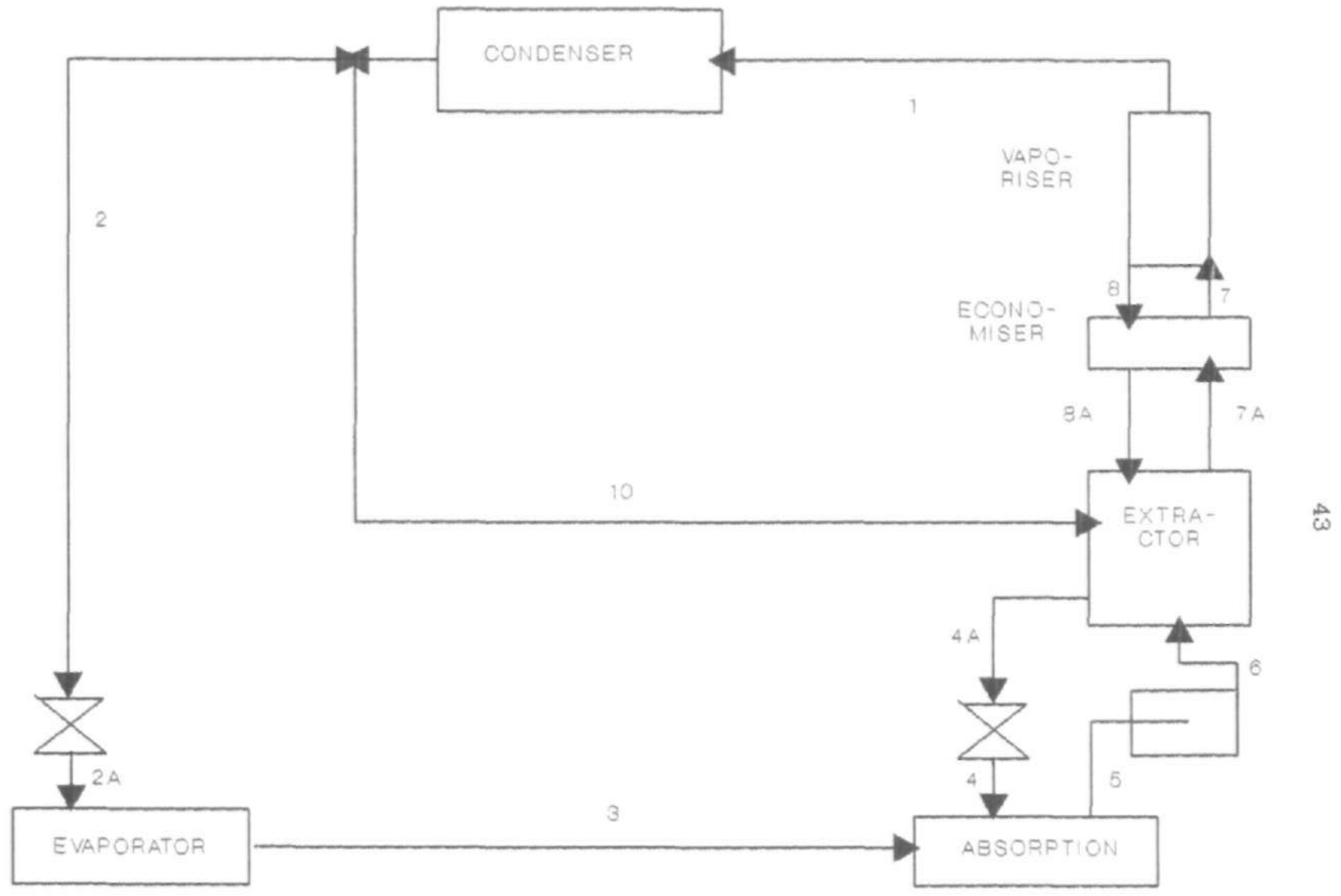


Fig 3.4a: Extraction-System-Attached Absorption Heat Pump Cycle Two without Rectification

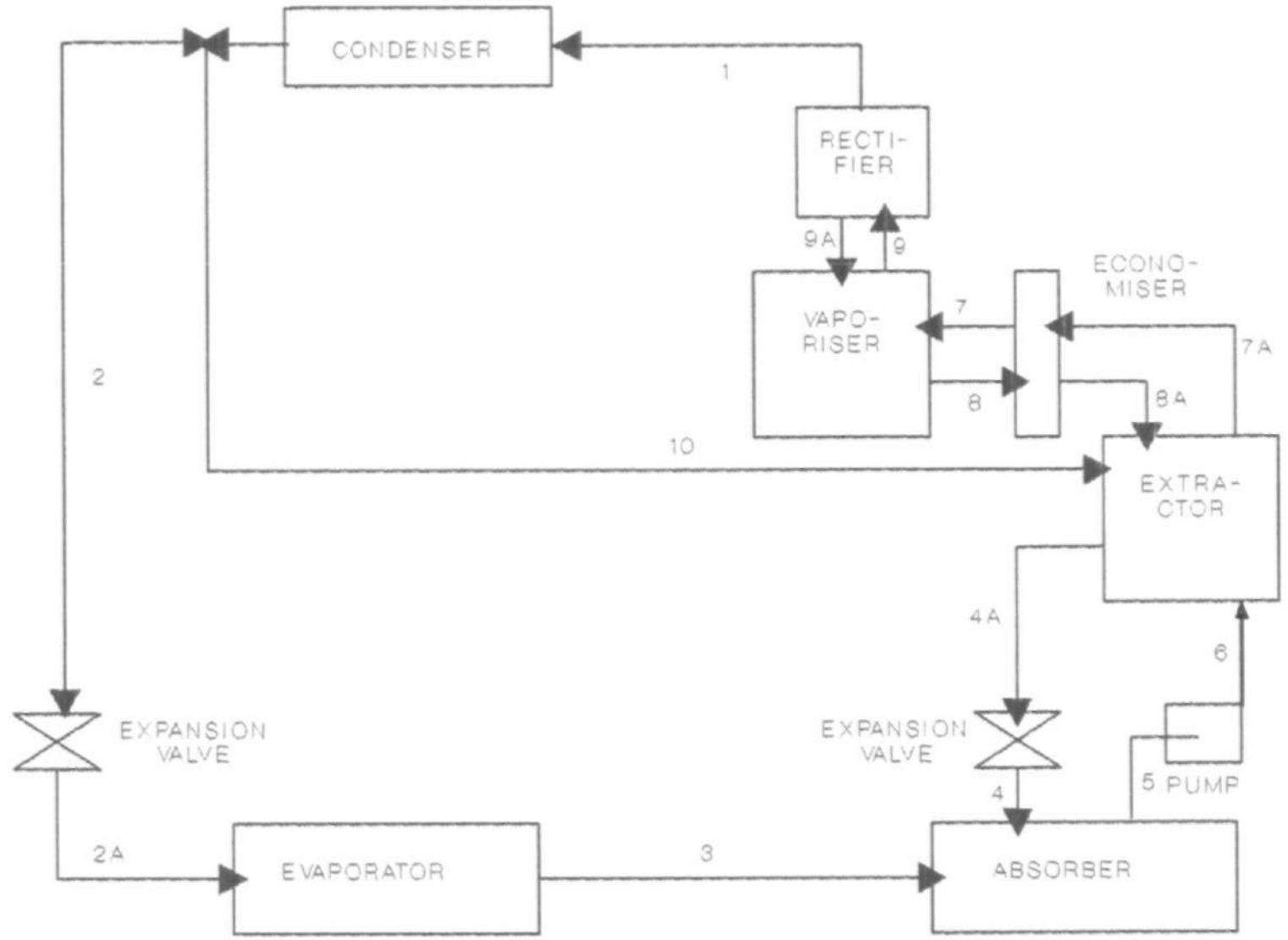


Fig 3.4b: Extraction-System-Attached Absorption Heat Pump Cycle Two with Rectification

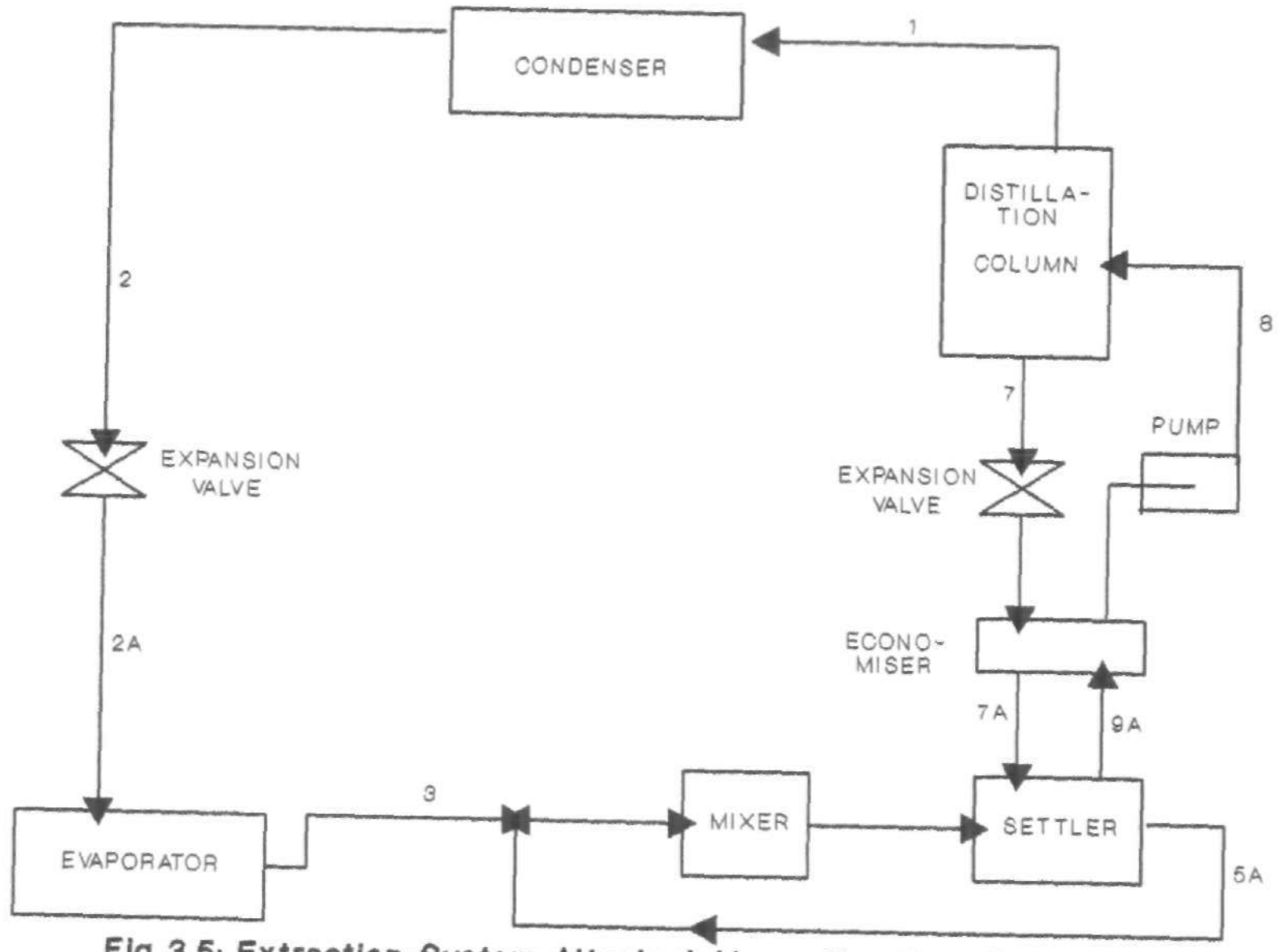


Fig 3.5: Extraction-System-Attached Absorption Heat Pump Cycle Three

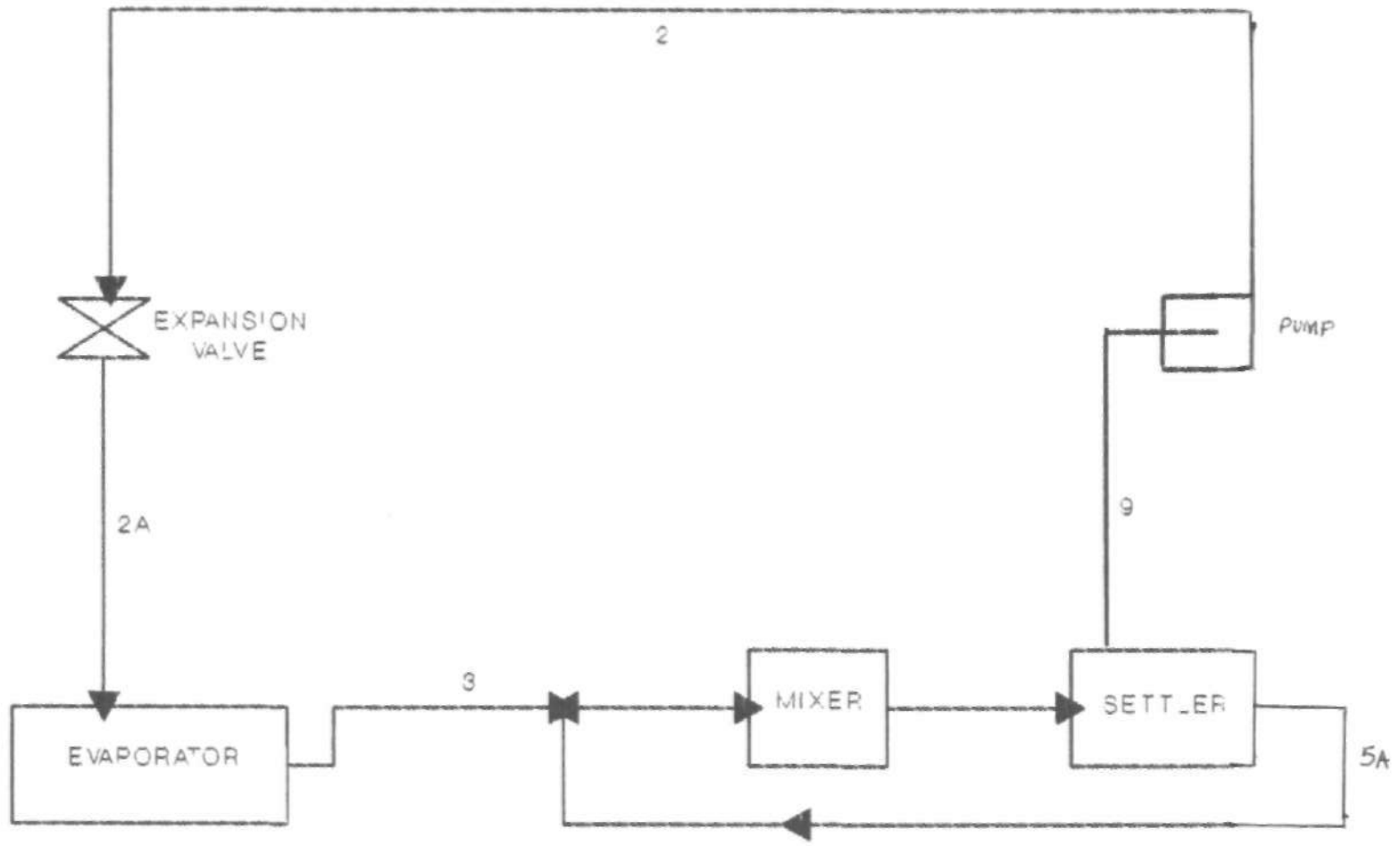


Fig 3.6: Extraction-System-Attached Absorption Heat Pump Cycle Four

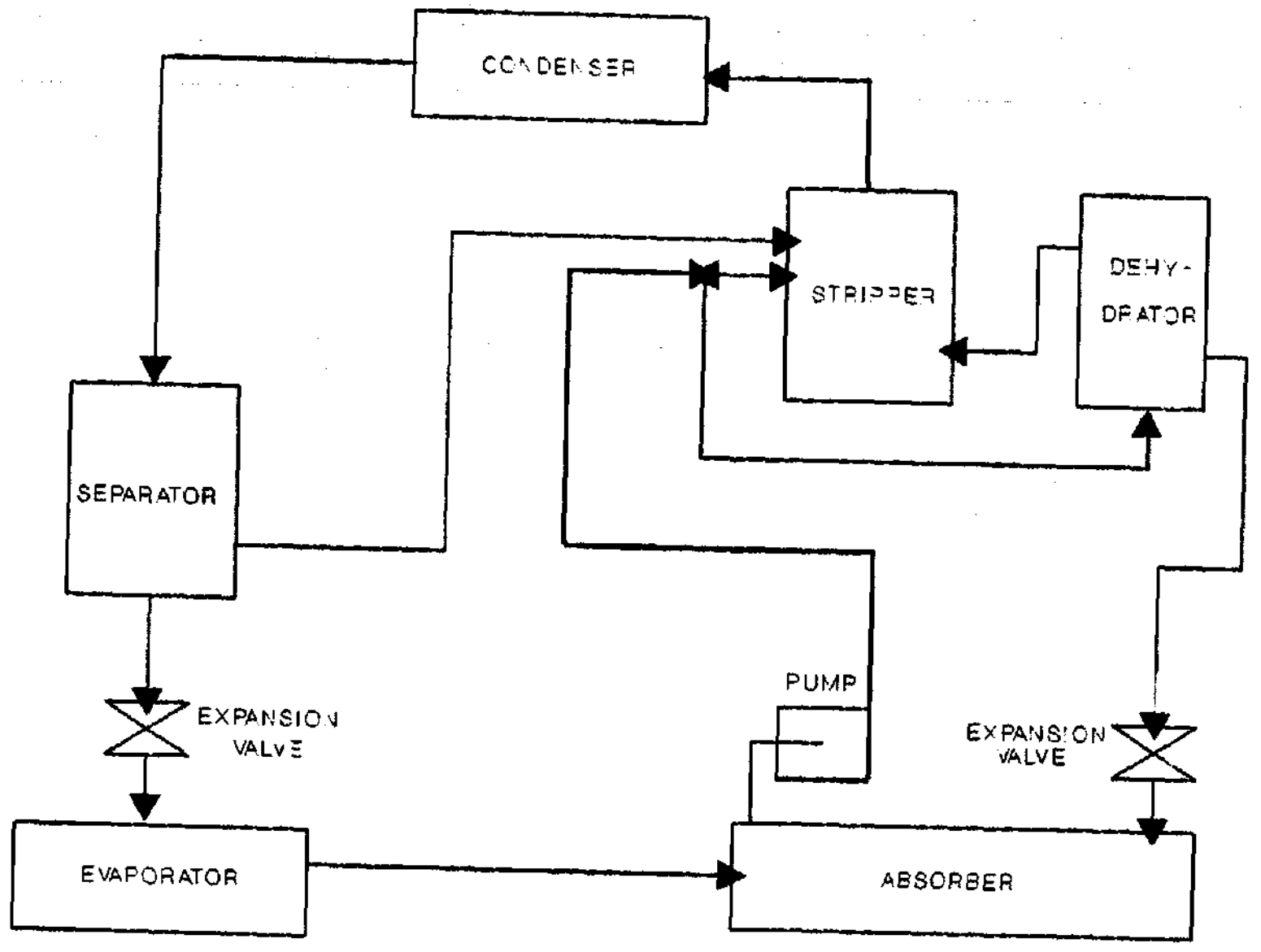


Fig 3.7: Stripping-System-Attached Absorption Heat Pump

Cycle Five:

This is a stripping-process-based cycle in which the strong aqua ammonia is pumped from the absorber into the stripper where it mixes with calcium hydroxide slurry from the generator to raise its pH. The stripping gas which may be hydrogen is introduced into the stripper counter-currently to the aqua ammonia and calcium hydroxide slurry. The alkaline condition (about pH 12) in the stripper ensures that ammonia vapour is easily desorbed from the mixture in the stripping column so that it can be 'swept off' by the stripping gas into the condenser. Ammonia vapour from the stripper is liquified at the condenser and throttled into the evaporator while the stripping gas recovered at the separator (in the high-pressure portion of the cycle) goes back to the stripping column. Ammonia vapour from the evaporator is sucked into the absorber to form strong agua-ammonia in the absorber. The aqueous ammonia solution is then pumped into the stripper.

The aqueous solution (devoid of ammonia) from the stripper may be separated into the weak aqueous ammonia solution and aqueous solution of calcium hydroxide by appropriate separation process. The weak aqueous ammonia solution is passed through an expansion valve into the absorber to form a mixture with ammonia vapour from the evaporator. The resulting solution is pumped to the higher pressure in the stripping column where it mixes with the strong aqueous ammonia solution and the cycle continues.

Some assumptions were made in developing this configuration. They include:

- Water vapour is not swept off along with ammonia from the stripper into the condenser.
- Ammonia is liquified sufficiently at the condenser and the quantity of ammonia vapour that returns with the stripping gas into the stripper is negligible.
- The quantity of ammonia left in aqueous calcium hydroxide solution is very small (this stripping procedure is also applied in the removal of micro quantity of ammonia from waste water).
- The temperature of the condenser and absorber are the same.

Stripping with hydrogen or any other gas miscible with ammonia but not soluble in water should be possible. The process cycle is shown in Figure 3.7.

3.3.2 Analysis of the cycles

Second law analyses of these two schemes - extraction and stripping - should give indications of their suitability or otherwise for this work. While the stripping-scheme based cycle will not be discussed any further in this work, the result of analyses of cycles one and two (based on extraction scheme) already developed are presented in Chapter 5. The analysis of cycles Three and Four are not carried out in this work because none of the five solvents we are constrained to work on possesses adequate capacity and selectivity properties required by the cycle.

CHAPTER FOUR

4. COMPUTER SIMULATION OF EXTRACTION SCHEMES

4.1 Introduction

Simulation procedure is used in chemical processing because of the following advantages:

- Economic experimentations is made possible.
- Limited experimental data can be interpolated or extrapolated.
- Alternative policies can be easily evaluated.
- System stability can be studied with and without operating the system.

Usually a model of the process of interest has to be developed before simulation takes place. The quality of result obtained from simulation of the model depends on:

- the extent to which the model is able to describe the physical process accurately.
- the quality of the data used in obtaining the parameters of the model.

For the purpose of this work, semi-empirical models based on thermodynamic principle are used in the phase-equilibria determination. The economic necessity of modelling and simulation in obtaining phase equilibria for multi-component systems has been pointed out [Prausnitz et al, 1980]. Simulation of such models require only limited experimental data. The models are based on sound theoretical foundation so that reliable results can be obtained from interpolation and extrapolation with respect to temperature, pressure and composition.

4.2 Liquid - Liquid Equilibria

The principle of two-phase liquid-liquid equilibria is applicable in the simulation of liquid-liquid extraction process. The liquid -liquid equilibria for multi-component mixture can be correlated and/or predicted using some of the semi-empirical models for excess Gibbs free energy of liquid mixture. The applicable model must be capable of predicting phase splitting of liquid mixtures that is unstable as a single phase at a given pressure over a temperature range, i.e. liquid mixture for which Equation 4.1 applies.

$$\partial^2 g^m / \partial x_i^2 < 0 \quad \text{.....4.1}$$

where:

g^m is the partial Gibbs free energy of component m

x_i is the mole fraction of component i

Other methods can be used to correlate liquid-liquid equilibria of ternary systems. Some of these are:

- Graphical methods which require extensive line construction to interpolate or extrapolate tie-line data [Treybal,1963,1981].
- The method in which the solubility surface of a polynomial in conjunction with experimental tie-line data are used to correlate the liquid-liquid equilibria [Chimowitz et al, 1983; Ruiz et al, 1986]

However with these aforementioned methods simplifying assumptions are made in some cases and all of them require experimental tie-

line data to correlate the liquid-liquid equilibria of any multi-component system. On the other hand it is possible to employ semi-empirical methods, especially the UNIQUAC model for the type of systems being considered in this work without the need for ternary tie-line data as explained in the latter part of this chapter.

4.2.1 UNIQUAC model

UNIQUAC model has been found to be the best of all the semi-empirical models for correlating or predicting liquid-liquid equilibria of systems containing polar compounds such as water and ammonia [Prausnitz et al., 1975,1978,1980]. But lack of adequate experimental ternary data needed to obtain the most accurate binary parameters from vapour-liquid-equilibrium data is a serious constraint. However, it has been consistently observed that [Prausnitz et al, 1978, 1980]:-

- the model is able to accurately predict and/or correlate liquid-liquid equilibria for type I system where the mutual solubility of the extract and raffinate solvents are very low and,
- the parameters obtained from mutual solubility and infinite dilution data gave better correlation than parameters obtained from vapour-liquid-equilibrium data.

Fortunately, all the solvents used in the phase equilibria computation in this work have low mutual solubility with water. In addition, mutual solubility data and binary infinite dilution coefficient data were used to obtain adjustable binary parameters in this work. Another point worth noting is the fact that though

ammonia in aqueous solution might exist in ionic state the proportion of ammonia that is expected to ionize at the concentration level of the aqueous ammonia solution at which the correlations in this work were carried out (minimum concentration is 15% by weight) is negligible since these concentration levels do not fall in the dilute region [Edward et al, 1978].

From the foregoing it is thus expected that the UNIQUAC model would be able to predict phase equilibria for ammonia-water-solvent system with adequate accuracy. Therefore this is the model used, as phase equilibrium model, for predicting conjugate phase compositions of ternary systems in this project. The applicable UNIQUAC equations are given in Appendix A while the program listing for the correlation of the liquid-liquid equilibria for the ammonia-water-solvent ternary systems is given in Appendix C.

4.2.2. Selection of Solvent

Solvents' selection for the simulation of the extraction of ammonia from aqueous ammonia solution was based on possession of the desirable characteristics of extracting solvent listed in Appendix F. The screening of the solvents was based on the following criteria in the order of listing:

- Very low mutual solubility with water.
- Infinite mutual solubility with ammonia or CST of mixture of ammonia and the solvent less than the expected temperature in the system, i.e. high capacity for ammonia.
- High selectivity for ammonia.

- Possession of all physical properties required to make the liquid-liquid extraction process feasible under the condition of the system as listed in Appendix F.
- Safety and other properties of economic importance.

The number of solvents that meet the properties listed above are many [Riddick & Bunger,1978; Stephens & Stephens, 1964] but the vapour liquid equilibrium data, mutual solubility data, azeotropic data, infinite dilution coefficient data, and other data of binary mixtures of each of the organic solvents, ammonia and water which are needed to obtain the UNIQUAC binary parameters required for computer simulation of the extraction schemes are available for only very few of the solvents. Some of the pure component parameters needed for the utilization of UNIQUAC equation are also not available for most of the solvents having the desirable properties. Due to these problems only the following five solvents could be used as solvents in the simulation operations.

1. Nitrobenzene.
2. M-xylene
3. Ethyl benzene
4. Styrene
5. Toluene

Table 4.1 gives the values of some of the desirable properties of these solvents.

PROPERTIES	EXTRACTING SOLVENTS				
	NB	MX	EB	SR	TL
boiling pt, K	483.95	412.25	409.34	418.29	383.78
sol in water, %	19.0	2.0	1.5	3.1	3.3
water sol in, %	24.0	4.0	4.3	6.6	5.5
CST with NH3, K	<293.1	<293.1	<293.1	<293.1	<293.1
heat cap,kJ/kgK	1.42	1.68	1.70	1.75	1.84
vap heat,kJ/kg	331.16	343.09	338.90	371.59	363.17
viscos, poise	1.63	0.86	0.64	0.70	0.86
sp. gravity	1.20	0.58	0.86	0.90	0.55
sol in NH3, %	24.0	4.1	5.3	7.1	4.7
NH3 sol in, %	15.5	45.0	50.3	62.5	43.8

Table 4.1: Selected Properties of Extracting Solvents
[Shinoda, 1978; Stephens & Stephens, 1964; Riddick & Bunger, 1978; Reid et al, 1987]

LEGEND FOR TABLE 4.1:

NB stands for nitrobenzene
MX stands for m-xylene
EB stands for ethylbenzene
SR stands for styrene
TL stands for toluene
NH3 stands for ammonia
CST stands for consolute solution temperature

Capacity and selectivity diagrams were drawn from the conjugate phase data obtained from computer simulation of the ternary systems expected to be formed by mixing the aqueous ammonia solution and each of the five solvents listed above, using UNIQUAC equation. By comparing these diagrams with the standard diagrams adapted from Somekh [1966] which is presented in Figures 4.1 and 4.2, the extent to which extraction can be

attained, which system type would be appropriate for extraction and the purity level that can be attained in the extract and/or raffinate phase can be determined.

The estimated binary parameters, the liquid-liquid equilibrium of ammonia-water-toluene system and, the capacity and selectivity diagrams are presented in Chapter 6. The arithmetic expressions and the listings of the computer programs used to obtain the UNIQUAC binary parameters are respectively presented in Appendices B and D.

	ORG SOLV PHASE (mf of NH3 in)	AMMONIA PHASE (mf of org sol in)	ORGANIC SOLVENT	TEMP.K
1.	0.6250	0.0710	STYRENE	253.15
2.	0.4375	0.0471	TOLUENE	253.15
3.	0.5031	0.0529	ETHYLBENZENE	273.15
4.	0.4850	0.0529	O-XYLENE	273.15
5.	0.2750	0.0529	P-XYLENE	273.15
6.	0.4500	0.0412	M-XYLENE	273.15
7.	0.4281	0.0235	ISOPROPYLBENZENE	273.15
8.	0.4063	0.01765	N-PROPYLBENZENE	273.15

Table 4.2: **Mutual Solubility Data of Binary Mixtures of Ammonia and Organic Solvents [Shinoda, 1978]**

LEGEND

ORG	ORGANIC
SOLV, SOL	SOLVENT
NH3	AMMONIA
mf	MOL FRACTION

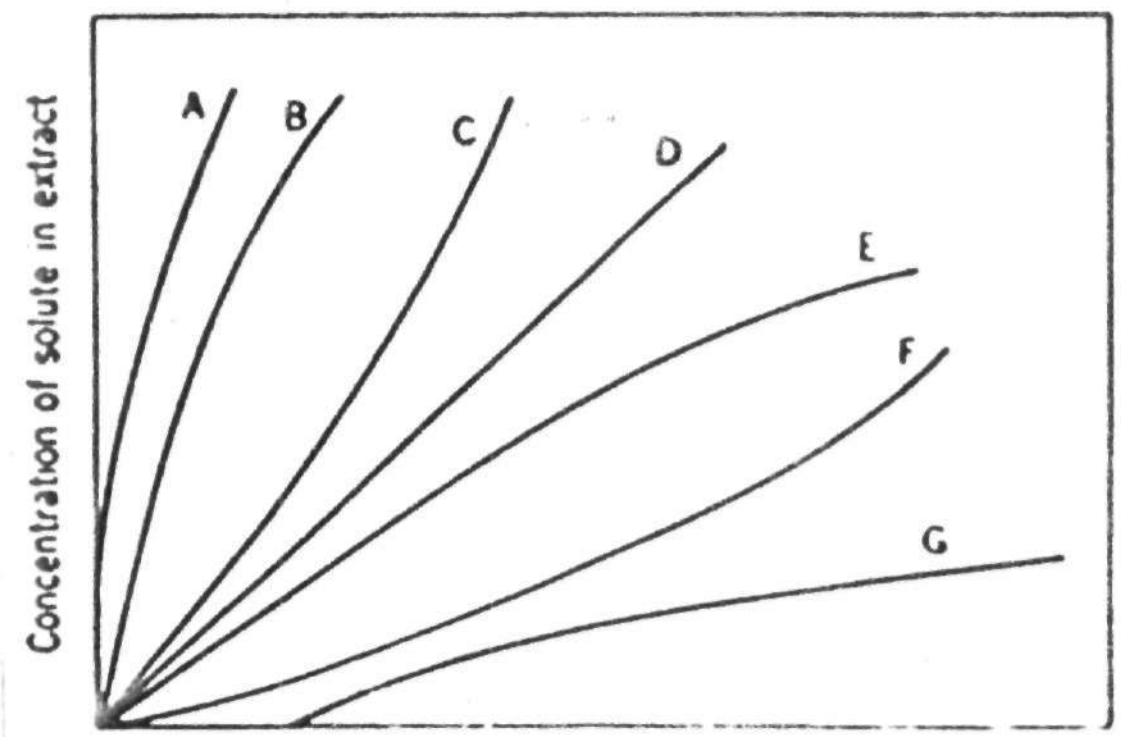


Figure 4.1: Capacity Diagram [Somekh ,1966]

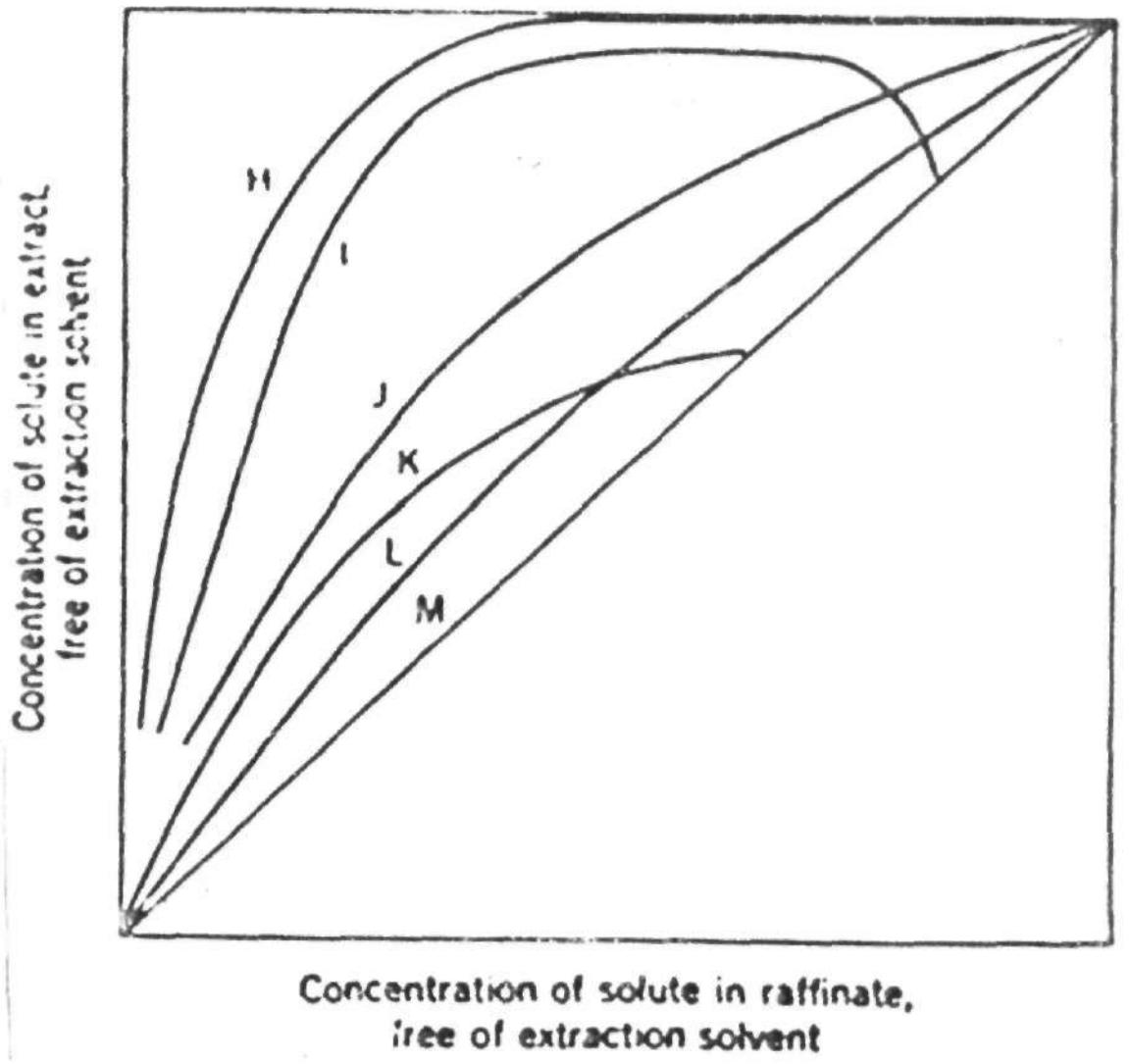


Figure 4.2: Selectivity Diagram [Somekh, 1966]

CHAPTER FIVE

SIMULATION OF THE CYCLES OF DERIVED SYSTEMS

5.1 Introduction

The first and second laws of thermodynamics are useful tools in the process industries. While the first law stipulates the conservation of energy, the second law helps to discriminate between the permissible and impossible energy transfer. In other words the second law differentiates between energy of various qualities and identify which energy conversion or flow is possible and which is impossible.

Essentially, the analysis of any process on the basis of second law of thermodynamics, usually referred to as second law analysis is used for energy auditing of the system. The importance of the second law analysis can be appreciated if it is realised that in real processes some quantity of energy is lost during energy conversion, energy consumption and/or energy transportation or transmission. It is thus necessary to quantify this energy loss occurring in a physical or chemical process so that the energy needed for the process to be realised is known apriori. The energy loss is due to the irreversibility accompanying the process and the extent of this energy loss is measured by the second law efficiency of the system. In addition to allowing the apriori determination of the actual energy need of a system the second law analysis makes it possible to locate the point(s) at which the energy loss(es) occur(s). Having pinpointed the source(s) of energy loss, it is possible to

techno-economic themes of Linnhoff [1979] discussed below make the interpretation of the results of second law analysis, with great certainty, possible.

5.2 Techno-economic Themes

Linnhoff [1979] identified some regularly recurring themes that "...relate to technical and economic constraints which either support or counterbalance strict thermodynamic evidence..." [Flower and Linnhoff, 1979]. The major ones among these themes are discussed in relation to the subject of this work below. The discussions treat the themes as 'pitfalls' in which capacity they help prevent premature and fallible conclusions to be drawn from the results of second law analysis.

Themes as 'pitfalls'

1. Thermodynamic potential is not the same as cost:

   This theme is a reminder of the fact that removal or reduction of irreversibility may not necessarily lead to lowering of cost. This theme is the reason usually given for not carrying out the second law analysis of process flowsheets. A good practical example of the truism of this theme as it relates to absorption heat pump is the case of irreversibility due to heat transfer in the absorber. To obtain a negligible energy loss in absorption process a very large sized absorber and pipes are required which means higher cost of the materials of construction. Thus the cost

factor may render the requirement for thermodynamic perfection untenable

2. Replacement and alteration of equipment are not equivalent: If an equipment is not the right one for a given duty, replacing it with a more appropriate equipment produces changes confined to that equipment given that the input stream is not changed. In a case like this, the two equipment that swap places might have the same efficiency but one is more appropriate for the task than the other. However where there is the need for alteration in an equipment to make it perform better because of its inherent inefficiency, then this change leads to change in the output of the equipment given the same input as obtained before the alteration. This changes causes other changes in the flow-sheet and there is the need to carry out mass and energy balance of the system to know the consequence of this change on the flow-sheet. Changing one unit operation equipment with another is alteration. A great deal of energy loss occurs in the non-isothermal separation process equipment and associated equipment in the conventional ammonia-water heat pump system, and by changing the equipment with isothermal process equipment, with the aim of increasing the energy efficiency as we are attempting to do in this project, would alter the flowsheet . The second law analysis of

the flow-sheet obtained as a result of the modification is therefore necessary.

3. Minimum driving force cause considerable change in the practical significance of losses:

To have a realistic size of equipment and make a given process take place in finite time requires a minimum driving force. It is thus always necessary to give allowance for the minimum potential difference while carrying out the analysis of a system with the aim of reducing the energy loss. For example, in the heat transfer accompanying the absorption process, a minimum temperature difference of 5°C is usually requested. A lower value would mean that an unrealistically large sized reactor is required for the given duty. The energy loss can only be significant if the potential gradient makes it recoverable, otherwise the loss is regarded as an inevitable one.

4. Network interactions often cause drastic changes in the overall state of the process following a change in one operation:

A change from non-isothermal processes, where heat transfer occurs, to isothermal separation processes where there is no heat transfer is bound to affect

other processes in the flow-sheet. For example the heat load is bound to reduce; it is also possible that the composition of the stream in the cycle of ammonia-water heat pump where isothermal or nearly isothermal separation process is used is different from that of the streams where the non-isothermal separation process (as in conventional system) is used. The change in the properties of the stream and the condition of the system is due to the network interaction.

5. Choice of energy sources and sinks:

The energy sources and sinks have serious effects on the efficiency of the system. The choice of right energy sources and sink is derived from the first law analysis. Carrying out the mass and heat balance makes it possible to determine whether a particular heat source and/or sink is the appropriate one for the given duty.

These techno-economic themes can also be used to identify ways of avoiding irreversibility in a given flow-sheet [Flower and Linnhoff, 1979]. Optimal design can result by using these themes as checklist. Optimality ensues when the energy loss(es) identified in the flow-sheet can not be eliminated for technical or economic reason or if its elimination is counterproductive due to network interaction. One consequence of the network interaction theme is that **thermodynamic loss are not necessarily**

caused where they are pinpointed [Linnhoff, 1979]. It is thus necessary for a given irreversibility to be traced to its source so that irreversibilities are not credited to wrong sources.

5.3 Entropy Estimation

Entropy gains accompanying process operations is one of the well known ways of reporting the results of second law analysis of the process operations; irreversibility and availability are also used. Irreversibility accompanying a process is sometimes calculated using the entropy gains in the process operation since all irreversible processes are accompanied by entropy gain.

The non-readily availability of entropy data in the open literature has always made the completion of second law analysis of process operations tedious. Even entropy calculation or correlation routines are not common part of the physical property packages usually used in the flow-sheet balancing programs. This scarcity of entropy data and entropy correlation routine packages are probably due to the fact that second law analysis does not enjoy widespread utilisation. Looking at it the other way, the limited use of second law analysis could be attributed to lack of sufficient entropy data and/or entropy correlation routines needed to carry out this analysis. Whichever way we look at it the primary cause of the problem could be ascribed to the demand usually made for accurate entropy data or entropy correlation routines which for practical purposes is not very important for second law analysis; at least not as important as it is for

equipment sizing and specification in plant designs [Linnhoff, 1983].

The use of correlation equations to obtain the physical properties of process streams require accurate experimental data. The entropy data obtained from such correlation procedure are expected to be of high accuracy if the data used for correlation are of high quality. Apart from the experimental thermodynamic data the composition of the stream is required for this correlation procedure. One of such correlation routines developed by Mumah [1987, 1990] which was used to obtain many of the thermodynamic properties of ammonia-water mixtures used Chebyshev polynomials procedure. However this procedure can only be used to generate the needed thermophysical data if high quality experimental data are available. No such data is available for the streams of the compounds used in this project.

The approximation methods developed by Linnhoff [1979] to obtain the entropy data neither require the process stream composition data nor experimental entropy or other thermophysical data apart from the temperature and pressure which can be obtained relatively easily and the enthalpy data which can be easily calculated if not available. It is obvious, as it has been pointed out before, that this method is easier to use. However some simplifying assumptions were made in deriving the relationships. They include:

1. Mixing contribution to the entropy of a stream is neglected unless obviously important in the context of the process step.

2. Specific heat capacity of the stream is independent of temperature.

So from the following relationships:

$$dS = C_p/T\,dT \quad \text{..... 5.1a}$$

$$dH = C_p\,dT \quad \text{..... 5.1b}$$

and on the basis of the second assumption, integrating the equations, substituting and rearranging the terms give:

$$S_2 - S_1 = (H_2 - H_1)\ln(T_2/T_1)/(T_2-T_1) \quad \text{..... 5.1c}$$

It is seen, as stated by Linnhoff [1979] that "...the entropy change can be calculated directly from the results of first law analysis.." The good thing about this approach is that despite its simplicity and speed, a typical accuracy better than 1% has been reported [Flower and Linnhoff, 1979; Linnhoff and Carpenter, 1981].

Where pressure change of gases occur, by making the ideal gas assumption we have:

$$dS = (C_p/T)dT - (R/P)dP \quad \text{.....5.2}$$

$$S_2 - S_1 = (H_2 - H_1)\ln(T_2/T_1)/(T_2 -T_1) - R\ln P_2/P_1 \quad \text{....5.3}$$

A more detailed derivation of these equations is given by Townsend [1980].

5.4 Calculation of Irreversibility

Irreversibility in a system may be defined as the lost opportunity for performing work by that system. Thus any part of the expended energy that is not utilised to perform useful work is referred to as irreversibility. In other word, the component of energy that is not available for doing work is the lost energy called irreversibility.

Based on this definition, irreversibility can simply be represented by equation 5.5 below:

$$\Sigma Ex_{in} = \Sigma Ex_{out} + \Delta Ex_{irr} \quad \text{.....5.4}$$

$$\Delta Ex_{irr} = \Sigma Ex_{in} - \Sigma Ex_{out} \quad \text{..... 5.5}$$

where:

ΣEx_{in} = total exergy in

ΣEx_{out} = total exergy out

ΔEx_{irr} = irreversibility

As pointed out by Linnhoff and Carpenter [1981], this equation has three problems, viz:

1. The calculation of the terms requires physical property data covering the full range of temperature and pressure between the operating and ambient conditions which may not be readily available.
2. Where the last two terms in equation 5.5 are large numbers and the first term is comparatively small,

taking the difference of the last two terms could lead to considerable error.

3. The nature of the process is not easily understood from the equation.

These problems are taken care of by using what Linnhoff and Carpenter [1981] called the concept of exergy change (ΔEx) as shown in equation 5.6 below:

$$W_{in} - W_{out} + \Sigma(Ex_Q)_{in} - \Sigma(Ex_Q)_{out} - \Sigma\Delta Ex = \Delta E_{xirr} \quad ....5.6$$

where:

W - work done

Ex_Q - heat exergy

The exergy changes (ΔEx) can be calculated by shortcut methods shown in Equations 5.7-5.9 below [Linnhoff and Carpenter, 1981] as first derived by Linnhoff [1979] using heat and mass balance data only. For:

- T and P constant: $\Delta Ex = \Delta H(1 - T_o/T)$ 5.7

- P constant: $\Delta Ex = \Delta H(1 - T_o/T_{lm})$ 5.8

- H constant: $\Delta EX = nRT_o \ln P_2/P_1$ 5.9

where: T_{lm} =log mean temperature

Irreversibilities are sometimes better calculated from the first principle if the needed data are available. Some of the

definitions of irreversibility from the first principle are given below [Young, 1952; van Wylen & Sonntag, 1961] :

$$dI = \int_1^2 \left(\frac{T - T_0}{T}\right)\delta Q - (Wu_2 - Wu_1) - \Delta Ex \qquad \text{5.10a}$$

At constant pressure :

$$\delta Q = dH$$

$$\therefore dI = \int_1^2 \left(\frac{T - T_0}{T}\right)dH - \Delta Wu - \Delta Ex \qquad \text{5.10b}$$

Integrating, neglecting temperature dependence, we have :

$$I = \frac{T - T_0}{T}(H_2 - H_1) - (Wu_2 - Wu_1) - T_0(S_2 - S_1) \qquad \text{5.10c}$$

If no mechanical work is done Equation 5.11 below results from:

- Equation 5.10a under adiabatic condition (i.e. $\delta Q = 0$.)
- Equation 5.10 under isothermal condition (i.e. $dH = 0$.)

$$I = -\Delta Ex \quad \text{.....5.11}$$

For non-adiabatic process, when no work is done, Equation 5.10 becomes :

$$I = \left(\frac{T - T_0}{T}\right)\Delta H - \Delta Ex \quad \text{.....5.12}$$

For the purpose of easy estimation of irreversibility, Young [1952] has classified the various process equipment into two broad classes. These are:

- **Engine**: Turbine and compressor belong to this class. Equipment in this group carry out essentially adiabatic process and so **irreversibility** is calculated by substracting the **useful work** delivered by the system from the decrease in **exergy** (availability) of the process.
- **Heat Exchangers**: Useful work is negligible in this case. Two types could be identified.

- Type One:

  Two or more streams are mixed together in equipment in this group types. If exchanging of heat is expected to take place between the fluids of the streams, the process can be justifiably regarded as adiabatic if all streams are included in the system. So for the processes carried out by equipment in this category, **Irreversibility** is given by :

$$I = \Sigma m(\Delta Ex) \quad \text{.....5.12b}$$

where:

m is mass flow rate (or ratio) of streams

Ex is exergy of the process

- Type Two:

All streams are kept separate and heat is exchanged between these streams through surfaces such as the walls of tubes. Equation **5.12b** may be used again in this case provided the source and sink (of energy) are considered as a single system.

Where mixing is involved:

$$I = (\Delta H_{mix}(1 - \frac{T_0}{T}) - \Delta H_{mix}(1 - \frac{T_0}{T_{lm}})) + RT_0 m_{tot} \sum (x_R \ln(x_R \gamma_R)) \quad \text{.....5.13}$$

where:

ΔHmix is the heat of mixing

R is gas constant

m_{tot} is mass rate

Irreversibility in this case is the sum total of that due to heat transfer (represented by the first two terms on the right hand side of the equation) and that due to mixing.

Throttling process:

Equation 5.14a is based on the premise that the irreversibility in the throttling process is due to the friction experienced by the fluid at the obstacle in the valve. [Beek and Muttzall, 1983].

$$\int_1^2 \frac{m}{\rho} dP + g(h_2 - h_1) + \frac{1}{2}(v_2^2 - v_1^2) + \phi_A - E_{fr} = 0 \quad \text{.....5.14a}$$

In throttling process:

$h_2 = h_1$

$v_2 = v_1$

$\phi_A = 0.$

Thus equation 5.14a can be written as:

$$-\int_1^2 \frac{m}{\rho} dP = E_{fr} \quad \text{.....5.14b}$$

If ρ or $(1/V)$ is assumed to be independent of the pressure, equation 5.14b (noting that $E_{fr} = I$) becomes:

$$I = \frac{m}{\rho}(P_1 - P_2) \quad \text{.....5.14c}$$

where:

ρ = density of the fluid

P = pressure

v = velocity of fluid.

E_{rr} is the friction due to constriction.

$\dot{m}$ is mass flow rate

ϕ_A is the added energy

V is the specific volume

The enthalpy data needed for the use of the short-cut method of Linnhoff [1979], Flower and Linnhoff [1979] and, Linnhoff and Carpenter [1981] are obtained from the solution of subroutine 'Enth' developed by Prausnitz et al [1980] based on the UNIQUAC model. The 'Enth' subprogram is capable of returning fairly accurate enthalpy data [Prausnitz et al, 1980]. It is not difficult to obtain fairly accurate data for either the specific volume or specific density that can be used in Equation 5.14 above to calculate irreversibility in the throttling process

5.5 Modelling for Second Law Analysis

The coefficient of performance (COP) of the cycles described in Chapter 3 could be expressed in terms of the variable parameters such as the recirculation or reflux ratio (r), solvent-to-feed ratio (sfr), concentration of the strong aqueous ammonia solution (xst), concentration of the weak aqueous solution (xwk), composition (x or y) and enthalpy change (Δh) of the fluid in the system. The mathematical expression of this statement is given by Equation 15.5a.

$$COP = f(sfr, r, xst, xwk, x(y), \Delta h) \quad \text{..... 5.15a}$$

The mass flow rates of the streams (fm) are functions of the first five independent variables in Equation 5.15a. The enthalpy change and mass flow rates of the streams around the under-listed equipment are the basis of the models developed for COP calculation.

- Generator or Vaporiser
- Absorber
- Evaporator
- Condenser
- Rectifier

The enthalpy (h) of the streams are returned from subroutine 'Enth' based on UNIQUAC model (see Appendix E) developed by Prausnitz et al [1979]. The flow rates of the streams are expressed relative to that of the working fluid which, figuratively, is given as the concentration gradient of the working fluid pair mixture (i.e. xst-xwk). The mass flow rate of the working fluid is given a value of 1.0. Thus all enthalpy changes across any equipment is expressed as **xkJ/kg working fluid.**

The models for calculation of COP, in the cooling and heating modes, of the conventional absorption heat pump and the extraction-system-attached (ESA) absorption heat pump cycles are given below.

5.5.1 Conventional ammonia-water absorption heat pump

The subscripts used in the following expressions correspond to the parametric labels shown in Figure 1.3.

(a) **Mass flow rates**

fm1 = 1.0 + r

fm2 = fm2a = fm3 = 1.0

fm5 =fm6 = fm7 = 1.0/(xst-xwk)

fm4 = fm4a = fm8 = fm7 - 1.0

fm9 = ((xst-xwk)/(yamv-xwk)) * fm6

fm9a = fm9 - 1.0

$$yamv = \frac{y(2) * mw(2)}{y(2) * mw(2) + y(3) * mw(3)} \quad \text{.....5.15b}$$

(b) **Enthalpy change/unit mass of working fluid** across:

- Evaporator is given as:

$$Q_{ev} = fm3 * h3 - fm2 * h2a \quad \text{..... 5.16a}$$

Substituting appropriate mass flow expressions in Equation (5.16a) and rearranging, we have:

$$Q_{ev} = h3 - h2a \quad \text{..... 5.16b}$$

- Absorber is given as:

$$Q_{AB} = fm5 * h5 - (fm3 * h3 + fm4 * h4 + hmx) \quad \text{..... 5.17a}$$

$$hmx = fm5 * (h4d - h5) \quad \text{..... 5.17b}$$

Substituting Equation (5.17b) and appropriate mass flow expressions in Equation (5.17a) and rearranging, we have:

$$Q_{REC} = \frac{(yamv - xwk)(h1 - h10 + r(h1 - h2)) + h10 - h9}{yamv - xwk} \quad \text{.....5.20b}$$

(c) Coefficient of Performance (COP)

Models for COP in the heating and cooling modes are given below:

- COP in the cooling mode

$COP_{CCV} = Q_{EV}/Q_{GEN}$ 5.21a

Subetituting Equations (5.16b) and (5.18b) in Equation (5.21a) and rearranging, we have:

$$COP_{CCV} = \frac{(xst - xwk)(yamv - xwk)(h3 - h2a)}{(xst-xwk)(yamv-xwk)(h10-h8)+(yamv-xwk)(h8-h7)+(xst-xwk)(h9-h10)} \quad \text{.5.21b}$$

- COP in the heating mode

$$COP_{HCV} = \frac{Q_{AB} + Q_{CON} + Q_{REC}}{Q_{GEN}} \quad \text{.....5.22a}$$

Substituting Equations (5.17b), (5.18b), (5.19b) and 5.20b) in Equation (5.22a) and rearranging, we have:

$$COP_{HCV} = \frac{(xst-xwk)(yamv-xwk)(h4-h3+h2)-(r+1)h1-h10+r(h1-h2)}{(xst-xwk)(yamv-xwk)(h8+h10)+(xst-xwk)(h9-h8)+(yamv-xwk)(h8-h7)}$$

$$+ \frac{(yamv-xwk)(2h5-h4d-h4)+(xst-xwk)(h10-h9)}{(xst-xwk)(yamv-xwk)(h8+h10)+(xst-xwk)(h9-h8)+(yamv-xwk)(h8-h7)} \quad \text{.....5.22b}$$

5.5.2 ESA-absorption heat pump

Two sets of models are applicable for these derived absorption heat pump systems depending on whether or not rectification process is included in the cycle of the heat pump. The subscripts identifying the mass flow rates of various streams correspond to the parametric labels indicated in Figures 3.3a, 3.3b, 3.4a and 3.4b.

(a) **Mass flow rates**

```
fm1  =  1.0 + r
fm2a  =  fm3  =  1.0
fm5  =  1.0/(xst -xwk)
fm4  =  fm5 - 1.0
fm10  =  r
fm8  =  fm8a  =  fm8b  =  (sfr * saw)/(xst - xwk)
fm7  =  fm8 + fm1
fm9  =(fm - faw)fm7/rf
fm9a  =  fm9 - fm1
```

Some definitions:

```
xst  =  cst1/100
xwk  =  cwk1/100
faw  =  xw(2)*mw(2)/(xw(2)*mw(2) + xw(3)*mw(3))
```

saw = (sfr * faw)/(1.0 - r)

fm = 1.0 - sfr/((r+1.0)(xst-xwk)+sfr+saw)

rf = (yamv-faw)/(1.0-r)

(b) Enthalpy change/(unit mass working fluid) across:

- Evaporator is given as:

$$Q_{EV} = fm3 * h3 - fm2 * h2a \quad \text{..... 5.23a}$$

Substituting appropriate mass flow expressions in Equation (5.16a) and rearranging, we have:

$$Q_{REV} = h3 - h2a \quad \text{..... 5.23b}$$

- Condenseer is given as:

$$Q_{CON} = fm1(h2 - h1) \quad \text{..... 5.24a}$$

Substituting appropriate mass flow expressions in Equation (5.19a) and rearranging, we have:

$$Q_{CON} = (1.0 + r)(h2 - h1) \quad \text{..... 5.24b}$$

- Absorber is given as:

$$Q_{AB} = fm5 * h5 - (fm3 * h3 + fm4 * h4 + hmx) \quad \text{..... 5.25a}$$

Substituting Equation (5.17b) and appropriate mass flow expressions in Equation (5.17a) and rearranging, we have:

$$Q_{AB} = \frac{(h4 - h3 - hmx)(xst - xwk) + h5 - h4}{xst - xwk} \quad \text{.....5.25b}$$

- Vaporiser (where rectification is needed) is given as:

$$Q_{VAP} = fm8 * h8 + fm9 * h9 - fm9a * h9a - fm7 * h7 \quad \text{...} \quad 5.26a$$

$$Q_{VAP} = fm8(h8 - h7) + fm9(h9 - h9a) - (r+1)(h9a + h7). \quad 5.26b$$

Substituting appropriate mass flow expressions in Equation (5.26b) and rearranging, we have:

$$Q_{VAP} = \frac{(sfr + saw)(rf(h8 - h7)+(fm - faw)(h9 - h9a))}{xst - xwk}$$

$$- \frac{(r + 1)(xst - xwk)((fm - faw)(h9a - h9) - rf(h9a + h7))}{xst - xwk} \quad \text{.....5.26c}$$

- Vaporiser (where no rectification is needed) is given as:

$$Q_{VAP} = fm8 * h8 + fm1 * h1 - fm1 * h7a - fm7 * h7 \quad \text{....} \quad 5.27a$$

$$Q_{VAP} = fm1(h1 - h7 - h7a) + fm8(h8 - h7) \quad \text{.....} \quad 5.27b$$

Substituting appropriate mass flow expressions in Equation (5.27b) and rearranging, we have:

$$COP_{CESA} = \frac{(h3 - h2a)(xst - xwk)rf}{(sfr+saw)(rf(h8-h7)+(fm-faw)(h9-h9a))-(r+1)(xst-xwk)(cbm)} \quad \text{.....5.29b}$$

where:

cbm = (fm - faw)(h9a - h9) - rf(h9a - h7) 5.29c

- COP in the heating mode is given by:

COP_{HESA} = $(Q_{AB} + Q_{REC} + Q_{CON})/Q_{VAP}$ 5.30a

Substituting Equations (5.24b), (5.25b), (5.26b) and (5.28c) in Equation (5.30a) and rearranging, we have:

$$COP_{HESA} = \frac{rf(xst-xwk)(1+r)(h2-h9a)+(fm-faw)(h9a-h9)((xst-xwk)(1+r)+(sfr+saw))+b}{(fm-faw)(h9-h9a)((sfr+saw)-(r+1)(xst-xwk))+cf} \quad 5.30b$$

where:

b = rf((xst -xwk)(h4 - h3 - hmx) + h5 - h4) 5.30c

cf = rf((sfr+saw)(h8-h7)-(r+1)(xst-xwk)(h9a+h7) 5.30d

For systems incorporating no rectification:

- COP in the cooling mode

Substituting Equations (5.23b) and (5.27b) in Equation (5.29a) and rearranging, we have:

$$COP_{CESA} = \frac{(xst - xwk)(h3 - h2a)}{(xst-xwk)(r+1)(h1-h7a-h7)+(sfr+saw)(h8-h7)} \quad .....5.31$$

- COP in the heating mode

Substituting Equations (5.24b), (5.25b) and (5.27c) in Equation (5.30a), noting that Q_{REC} = 0.0 ,and rearranging, we have:

$$COP_{HESA} = \frac{xst-xwk)(h4-h3-hmx)+h5+h4+9r+1)(h2-h1)(xst-xwk)}{(r+1)(h1+h7a-h7)(xst-xwk)+(sfr+saw)(h8-h7)} \quad .....5.32$$

The entropy change, enthalpy change and irreversibility were calculated while carrying out the second law analyses on some of the thermodynamic cycles of heat pump developed in Chapter 3. These cycles are shown in Figures 1.3 and 3.3a to 3.4b. The listing of the fortran program used for the second law analysis including the subprogram 'Enth' is given in Appendix E.

CHAPTER SIX

6. RESULTS AND DISCUSSION

6.1 Simulation of Extraction Schemes

Results of the simulation of the extraction scheme showed that all the five ternary systems studied split into two layers at 25°C and 60°C at 1 atmosphere. The phase splitting is as expected from the binary solubility data of the streams. Table 6.1 gives a typical result of the simulation exercise while the UNIQUAC parameters used for the simulation are given in Table 6.2.

Table 6.1: **Liqui-liquid Equilibrium for a Three Component System at T= 333.15K**

INDEX	COMPONENT	FEED	R PHASE	E PHASE	R/E	EQUIL CONS
		======= mole fraction =====				
1	WATER	.1000	.7305	.0659		9.02E-02
2	AMMONIA	.1000	.2694	.0908	9.49E-01	3.37E-01
3	TOLUENE	.8000	.0001	.8432		7.59E+03
1	WATER	.1000	.5602	.0594		1.06E-01
2	AMMONIA	.2000	.4389	.1789	9.19E-01	4.08E-01
3	TOLUENE	.7000	.0008	.7616		9.01E+02
1	WATER	.1000	.4259	.0541		1.27E-01
2	AMMONIA	.3000	.5711	.2618	8.77E-01	4.58E-01
3	TOLUENE	.6000	.0030	.6841		2.28E+02
1	WATER	.1000	.3204	.0492		1.54E-01
2	AMMONIA	.4000	.6722	.3373	8.13E-01	5.02E-01
3	TOLUENE	.5000	.0074	.6135		8.33E+01
1	WATER	.2000	.3355	.0498		1.49E-01
2	AMMONIA	.5000	.6580	.3250	4.74E-01	4.94E-01
3	TOLUENE	.3000	.0065	.6251		9.62E+01
1	WATER	.2000	.4113	.0534		1.30E-01
2	AMMONIA	.4000	.5853	.2715	5.90E-01	4.64E-01
3	TOLUENE	.4000	.0034	.6751		1.98E+02

1	WATER	.2000	.5065	.0574		1.13E-01
2	AMMONIA	.3000	.4921	.2106	6.82E-01	4.28E-01
3	TOLUENE	.5000	.0014	.1320		5.10E+02
1	WATER	.2000	.6249	.0618		9.90E-02
2	AMMONIA	.2000	.3746	.1432	7.55E-01	3.82E-01
3	TOLUENE	.6000	.0004	.7949		1.89E+03
1	WATER	.2000	.7748	.0677		8.74E-02
2	AMMONIA	.1000	.2251	.0712	8.13E-01	3.16E-01
3	TOLUENE	.7000	.0001	.8611		1.51E+04
1	WATER	.3000	.8073	.0691		8.56E-02
2	AMMONIA	.1000	.1927	.0578	6.87E-01	3.00E-01
3	TOLUENE	.6000	.0000	.8731		2.67E+04
1	WATER	.3000	.6721	.0636		9.47E-02
2	AMMONIA	.2000	.3277	.1189	6.12E-01	3.63E-01
3	TOLUENE	.5000	.0002	.8173		3.39E+03
1	WATER	.3000	.5639	.0595		1.06E-01
2	AMMONIA	.3000	.4353	.1768	5.23E-01	4.06E-01
3	TOLUENE	.4000	.0008	.7637		9.38E+02
1	WATER	.3000	.4755	.0561		1.18E-01
2	AMMONIA	.4000	.5226	.2296	4.18E-01	4.39E-01
3	TOLUENE	.3000	.0019	.7147		3.72E+02
1	WATER	.3000	.4031	.0530		1.32E-01
2	AMMONIA	.5000	.5932	.2767	2.95E-01	4.67E-01
3	TOLUENE	.2000	.0037	.6703		1.83E+03
1	WATER	.4000	.8321	.0702		8.43E-02
2	AMMONIA	.1000	.1679	.0482	5.67E-01	2.87E-01
3	TOLUENE	.5000	.0000	.8817		4.32E+04
1	WATER	.4000	.7087	.0651		9.18E-02
2	AMMONIA	.2000	.2912	.1011	4.80E-01	3.47E-01
3	TOLUENE	.4000	.0002	.8339		5.55E+03
1	WATER	.4000	.6085	.0612		1.01E-01
2	AMMONIA	.3000	.3910	.1521	3.81E-01	3.89E-01
3	TOLUENE	.3000	.0005	.7867		1.55E+03
1	WATER	.4000	.5253	.0581		1.11E-01
2	AMMONIA	.4000	.4735	.1992	2.68E-01	4.21E-01
3	TOLUENE	.2000	.0012	.7427		6.20E+02

COMPONENT 1	COMPONENT 2	UNIQUAC BINARY PARAMETERS A12	A21	TEMP.K
WATER	M-XYLENE	318.16	1504.56	298.15
WATER	ETHYLBENZENE	351.27	1473.84	298.15
WATER	TOLUENE	339.13	1552.37	298.15
WATER	TOLUENE	305.43	1378.76	333.15
WATER	NITROBENZENE	217.75	938.44	293.15
WATER	STYRENE	322.92	1339.23	293.15
AMMONIA	ETHYLBENZENE	154.77	519.13	273.15
AMMONIA	M-XYLENE	161.54	539.10	273.15
AMMONIA	STYRENE	152.73	383.01	253.15
AMMONIA	TOLUENE	179.04	449.27	253.15
AMMONIA	NITROBENZENE	642.52	-202.13	293.15
AMMONIA	O-XYLENE	150.60	541.16	273.15
WATER**	AMMONIA	202.57	-330.21	333.15

Figure 6.2: Uniquac Parameters estimated from Mutual Solubility and Infinite Dilution Activity Coefficient Data

LEGEND

** BINARY PARAMETERS OBTAINED FROM INFINITE DILUTION DATA

A12 PARAMETER OF COMPONENT 1 IN COMPONENT 2

A21 PARAMETER OF COMPONENT 2 IN COMPONENT 1

Having established that a given ternary system can separate into two layers, the adequacy of the extract (or raffinate) solvent was further investigated with the help of the capacity and selectivity diagrams. The results are discussed below.

6.1.1 Capacity diagram

The capacity of the solvent, at all solute concentrations lower than that in the feed, affects the degree of completeness of recovery of solute from the feed [Somekh, 1966]. The higher the value of the tangent to the curves from the origin, the more the capacity of the solvent for the solute and so also the stronger the bond between the two.

The solvent desired should have adequate capacity for ammonia to ensure a high degree of extraction but the bond between the solvent and ammonia should not be too high so as not to make the recovery of solvent from the extract too difficult. Therefore the value of the tangent (to the curve) from the origin should not be too far from unity. On this basis, curves C,D and E in Figure 4.1 are the desirable ones .

On examining the curves of Figures 6.1 to 6.5 only nitrobenzene seems capable, on the basis advanced by Somekh[1966], of extracting all the ammonia from the ammonia-water mixture as its capacity diagram (Figure 6.1) is the only one comparable to curve A of Figure 4.1 (value of the tangent is greater than 1.0). The other four solvents studied, viz: ethylbenzene, m-xylene, styrene and toluene may not be capable of extracting ammonia completely from the ammonia-water mixture at 60°C, going by the low value of the tangents to the curves (Figures 6.2-6.5) that appear similar to curve F of Figure 4.1.

6.1.2 Selectivity diagram

A high concentration of raffinate solvent in the extract is not desirable either because of the resulting low purity of the solute or because of low yield of raffinate. Therefore the nature of the solvent and the extraction conditions should be such that the system is selective. The selectivity and purity relationships for a given liquid-liquid system can be obtained using selectivity graph.

It is desirable that ammonia is obtained as pure solute using the minimum number of extraction stage. This is possible if the values of the tangent to the curves is far greater than unity and, the curve starts at the origin and terminates at the points with co-ordinates of (1,1). The fulfilment of the latter condition is an indication of the possibility of obtaining pure solute, very easily, by extraction while the high tangent value ensures that less number of stages would be required for the process.

The shape of the selectivity diagrams obtained for the ternary systems involving ammonia, water and each of the five solvents mentioned earlier (see Figures 6.6 to 6.10) seem to suggest that high solute purity is achievable by extract refluxing [Somekh, 1966] but more extraction stages would be required for the systems having m-xylene, styrene, toluene and ethylbenzene as the extracting solvents than one using nitrobenzene.

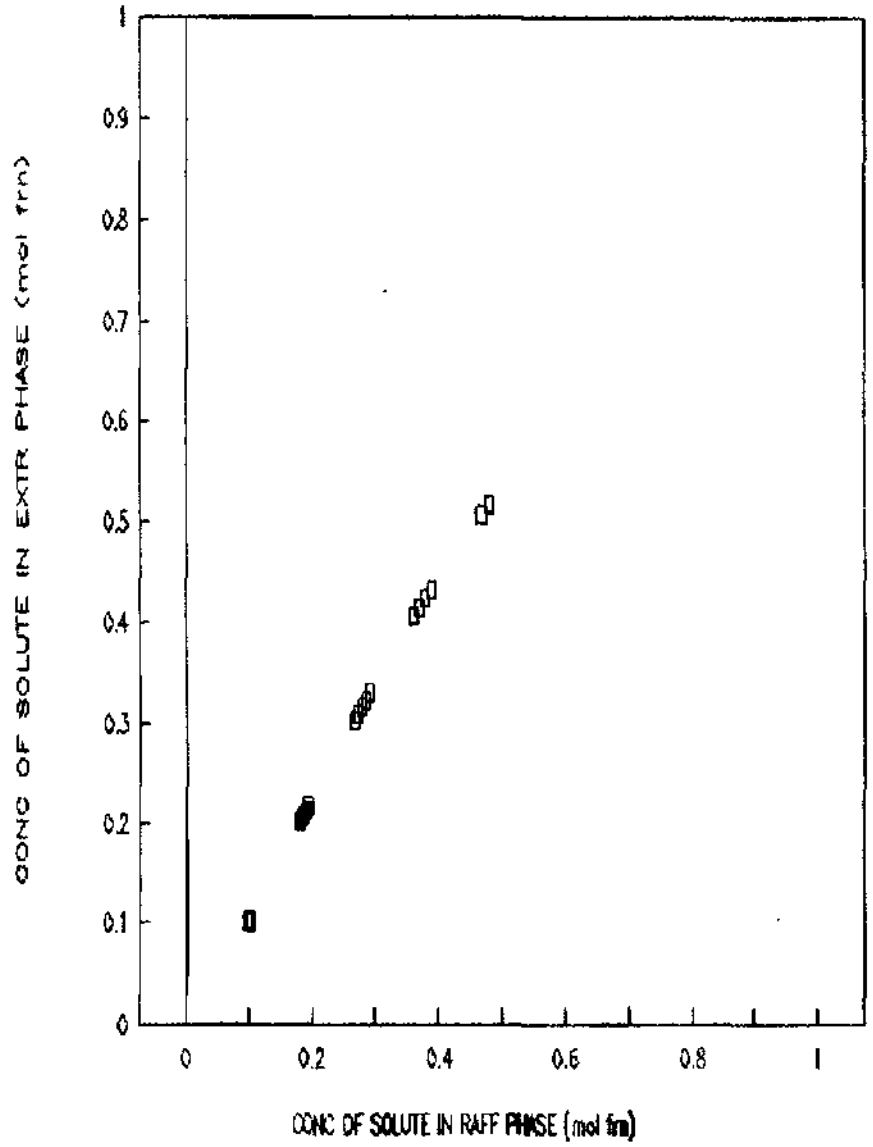


Figure 6.1: Capacity Diagram of Ammonia-Water-Nitrobenzene System at 60°C

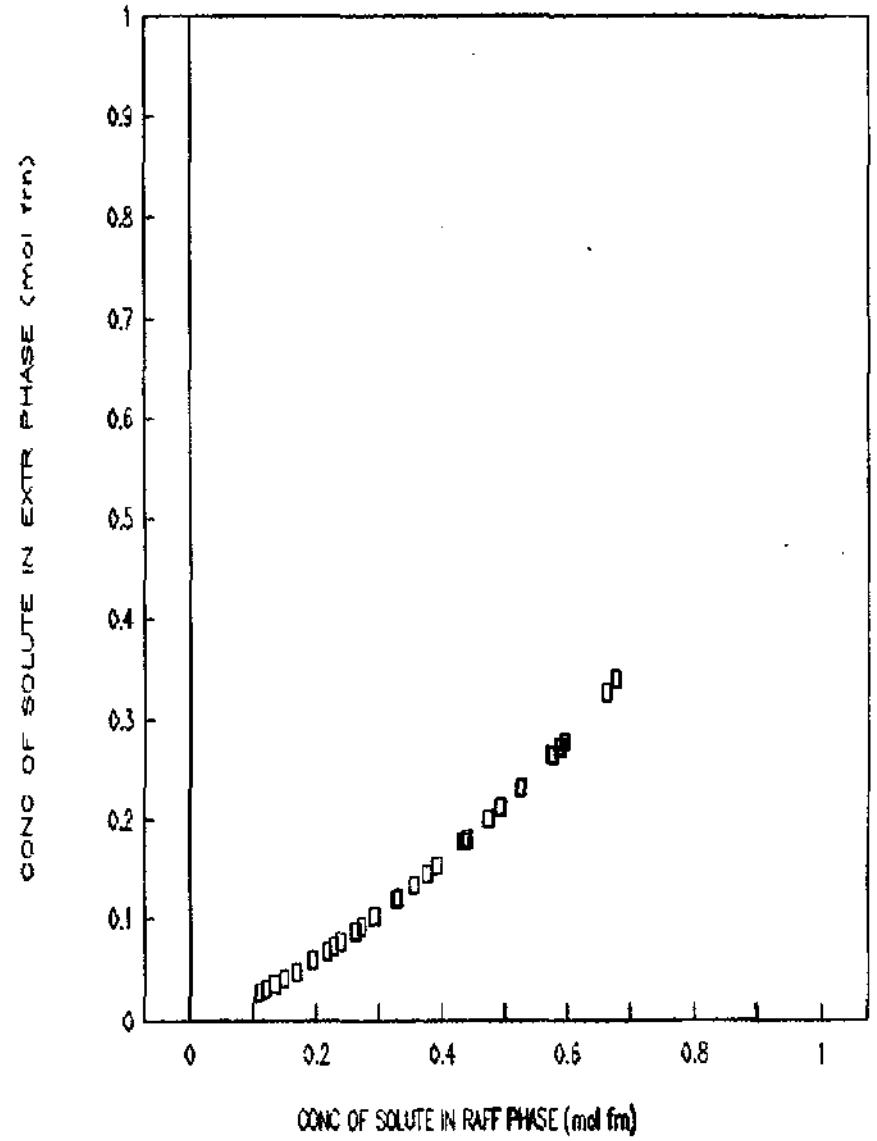


Figure 6.2: Capacity Diagram of Ammonia-Water-Toluene System at 60°C

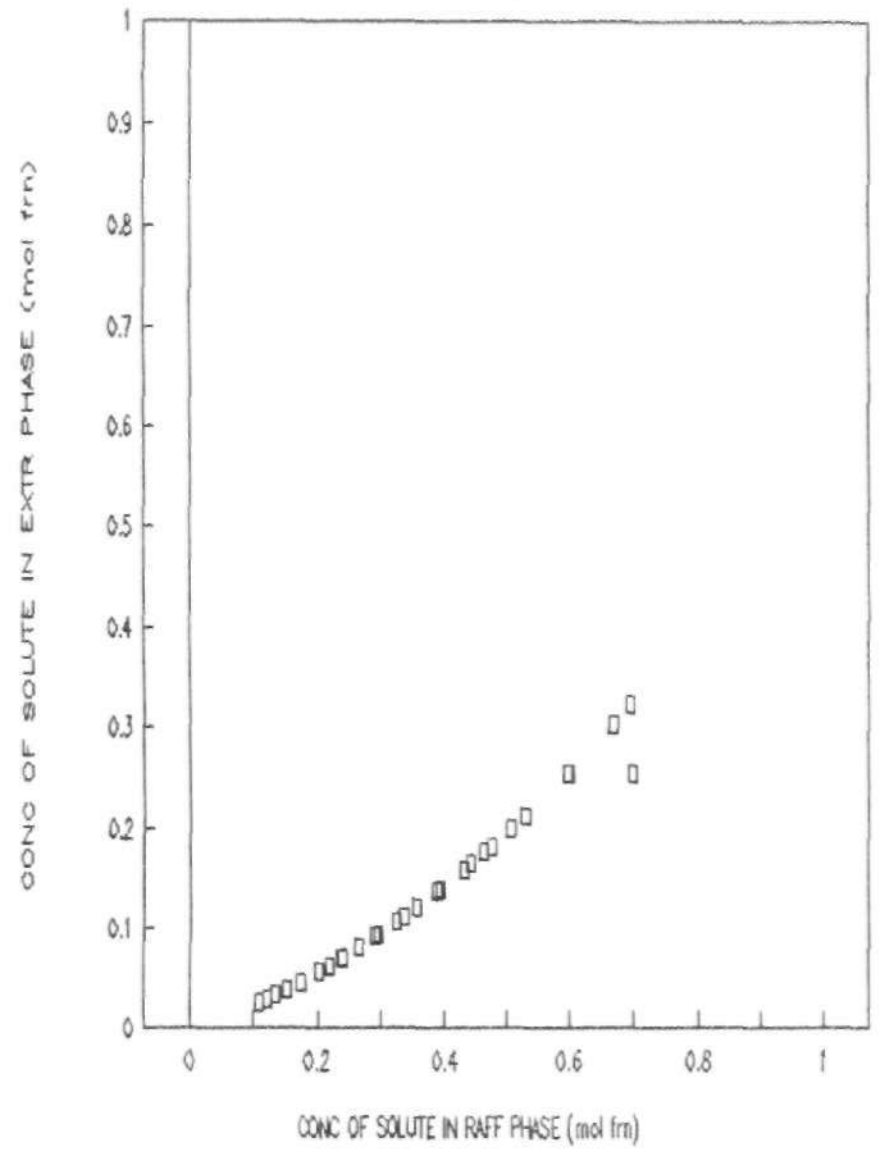


Figure 6.3: Capacity Diagram of Ammonia-Water-m-xylene System at 60°C

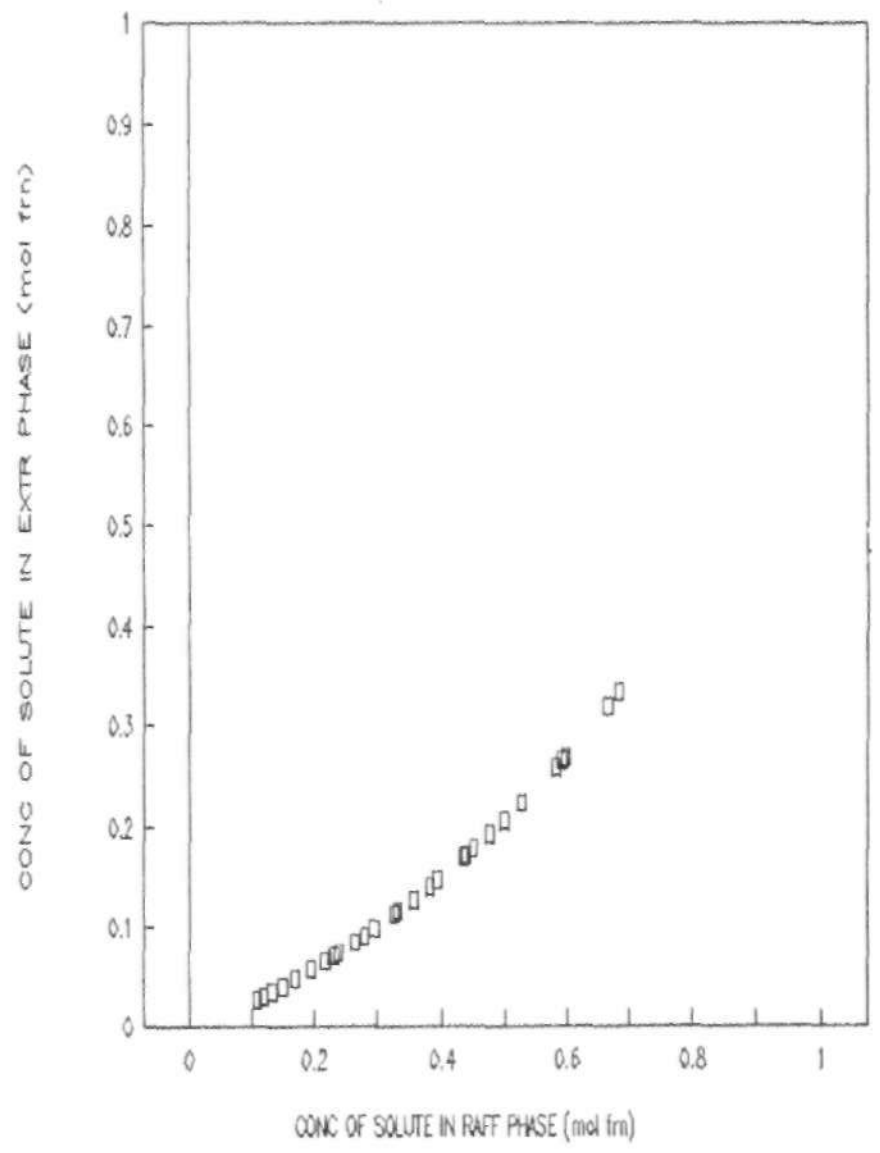


Figure 6.4: Capacity Diagram of Ammonia-Water-Ethylbenzene System at 60°C

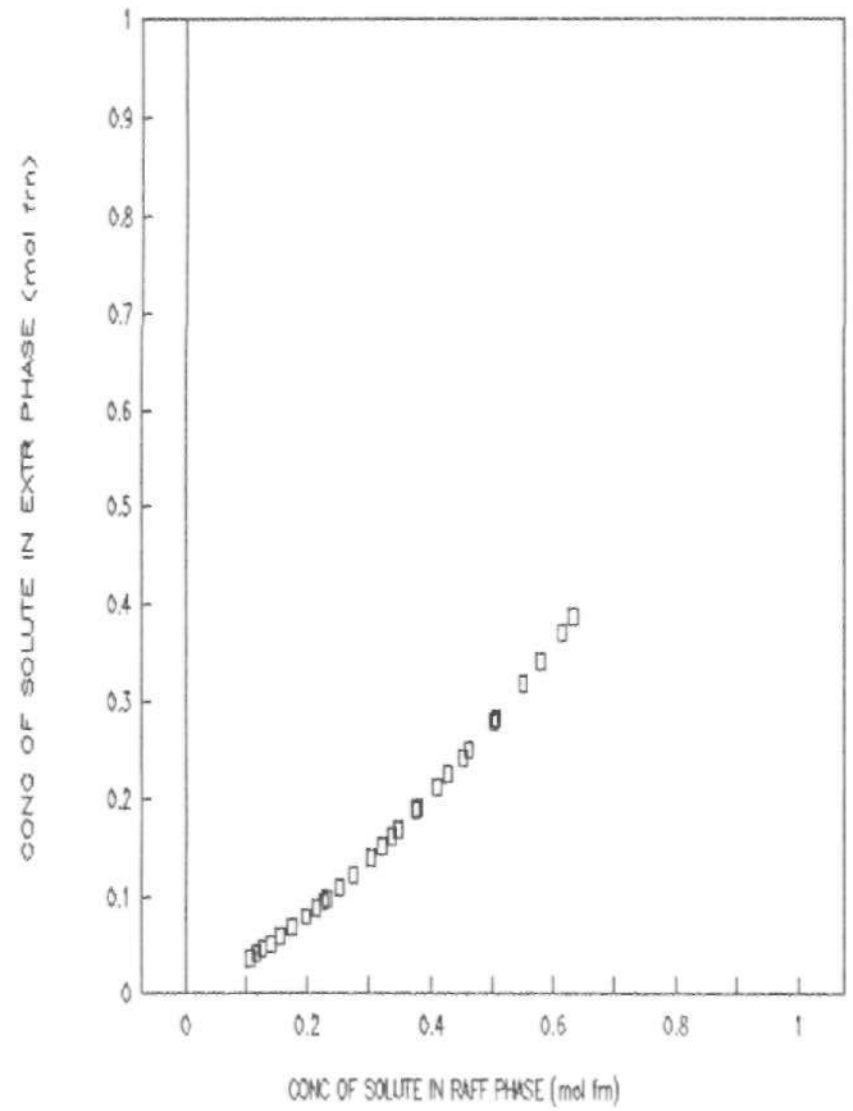


Figure 6.5: Capacity Diagram of Ammonia-Water-Styrene System at 60°C

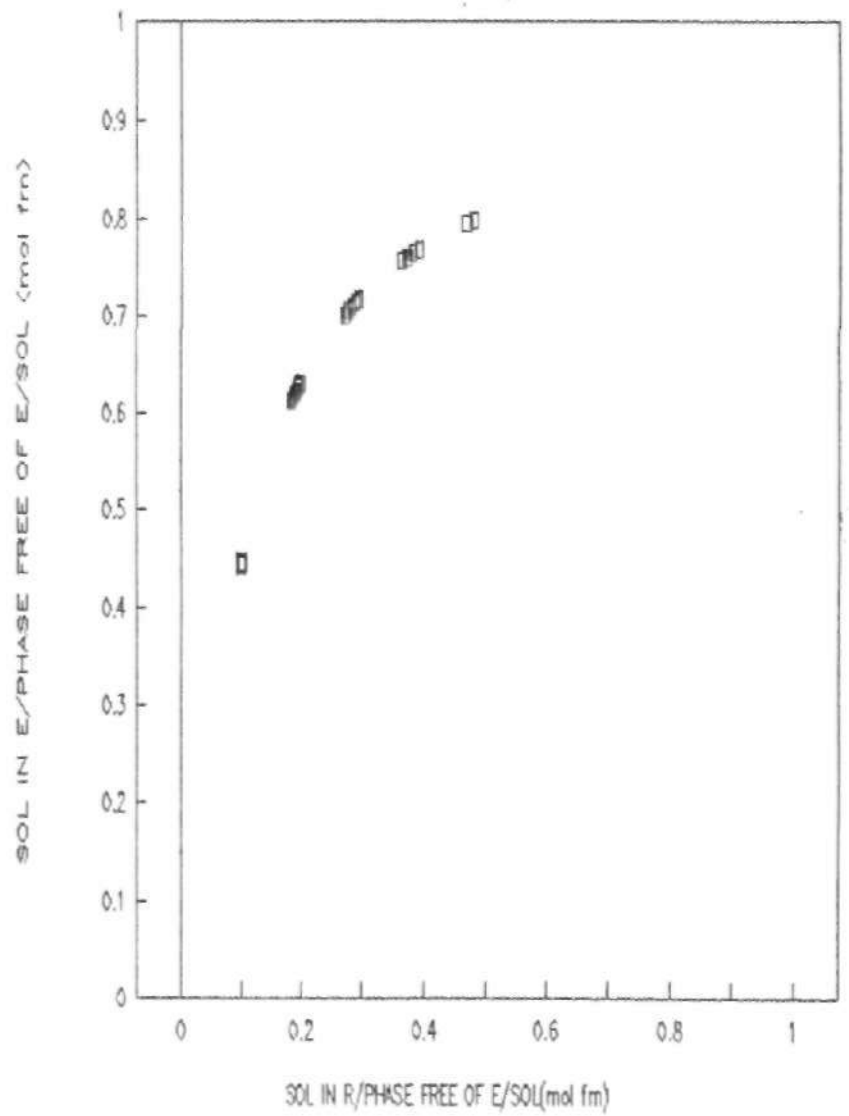


Figure 6.6: Selectivity Diagram of Ammonia-Water-Nitrobenzene System at 60°C

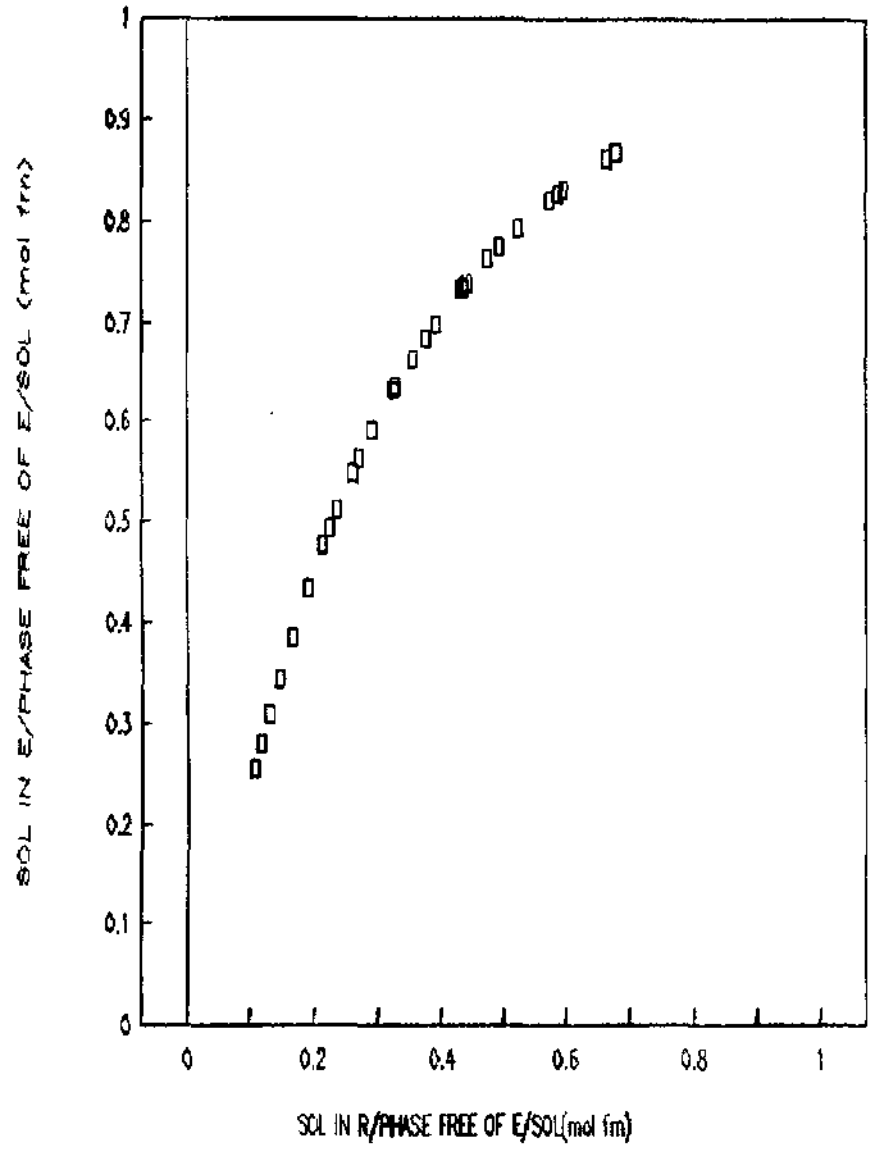


Figure 6.7: Selectivity Diagram of Ammonia-Water-Toluene System at 60°C

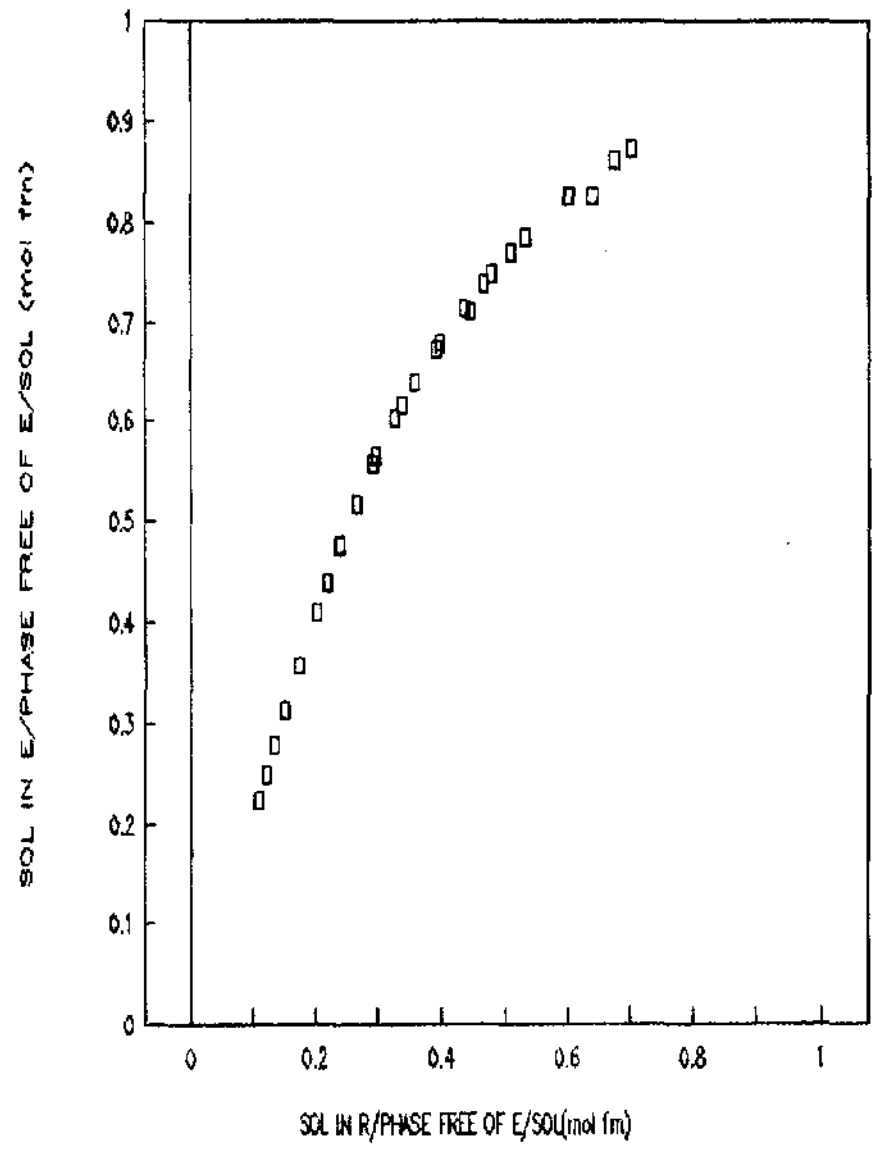


Figure 6.8: Selectivity Diagram of Ammonia-Water-m-xylene System at 60°C

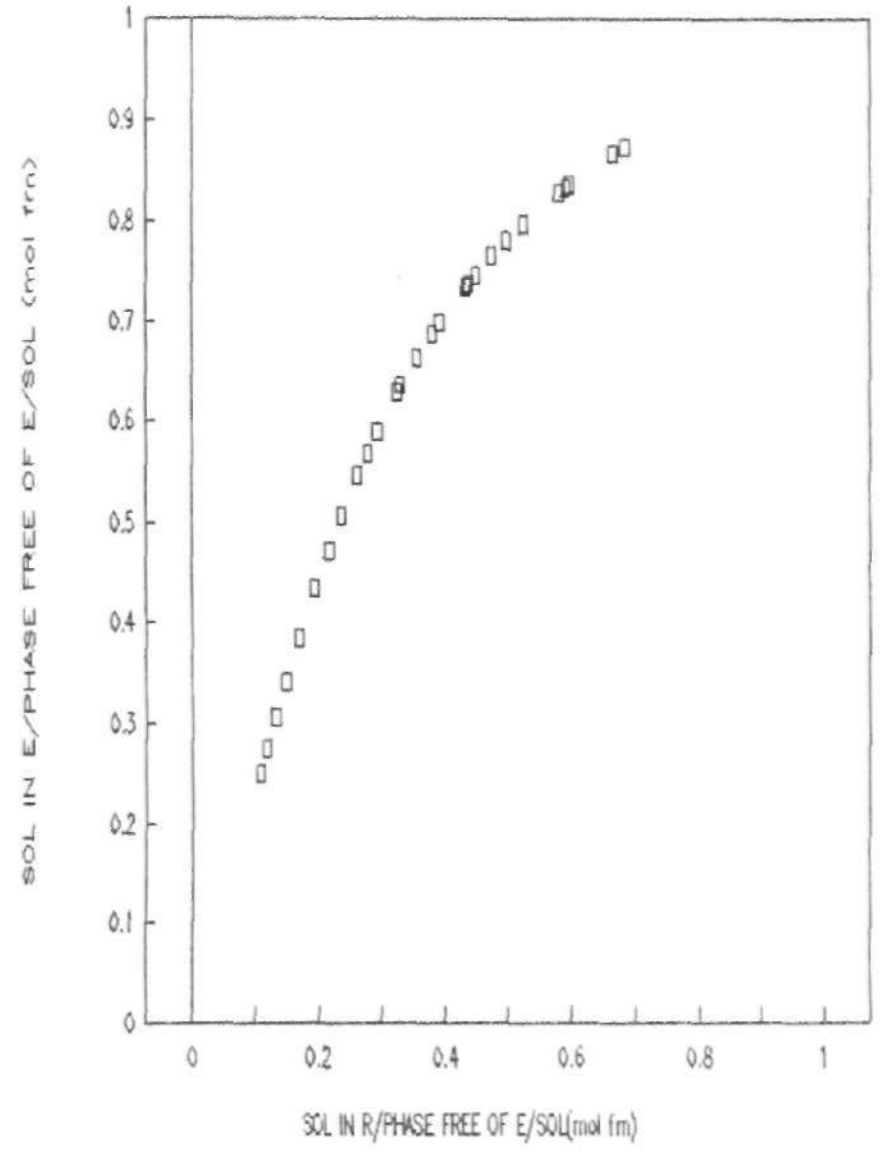


Figure 6.9: Selectivity Diagram of Ammonia-Water-Ethylbenzene System at 60°C

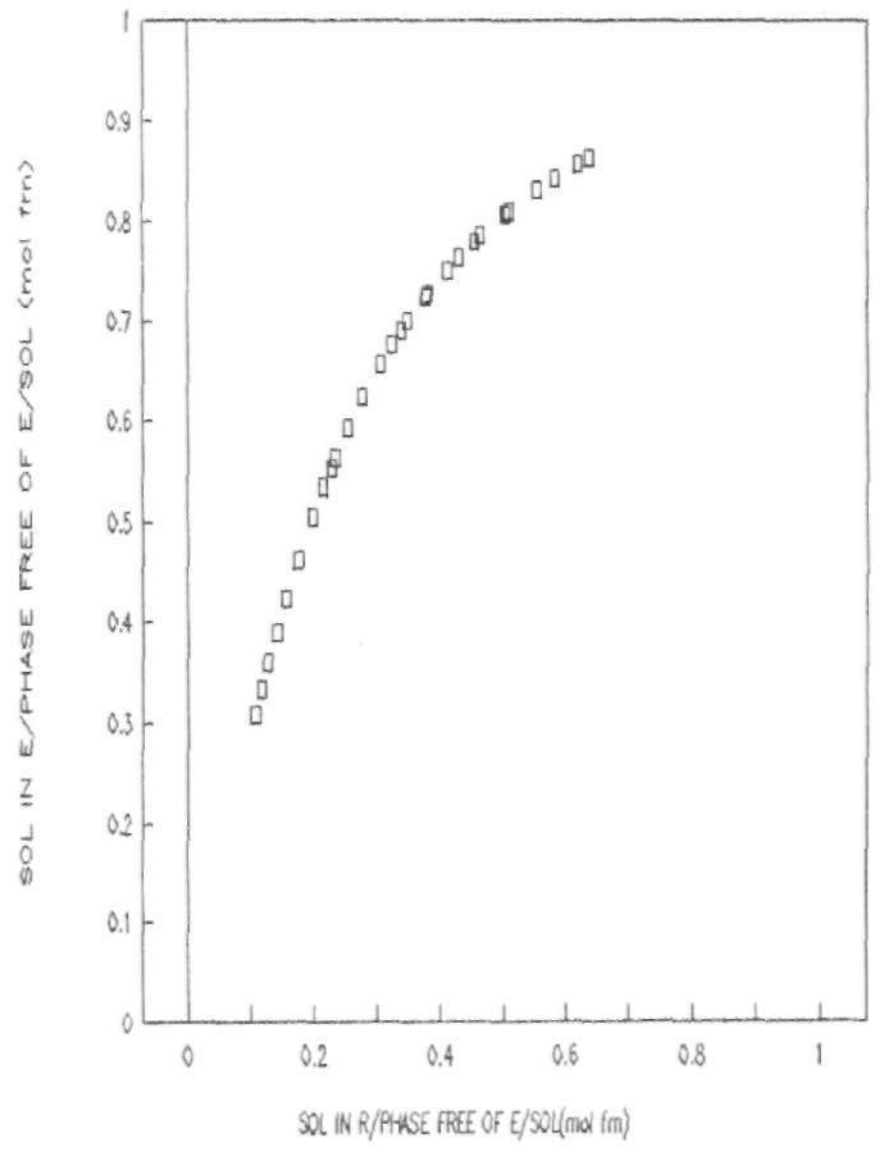


Figure 6.10: Selectivity Diagram of Ammonia-Water-Styrene System at 60°C

6.1.3 Binodal curves

The two plots (Capacity and Selectivity diagrams) can be combined together to obtain characteristic binodal curves on triangular co-ordinates for the ternary systems. The binodal curves based on the capacity and selectivity charts of the ternary systems formed by the aqua ammonia and each of the five selected solvents (which are given in Figures 6.1- 6.10) are presented in Figures 6.11 and 6.12.

The following observations (could be made) and inferences could drawn from the shape of the curve in Figure 6.11:

- Mutual solubility area of solvents very small. This implies than high purity solute can be obtained in the extract phase.
- The position of plait point is towards the raffinate solvent corner, making the tie-lines to form acute angles with the raffinate solvent corner. This implies that the number of stages required to extract all solute is not too many, i.e. the solvent has high capacity for the solute.

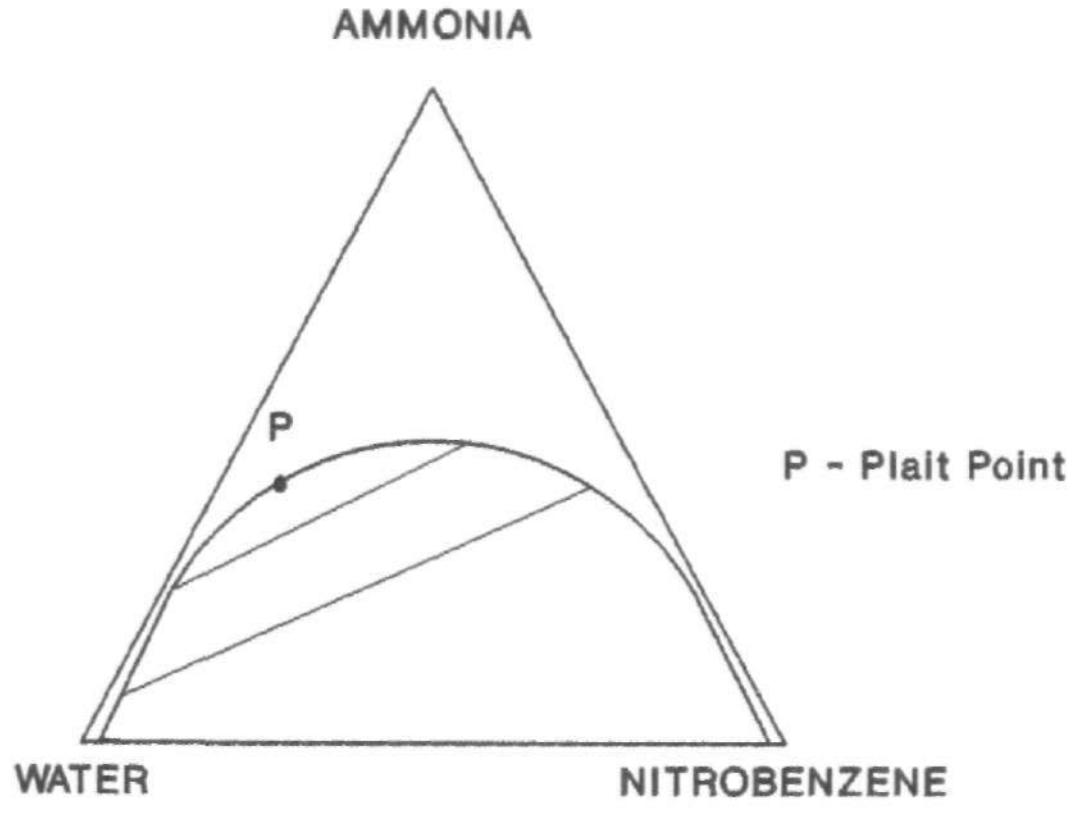


Figure 6.11: Binodal Curve Depicting Ammonia-Water-Nitrobenzene System Based on its Selectivity and Capacity Charts

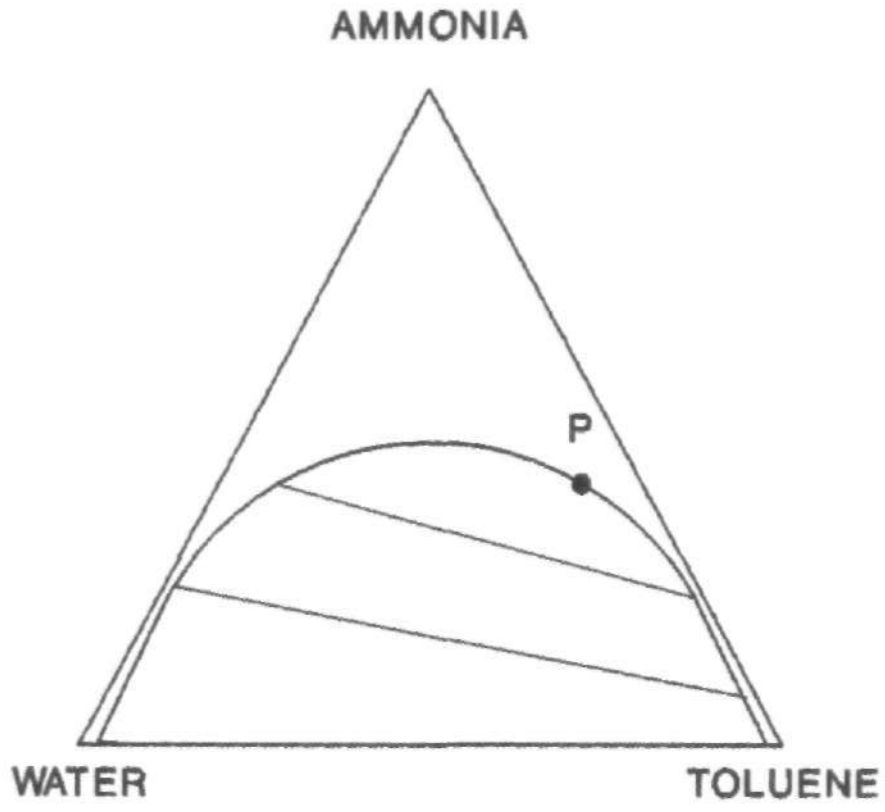


Figure 6.12: Binodal Curve depicting Ammonia-Water-Toluene System Based on its Selectivity and Capacity Charts

The curve shown in Figure 6.12 represents the general shape for ternary systems formed individually between aqua ammonia and the following solvents : m-xylene, styrene, toluene and ethylbenzene, though only toluene is indicated on the diagram. Observations and inferences that can be drawn from the shape of this curve are itemised below:

- Mutual solubility of solvents are very small. The inference is the same as for Figure 6.11.
- The position of plait point is towards the extract solvent corner making the tie-lines to form acute angles with the extract solvent edge. This implies that more extraction stages are required to recover the solute from the raffinate than that required for the system using nitrobenzene, every other thing being equal.

6.2 Simulation of Thermodynamic Cycles

Theoretical coefficient of performance (COP) and irreversibility values were obtained from the simulation of the conventional ammonia-water absorption heat pump and the modified forms of this system derived by introducing extraction process in the separation stage of the system (ESA). The results of these second law analyses for the conventional system are given in Tables 6.3 and 6.4 while those for the ESA systems are shown in Tables 6.5a to 6.14b. Recirculation ratio (R) values of 0.25 and 0.50 were used in the separation stages of the conventional and ESA systems. The values of the COP and irreversibility

obtained for these systems are discussed on the basis indicated below:

6.2.1 General comparison of the conventional and the extraction-step-attached (ESA) systems

The total irreversibility of the derived (ESA) systems were generally lower, than that of the conventional systems. Using weak aqueous ammonia solution concentration that ranged between 15% and 35% (by weight) and the strong solution concentration of 36% and 46% (by weight) at evaporator's temperatures of 268.15K and 273.15K, a maximum value of 1,283 kJ/kg (based on the working fluid) was obtained for the derived systems investigated while the highest value of irreversibility accompanying the processes of the conventional system was 2,231 kJ/kg. (based on the working fluid). The highest COP values in the cooling mode of 0.504 was obtained for the conventional system as against 0.743 for the ESA systems. Similarly, the modified systems gave higher COP values in the heating modes. This is obvious from the comparison of the results presented in Tables 6.3 and 6.4 and those in Tables 6.5a to 6.14b.

In the conventional system, the rectifier is the source of highest irreversibility. In contrast, only the absorber retains such characteristically high irreversibility values in the derived systems. Where the normal boiling points of the extracting solvent used in the derived systems is higher than 167^{o}C (e.g. nitrobenzene), it was observed that the rectifier unit and economizer could be omitted from the flow-chart of the systems. Lower irreversibility accompanied the vapour generation

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process (taking place in the vaporiser) in the derived systems than it did the same process (taking place in the generator) in the conventional system.

The relatively high irreversibility values credited to the generator and rectifier in the conventional ammonia-water absorption heat pump could be traced to the relatively high quantity of heat energy required to generate vapour from the aqueous solution of ammonia in the conventional system compared to the requirements for the same duty in the ESA systems considered. A comparison of the heat capacity (at 25°C) and enthalpy of vaporisation (at boiling point) of water and the five selected solvents shows that water has the highest values for the two thermodynamic properties. Consequently to raise the temperature of water and vaporise it requires more heat (energy) input than it takes to perform similar tasks on any of the five organic solvents listed in chapter 4. Heat capacity value for water (at 25°C) is more than twice that of the solvent with the highest value. For vaporization enthalpy (at boiling point) the factor is more than five.

The higher the enthalpy of vaporisation of the constituents of a given mixture, the higher the temperature at which vapour of a specified composition is generated under a given condition. Given the same sink, the higher temperature at which vaporisation takes place results in higher temperature gradient during the heat transfer that take place in the generator (or vaporiser) and rectifier and so greater the irreversibility accompanying the processes. Thus vapour containing a given mass fraction of ammonia is generated at higher temperature from aqua ammonia than

vapour of similar ammonia composition from a mixture of ammonia and any of the five selected organic solvents. The higher the enthalpy of vaporisation and/or heat capacity of water or solvent the less the COP of the system incorporating any of these fluid since this means more heat (HGE) input for vapour generation.

Network interaction phenomenon is easily demonstrated by comparing the relative values of irreversibility accompanying rectification process in the conventional and derived systems. The conventional system requiring relatively high energy input for vapour generation has relatively high irreversibility resulting from rectification process. That the large value is due to the high HGE input required for vapour generation is obvious from the relatively low irreversibility values accompanying rectification process in the derived system where relatively low quantity of HGE are needed for vapour generation. Thus the irreversibility in the **rectifier** is **caused** at the **vaporiser** (**or generator**); this observation validates one of the themes put forward by Linnhoff which asserts that **irreversibility is not necessarily caused where it is pinpointed.**

That the COP and irreversibility values for the ESA systems are completely different from that of the conventional system is another validation of one of the themes referred to above which states that "**Replacement is not equivalent to alteration**". And as expected, alteration (of process and equipment) leads to changes in the composition of the streams and/or system's conditions. This alteration is responsible for the change in the COP and irreversibility values discussed above.

6.2.2 Comparison of derived systems using different solvents

As already stated five solvents which were found to possess the required thermophysical and solubility properties for use as extracting solvents and for which necessary data for computer simulation using UNIQUAC equation are available in the literature accessible to us during the course of this work are: **Ethylbenzene, m-xylene, styrene, toluene and nitrobenzene.**

The system employing nitrobenzene as the extracting solvent was found to have the lowest irreversibility values and the highest COP values in the cooling COP_C and heating COP_H modes. It was possible to dispense with the use of rectifier and economizer in these systems because, as a result of the difference between the normal boiling point of ammonia and nitrobenzene being higher than 200K, pure ammonia could be obtained from ammonia-nitrobenzene mixture, without rectification, by adjusting the pressure of the systems [Renz, 1978; Mumah, 1990]. Heat recovery from the solvent's stream going back to the extracting unit becomes unnecessary since there is little or no temperature gradient in the process stream as it moves from the vaporiser to the extractor and vice-versa, and so economizer is not needed.

The systems using ethylbenzene which has the lowest enthalpy of vaporisation value at normal boiling point out of all the other four selected solvents, have the highest COP values in the heating mode; systems employing m-xylene which has the lowest specific enthalpy value at about 25°C recorded the highest COP values in the cooling mode. Thus it was observed that COP_H increased with decreasing enthalpy of vaporisation of the

extracting solvent while COPc increased with decreasing specific enthalpy. It could be inferred that in the cooling mode heat capacity influences the quantity of heat required while in the heating mode both heat capacity and heat of vaporisation of the stream determines the amount of heat transferred but heat of vaporisation is the more important determining factor. The effect of network interaction is visible here as well. In this case, it is the change in the composition of the systems' streams that cause the difference in the values of COP and irreversibility accompanying the processes of the systems. The network interaction of this change in the composition of the systems' streams when different solvents are used in the ESA is reflected in the differences observed in the irreversibility and COP values of these systems under the same conditions.

6.2.3. Influence of the process parameters on the conventional and extraction-step attached systems

The process parameters investigated for the conventional ammonia-water absorption heat pump were recirculation ratio (R), evaporator temperature (TEV), ammonia concentration in the strong aqueous ammonia solution (XST) and ammonia concentration in the weak aqueous ammonia solution (XWK). For the derived systems the solvent-to-feed ratio (SFR) was also studied, in addition to the listed parameters.

It was generally observed that irreversibility increased with recirculation or reflux ratio and the concentrations of the weak aqueous ammonia solution and reduced with increasing concentration of strong solution and the concentration gradient

(XST - XWK). The COP in the cooling mode increased with the solvent-to- feed ratio and reflux ratio while the reverse is the case in the heating mode. Total irreversibility reduced, and COP increased, with increasing evaporator temperature (TEV) for a given solvent. Irreversibility values in the evaporator at 268.15K were higher than at 273.15K. The lowerr the ammonia concentration of the strong and weak aqueous solutions, the higher the irreversibility values in the absorber and, generally, the higher the COP values in the heating and cooling mode.

COP values in the systems using the same extracting solvent was essentially the same whether the extractor was located in the lower or higher pressure side of the heat pump system. Except for the irreversibility occurring at the expansion valves, there were no significant difference in the irreversibility values recorded for the different units of the two sets of ESA systems. Lower irreversibility accompanied the process of throttling the working fluid from the condenser into the evaporator for the systems where the extracting unit is placed in the high pressure side. This values decrease at higher TEV VALUES. The other throttling valve recorded higher irreversibility values for these systems.

The effect of **heat source** is seen when the irreversibility and COP values at the two different evaporator's temperatures are compared. The different values at the two evaporator's temperatures if other parameters and the streams' compositions are kept constant, validates one of the techno-economic themes on the choice of energy sources and sinks which implies that the selection of these sources has effects on the irreversibility

accompanying the operations of the system and thus the COP of the system. The effects of R, SFR, XST and XWK on the values of irreversibility and COPs are some of the manifestations of **network interaction** phenomena.

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
WATER HEAT CAP.-ca. 303K (kJ/kg.K) = 4.18
WATER HEAT OF VAP.-normal b.pt. (kJ/kg.)= 2255.32
BOILING POINTS DIFFERENCE (K) = 133.50

PARAMETERS			********** IRREVERSIBILITIES **********									***COPs***	
R	XST	XWK	EVAPR	ABSOR	GENER	EXVA1	ECONO	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
	%	%	========== kJ/kg ==========										
.25	36.0	15.0	44.77	446.00	148.32	4.22	79.71	976.42	9.53	7.79	1716.751	.414	1.264
.25	36.0	25.0	44.72	900.00	236.51	15.33	86.07	756.51	9.47	7.92	2056.523	.451	1.197
.25	46.0	15.0	44.71	299.00	104.56	2.58	58.13	981.60	9.44	8.04	1508.066	.427	1.299
.25	46.0	25.0	44.65	468.00	135.64	7.35	48.79	759.87	9.37	8.17	1481.846	.498	1.313
.25	46.0	35.0	44.59	937.00	220.59	22.40	55.74	933.10	9.29	8.28	2230.996	.446	1.189
.50	36.0	15.0	44.61	446.00	147.79	4.55	78.83	764.44	9.18	8.39	1503.798	.414	1.153
.50	36.0	25.0	44.54	901.00	236.51	16.47	84.81	527.11	9.07	8.50	1827.998	.453	1.075
.50	46.0	15.0	44.53	299.00	103.52	2.76	57.24	777.52	9.02	8.61	1302.195	.427	1.184
.50	46.0	25.0	44.44	468.00	134.93	7.84	47.75	536.51	8.87	8.71	1257.052	.502	1.180
.50	46.0	35.0	44.36	937.00	220.48	23.81	54.14	690.68	8.71	8.80	1987.980	.453	1.069

Table 6.3: Theoretical COP and Irreversibility in the Main Units of Conventional Ammonia-Water Heat Pump

EVAPORATOR TEMPERATURE (K)	= 273.15
ABSORBER TEMPERATURE (K)	= 303.15
EVAPORATOR PRESSURE (BAR)	= 4.32
CONDENSER PRESSURE (BAR)	= 11.76
WATER HEAT CAP.-ca. 303K (kJ/kg.K)	= 4.18
WATER HEAT OF VAP.-normal b.pt. (kJ/kg.)	= 2255.32
BOILING POINTS DIFFERENCE (K)	= 133.50

PARAMETERS			********** IRREVERSIBILITIES **********								***COPs***	
R	XST	XWK	EVAPR	ABSOR	GENER	EXVA1	ECONO	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
	%	%	========== kJ/kg ==========										
.25	36.0	15.0	22.13	456.00	148.32	3.83	79.71	976.42	9.53	7.07	1703.009	.417	1.267
.25	36.0	25.0	22.10	909.00	236.51	14.00	86.07	756.51	9.47	7.23	2040.890	.454	1.200
.25	46.0	15.0	22.10	308.00	104.56	2.37	58.13	981.60	9.44	7.38	1493.578	.430	1.302
.25	46.0	25.0	22.06	476.00	135.64	6.78	48.79	759.87	9.37	7.53	1466.049	.501	1.317
.25	46.0	35.0	22.03	944.00	220.59	20.76	55.74	933.10	9.29	7.67	2213.172	.449	1.192
.50	36.0	15.0	22.04	456.00	147.79	4.23	78.83	764.44	9.18	7.81	1490.320	.416	1.155
.50	36.0	25.0	21.99	909.00	236.51	15.38	84.81	527.11	9.07	7.94	1811.800	.456	1.078
.50	46.0	15.0	21.99	308.00	103.52	2.59	57.24	777.52	9.02	8.06	1287.938	.429	1.187
.50	46.0	25.0	21.94	476.00	134.93	7.37	47.75	536.51	8.87	8.18	1241.556	.504	1.183
.50	46.0	35.0	21.89	944.00	220.48	22.46	54.14	690.68	8.71	8.30	1970.654	.455	1.071

Table 6.4: Theoretical COP and Irreversibility in the Main Units of Conventional Ammonia-Water Heat Pump

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : NITROBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.42
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 331.16
BOILING POINT DIFFERENCE (K) = 244.30

SYSTEMS	PARAMETERS		IRREVERSIBILITIES kJ/kg								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
.75	.25	36.0	15.0	45.18	459.00	30.21	.00	6.68	.00	12.52	5.83	559.423	.740	1.624
.75	.25	36.0	25.0	45.18	922.00	55.43	.00	12.39	.00	12.52	5.61	1053.132	.732	1.313
.75	.25	46.0	15.0	45.18	308.00	18.91	.00	4.66	.00	12.52	5.39	394.657	.748	1.721
.75	.25	46.0	25.0	45.18	480.00	26.83	.00	6.68	.00	12.52	5.18	576.397	.740	1.619
.75	.25	46.0	35.0	45.18	957.00	49.24	.00	12.39	.00	12.52	4.98	1081.313	.732	1.329
.75	.50	36.0	15.0	45.18	459.00	24.79	.00	6.76	.00	15.03	5.75	556.509	.733	1.631
.75	.50	36.0	25.0	45.18	922.00	45.50	.00	12.47	.00	15.03	5.52	1045.701	.721	1.360
.75	.50	46.0	15.0	45.18	308.00	15.52	.00	4.74	.00	15.03	5.31	393.774	.745	1.729
.75	.50	46.0	25.0	45.18	480.00	22.02	.00	6.76	.00	15.03	5.10	574.097	.740	1.670
.75	.50	46.0	35.0	45.18	957.00	40.42	.00	12.47	.00	15.03	4.91	1075.001	.721	1.319
1.50	.25	36.0	15.0	45.18	459.00	40.70	.00	12.96	.00	12.52	3.93	574.295	.728	1.716
1.50	.25	36.0	25.0	45.18	922.00	74.69	.00	24.38	.00	12.52	3.78	1082.552	.720	1.244
1.50	.25	46.0	15.0	45.18	308.00	25.48	.00	8.91	.00	12.52	3.63	403.722	.740	1.542
1.50	.25	46.0	25.0	45.18	480.00	36.15	.00	12.96	.00	12.52	3.49	590.309	.730	1.293
1.50	.25	46.0	35.0	45.18	957.00	66.35	.00	24.38	.00	12.52	3.36	1108.785	.720	1.182
1.50	.50	36.0	15.0	45.18	459.00	33.41	.00	13.04	.00	15.03	3.87	569.529	.728	1.342
1.50	.50	36.0	25.0	45.18	922.00	61.31	.00	24.46	.00	15.03	3.72	1071.697	.718	1.434
1.50	.50	46.0	15.0	45.18	308.00	20.91	.00	8.99	.00	15.03	3.58	401.688	.740	1.651
1.50	.50	46.0	25.0	45.18	480.00	29.68	.00	13.04	.00	15.03	3.44	586.364	.720	1.362
1.50	.50	46.0	35.0	45.18	957.00	54.46	.00	24.46	.00	15.03	3.31	1099.432	.718	1.373

Table 6.5a: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section**

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : NITROBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.42
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 331.16
BOILING POINT DIFFERENCE (K) = 244.30

SYSTEMS		PARAMETERS		IRREVERSIBILITIES kJ/kg									COPs	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
.75	.25	36.0	15.0	45.18	459.00	25.14	.00	6.68	.00	12.52	4.67	553.195	.740	1.624
.75	.25	36.0	25.0	45.18	922.00	43.98	.00	12.39	.00	12.52	4.49	1040.555	.732	1.313
.75	.25	46.0	15.0	45.18	308.00	15.74	.00	4.66	.00	12.52	4.31	390.411	.748	1.721
.75	.25	46.0	25.0	45.18	480.00	21.29	.00	6.68	.00	12.52	4.15	569.816	.740	1.619
.75	.25	46.0	35.0	45.18	957.00	37.14	.00	12.39	.00	12.52	3.99	1068.218	.732	1.329
.75	.50	36.0	15.0	45.18	459.00	20.64	.00	6.76	.00	15.03	3.83	550.440	.733	1.631
.75	.50	36.0	25.0	45.18	922.00	36.10	.00	12.47	.00	15.03	3.68	1034.460	.721	1.360
.75	.50	46.0	15.0	45.18	308.00	12.92	.00	4.74	.00	15.03	3.54	389.404	.745	1.729
.75	.50	46.0	25.0	45.18	480.00	17.47	.00	6.76	.00	15.03	3.40	567.847	.740	1.670
.75	.50	46.0	35.0	45.18	957.00	30.49	.00	12.47	.00	15.03	3.27	1063.440	.721	1.319
1.50	.25	36.0	15.0	45.18	459.00	33.89	.00	12.96	.00	12.52	3.14	566.696	.728	1.328
1.50	.25	36.0	25.0	45.18	922.00	59.28	.00	24.38	.00	12.52	3.02	1066.378	.720	1.244
1.50	.25	46.0	15.0	45.18	308.00	21.22	.00	8.91	.00	12.52	2.91	398.733	.740	1.542
1.50	.25	46.0	25.0	45.18	480.00	28.69	.00	12.96	.00	12.52	2.79	582.151	.730	1.293
1.50	.25	46.0	35.0	45.18	957.00	50.07	.00	24.38	.00	12.52	2.69	1091.836	.720	1.182
1.50	.50	36.0	15.0	45.18	459.00	27.82	.00	13.04	.00	15.03	2.58	562.653	.728	1.342
1.50	.50	36.0	25.0	45.18	922.00	48.67	.00	24.46	.00	15.03	2.48	1057.817	.718	1.434
1.50	.50	46.0	15.0	45.18	308.00	17.42	.00	8.99	.00	15.03	2.39	397.002	.740	1.651
1.50	.50	46.0	25.0	45.18	480.00	23.56	.00	13.04	.00	15.03	2.29	579.104	.720	1.362
1.50	.50	46.0	35.0	45.18	957.00	41.12	.00	24.46	.00	15.03	2.20	1084.992	.718	1.373

Table 6.5b: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section**

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : NITROBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.42
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 331.16
BOILING POINT DIFFERENCE (K) = 244.30

SYSTEMS		PARAMETERS		IRREVERSIBILITIES kJ/kg								***COPe***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
.75	.25	36.0	15.0	22.37	466.00	27.44	.00	6.68	.00	12.52	5.27	540.287	.745	1.625
.75	.25	36.0	25.0	22.37	926.00	50.36	.00	12.39	.00	12.52	5.06	1028.708	.734	1.316
.75	.25	46.0	15.0	22.37	315.00	17.18	.00	4.66	.00	12.52	4.87	376.598	.751	1.724
.75	.25	46.0	25.0	22.37	486.00	24.37	.00	6.68	.00	12.52	4.68	556.633	.742	1.620
.75	.25	46.0	35.0	22.37	960.00	44.73	.00	12.39	.00	12.52	4.50	1056.517	.734	1.310
.75	.50	36.0	15.0	22.37	466.00	22.52	.00	6.76	.00	15.03	5.19	537.877	.735	1.634
.75	.50	36.0	25.0	22.37	926.00	41.33	.00	12.47	.00	15.03	4.99	1022.195	.733	1.362
.75	.50	46.0	15.0	22.37	315.00	14.10	.00	4.74	.00	15.03	4.80	376.033	.750	1.730
.75	.50	46.0	25.0	22.37	486.00	20.01	.00	6.76	.00	15.03	4.61	554.781	.742	1.673
.75	.50	46.0	35.0	22.37	960.00	36.72	.00	12.47	.00	15.03	4.43	1051.020	.735	1.320
1.50	.25	36.0	15.0	22.37	466.00	36.98	.00	12.96	.00	12.52	3.55	554.383	.731	1.330
1.50	.25	36.0	25.0	22.37	926.00	67.86	.00	24.38	.00	12.52	3.41	1056.542	.727	1.251
1.50	.25	46.0	15.0	22.37	315.00	23.15	.00	8.91	.00	12.52	3.28	385.232	.741	1.533
1.50	.25	46.0	25.0	22.37	486.00	32.84	.00	12.96	.00	12.52	3.15	569.855	.733	1.300
1.50	.25	46.0	35.0	22.37	960.00	60.28	.00	24.38	.00	12.52	3.03	1082.580	.727	1.189
1.50	.50	36.0	15.0	22.37	466.00	30.35	.00	13.04	.00	15.03	3.50	550.290	.732	1.345
1.50	.50	36.0	25.0	22.37	926.00	55.70	.00	24.46	.00	15.03	3.36	1046.918	.724	1.441
1.50	.50	46.0	15.0	22.37	315.00	19.00	.00	8.99	.00	15.03	3.23	383.621	.742	1.654
1.50	.50	46.0	25.0	22.37	486.00	26.96	.00	13.04	.00	15.03	3.11	566.508	.737	1.367
1.50	.50	46.0	35.0	22.37	960.00	49.48	.00	24.46	.00	15.03	2.99	1074.320	.724	1.379

Table 6.6a: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : NITROBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.42
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 331.16
BOILING POINT DIFFERENCE (K) = 244.30

SYSTEMS SFR	R	PARAMETERS XST %	XWK %	IRREVERSIBILITIES EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR kJ/kg	COPc	COPh
.75	.25	36.0	15.0	22.37	466.00	22.84	.00	6.68	.00	12.52	4.22	534.635	.745	1.625
.75	.25	36.0	25.0	22.37	926.00	39.95	.00	12.39	.00	12.52	4.05	1017.290	.734	1.316
.75	.25	46.0	15.0	22.37	315.00	14.30	.00	4.66	.00	12.52	3.90	372.747	.751	1.724
.75	.25	46.0	25.0	22.37	486.00	19.34	.00	6.68	.00	12.52	3.74	550.661	.742	1.620
.75	.25	46.0	35.0	22.37	960.00	33.74	.00	12.39	.00	12.52	3.60	1044.628	.734	1.310
.75	.50	36.0	15.0	22.37	466.00	18.75	.00	6.76	.00	15.03	3.46	532.374	.735	1.634
.75	.50	36.0	25.0	22.37	926.00	32.80	.00	12.47	.00	15.03	3.33	1011.994	.733	1.632
.75	.50	46.0	15.0	22.37	315.00	11.74	.00	4.74	.00	15.03	3.20	372.073	.750	1.730
.75	.50	46.0	25.0	22.37	486.00	15.88	.00	6.76	.00	15.03	3.07	549.113	.742	1.623
.75	.50	46.0	35.0	22.37	960.00	27.70	.00	12.47	.00	15.03	2.95	1040.527	.735	1.320
1.50	.25	36.0	15.0	22.37	466.00	30.79	.00	12.96	.00	12.52	2.84	547.485	.731	1.330
1.50	.25	36.0	25.0	22.37	926.00	53.85	.00	24.38	.00	12.52	2.73	1041.856	.727	1.251
1.50	.25	46.0	15.0	22.37	315.00	19.27	.00	8.91	.00	12.52	2.62	380.705	.741	1.533
1.50	.25	46.0	25.0	22.37	486.00	26.07	.00	12.96	.00	12.52	2.52	562.449	.733	1.300
1.50	.25	46.0	35.0	22.37	960.00	45.49	.00	24.38	.00	12.52	2.43	1067.191	.727	1.189
1.50	.50	36.0	15.0	22.37	466.00	25.28	.00	13.04	.00	15.03	2.33	544.052	.732	1.345
1.50	.50	36.0	25.0	22.37	926.00	44.22	.00	24.46	.00	15.03	2.24	1034.319	.724	1.441
1.50	.50	46.0	15.0	22.37	315.00	15.83	.00	8.99	.00	15.03	2.15	379.372	.742	1.654
1.50	.50	46.0	25.0	22.37	486.00	21.41	.00	13.04	.00	15.03	2.07	559.921	.737	1.367
1.50	.50	46.0	35.0	22.37	960.00	37.36	.00	24.46	.00	15.03	1.99	1061.214	.724	1.379

Table 6.6b: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section**

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : TOLUENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.84
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 363.17
BOILING POINT DIFFERENCE (K) = 144.15

SYSTEMS	PARAMETERS			IRREVERSIBILITIES								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				kJ/kg										
.75	.25	36.0	15.0	45.18	459.00	24.93	8.79	51.32	26.50	12.31	5.83	633.865	.631	1.419
.75	.25	36.0	25.0	44.73	923.00	48.38	14.71	56.12	28.20	11.93	5.72	1132.783	.615	1.206
.75	.25	46.0	15.0	44.57	309.00	17.44	6.43	34.79	28.85	11.78	5.81	458.670	.640	1.474
.75	.25	46.0	25.0	44.53	481.00	26.12	8.61	42.04	28.37	11.72	5.90	648.306	.638	1.359
.75	.25	46.0	35.0	44.50	958.00	50.58	14.39	57.52	27.83	11.67	5.99	1170.470	.623	1.151
.75	.50	36.0	15.0	44.46	460.00	26.85	8.79	41.19	48.52	13.92	7.29	651.018	.496	1.331
.75	.50	36.0	25.0	44.42	923.00	51.90	14.54	55.56	47.30	13.83	7.39	1157.939	.490	1.167
.75	.50	46.0	15.0	44.37	309.00	18.64	6.35	31.80	45.84	13.74	7.48	477.207	.509	1.379
.75	.50	46.0	25.0	44.32	481.00	27.83	8.43	40.85	44.29	13.63	7.57	667.907	.512	1.290
.75	.50	46.0	35.0	44.26	958.00	53.70	13.91	57.55	42.53	13.50	7.65	1191.114	.507	1.125
1.50	.25	36.0	15.0	44.20	461.00	56.84	13.77	59.00	22.68	11.14	6.45	675.077	.657	1.392
1.50	.25	36.0	25.0	44.13	924.00	109.58	23.78	90.28	21.10	11.00	6.51	1230.385	.623	1.126
1.50	.25	46.0	15.0	44.04	309.00	39.25	9.47	45.81	19.44	10.83	6.58	484.421	.699	1.489
1.50	.25	46.0	25.0	43.93	482.00	58.45	12.74	58.90	17.66	10.62	6.64	690.948	.699	1.344
1.50	.25	46.0	35.0	43.81	958.00	112.54	21.83	92.21	15.66	10.38	6.70	1261.129	.667	1.069
1.50	.50	36.0	15.0	43.67	461.00	59.43	12.12	58.58	24.37	12.12	8.11	679.397	.593	1.353
1.50	.50	36.0	25.0	43.52	924.00	114.33	20.39	91.27	19.97	11.74	8.17	1233.386	.584	1.113
1.50	.50	46.0	15.0	43.35	310.00	40.87	7.82	43.15	15.07	11.30	8.24	479.797	.678	1.469
1.50	.50	46.0	25.0	43.17	482.00	60.75	10.14	57.91	9.67	10.79	8.30	682.722	.714	1.343
1.50	.50	46.0	35.0	42.96	959.00	116.76	16.66	93.86	3.74	10.21	8.35	1251.546	.724	1.058

Table 6.7a: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : TOLUENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.84
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 363.17
BOILING POINT DIFFERENCE (K) = 144.15

SYSTEMS PARAMETERS				********** IRREVERSIBILITIES **********								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				========== kJ/kg ==========										
.75	.25	36.0	15.0	45.18	459.00	26.46	8.79	51.32	26.50	12.31	4.67	634.226	.631	1.419
.75	.25	36.0	25.0	44.73	923.00	48.94	14.71	56.12	28.20	11.93	4.57	1132.204	.615	1.206
.75	.25	46.0	15.0	44.57	309.00	18.51	6.43	34.80	28.86	11.78	4.65	458.589	.640	1.474
.75	.25	46.0	25.0	44.53	481.00	26.43	8.61	42.05	28.38	11.72	4.72	647.446	.638	1.359
.75	.25	46.0	35.0	44.50	958.00	48.64	14.40	57.53	27.84	11.67	4.79	1167.364	.623	1.151
.75	.50	36.0	15.0	44.46	460.00	28.50	8.80	41.22	48.55	13.92	4.86	650.301	.496	1.331
.75	.50	36.0	25.0	44.42	923.00	52.51	14.56	55.59	47.34	13.83	4.92	1156.171	.490	1.167
.75	.50	46.0	15.0	44.37	309.00	19.79	6.36	31.86	45.98	13.74	4.99	476.079	.508	1.379
.75	.50	46.0	25.0	44.32	481.00	28.16	8.45	40.91	44.37	13.63	5.05	665.879	.512	1.290
.75	.50	46.0	35.0	44.26	958.00	51.67	13.95	57.61	42.64	13.50	5.10	1186.739	.507	1.125
1.50	.25	36.0	15.0	44.20	461.00	60.35	13.82	59.05	22.77	11.14	5.16	677.487	.657	1.393
1.50	.25	36.0	25.0	44.13	924.00	110.91	23.88	90.29	21.22	11.00	5.21	1230.655	.623	1.126
1.50	.25	46.0	15.0	44.04	309.00	41.68	9.53	45.91	19.60	10.83	5.26	485.854	.699	1.488
1.50	.25	46.0	25.0	43.93	482.00	59.18	12.84	58.98	17.87	10.62	5.31	690.733	.698	1.344
1.50	.25	46.0	35.0	43.81	958.00	108.38	22.05	92.20	15.93	10.38	5.36	1256.109	.666	1.069
1.50	.50	36.0	15.0	43.67	461.00	63.14	12.28	58.77	24.91	12.12	5.40	681.298	.592	1.353
1.50	.50	36.0	25.0	43.52	924.00	115.83	20.73	91.36	20.64	11.74	5.45	1233.275	.582	1.114
1.50	.50	46.0	15.0	43.36	310.00	43.44	8.00	43.54	15.92	11.31	5.49	481.050	.674	1.467
1.50	.50	46.0	25.0	43.17	482.00	61.59	10.44	58.26	10.73	10.80	5.53	682.525	.709	1.342
1.50	.50	46.0	35.0	42.97	959.00	112.65	17.28	94.00	5.05	10.22	5.57	1246.741	.716	1.059

Table 6.7b: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section**

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : TOLUENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.84
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 363.17
BOILING POINT DIFFERENCE (K) = 144.15

SYSTEMS		PARAMETERS		IRREVERSIBILITIES								COPs	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				kJ/kg										
.75	.25	36.0	15.0	22.37	466.00	22.69	8.79	51.32	26.50	12.31	5.27	615.254	.636	1.425
.75	.25	36.0	25.0	22.10	927.00	44.27	14.71	56.12	28.20	11.93	5.17	1109.508	.619	1.210
.75	.25	46.0	15.0	22.01	316.00	16.04	6.43	34.79	28.85	11.78	5.29	441.185	.644	1.478
.75	.25	46.0	25.0	21.99	487.00	24.14	8.61	42.04	28.37	11.72	5.39	629.267	.642	1.363
.75	.25	46.0	35.0	21.97	960.00	46.93	14.39	57.52	27.83	11.67	5.50	1145.802	.627	1.155
.75	.50	36.0	15.0	21.95	467.00	25.01	8.79	41.19	48.52	13.92	6.72	633.102	.499	1.334
.75	.50	36.0	25.0	21.92	927.00	48.53	14.54	55.56	47.30	13.83	6.84	1135.524	.493	1.169
.75	.50	46.0	15.0	21.89	316.00	17.49	6.35	31.80	45.84	13.74	6.95	460.052	.511	1.381
.75	.50	46.0	25.0	21.86	487.00	26.19	8.43	40.85	44.29	13.63	7.06	649.309	.514	1.293
.75	.50	46.0	35.0	21.83	961.00	50.70	13.91	57.55	42.53	13.50	7.16	1168.192	.509	1.128
1.50	.25	36.0	15.0	21.79	467.00	53.82	13.77	59.00	22.68	11.14	6.05	655.255	.660	1.395
1.50	.25	36.0	25.0	21.75	927.00	104.04	23.78	90.28	21.10	11.00	6.13	1205.084	.625	1.129
1.50	.25	46.0	15.0	21.70	317.00	37.36	9.47	45.81	19.44	10.83	6.21	467.820	.702	1.491
1.50	.25	46.0	25.0	21.63	487.00	55.77	12.74	58.90	17.66	10.62	6.28	670.614	.701	1.347
1.50	.25	46.0	35.0	21.56	961.00	107.62	21.83	92.21	15.66	10.38	6.35	1236.617	.668	1.070
1.50	.50	36.0	15.0	21.48	468.00	56.95	12.12	58.58	24.37	12.12	7.71	661.328	.594	1.354
1.50	.50	36.0	25.0	21.39	928.00	109.78	20.39	91.27	19.97	11.74	7.79	1210.322	.584	1.114
1.50	.50	46.0	15.0	21.29	317.00	39.32	7.82	43.15	15.07	11.30	7.86	462.809	.678	1.469
1.50	.50	46.0	25.0	21.18	488.00	58.55	10.14	57.91	9.67	10.79	7.93	664.172	.714	1.343
1.50	.50	46.0	35.0	21.06	962.00	112.72	16.66	93.86	3.74	10.21	8.00	1228.253	.723	1.057

Table 6.8a: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section**

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : TOLUENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.84
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 363.17
BOILING POINT DIFFERENCE (K) = 144.15

SYSTEMS		PARAMETERS		IRREVERSIBILITIES kJ/kg								COPs	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
.75	.25	36.0	15.0	22.37	466.00	24.08	8.79	51.32	26.50	12.31	4.22	615.592	.636	1.425
.75	.25	36.0	25.0	22.10	927.00	44.78	14.71	56.12	28.20	11.93	4.14	1108.991	.619	1.210
.75	.25	46.0	15.0	22.01	316.00	17.02	6.43	34.80	28.86	11.78	4.23	441.124	.644	1.478
.75	.25	46.0	25.0	21.99	487.00	24.41	8.61	42.05	28.38	11.72	4.32	628.485	.642	1.363
.75	.25	46.0	35.0	21.97	960.00	45.13	14.40	57.53	27.84	11.67	4.40	1142.934	.627	1.155
.75	.50	36.0	15.0	21.95	467.00	26.55	8.80	41.22	48.55	13.92	4.48	632.460	.499	1.334
.75	.50	36.0	25.0	21.92	927.00	49.10	14.56	55.59	47.34	13.83	4.56	1133.900	.493	1.169
.75	.50	46.0	15.0	21.89	316.00	18.56	6.36	31.86	45.98	13.74	4.63	459.030	.511	1.381
.75	.50	46.0	25.0	21.86	487.00	26.51	8.45	40.91	44.37	13.63	4.71	647.432	.514	1.293
.75	.50	46.0	35.0	21.83	961.00	48.79	13.95	57.61	42.64	13.50	4.78	1164.096	.509	1.128
1.50	.25	36.0	15.0	21.79	467.00	57.15	13.82	59.05	22.77	11.14	4.84	657.560	.659	1.395
1.50	.25	36.0	25.0	21.75	927.00	105.31	23.88	90.29	21.22	11.00	4.91	1205.367	.625	1.129
1.50	.25	46.0	15.0	21.70	317.00	39.67	9.53	45.91	19.60	10.83	4.97	469.212	.701	1.491
1.50	.25	46.0	25.0	21.63	487.00	56.47	12.84	58.98	17.87	10.62	5.03	670.439	.700	1.347
1.50	.25	46.0	35.0	21.56	961.00	103.65	22.05	92.20	15.93	10.38	5.08	1231.855	.668	1.071
1.50	.50	36.0	15.0	21.48	468.00	60.51	12.28	58.77	24.91	12.12	5.14	663.209	.593	1.354
1.50	.50	36.0	25.0	21.39	928.00	111.23	20.73	91.36	20.64	11.74	5.19	1210.287	.583	1.114
1.50	.50	46.0	15.0	21.29	317.00	41.79	8.00	43.54	15.92	11.31	5.24	464.090	.675	1.468
1.50	.50	46.0	25.0	21.18	488.00	59.36	10.44	58.26	10.73	10.80	5.29	664.069	.709	1.341
1.50	.50	46.0	35.0	21.06	962.00	108.77	17.28	94.00	5.05	10.22	5.34	1223.718	.715	1.058

Table 6.8b: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section**

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : M-XYLENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.68
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 343.09
BOILING POINT DIFFERENCE (K) = 172.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES kJ/kg								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC COPH
.75	.25	36.0	15.0	45.18	459.00	24.46	7.83	50.47	19.05	12.31	5.83	624.127	.654 1.430
.75	.25	36.0	25.0	44.72	923.00	47.47	13.22	56.84	20.69	11.93	5.72	1123.579	.638 1.207
.75	.25	46.0	15.0	44.56	309.00	17.11	5.69	36.72	21.46	11.77	5.81	452.118	.664 1.487
.75	.25	46.0	25.0	44.52	481.00	25.63	7.67	43.10	21.09	11.71	5.90	640.633	.662 1.367
.75	.25	46.0	35.0	44.48	958.00	49.62	12.96	57.95	20.68	11.65	5.99	1161.323	.645 1.150
.75	.50	36.0	15.0	44.44	460.00	26.34	7.82	43.60	37.61	13.90	7.29	641.009	.518 1.341
.75	.50	36.0	25.0	44.40	923.00	50.92	13.08	57.37	36.64	13.82	7.39	1146.603	.511 1.168
.75	.50	46.0	15.0	44.35	309.00	18.28	5.62	35.58	35.54	13.72	7.48	469.581	.531 1.391
.75	.50	46.0	25.0	44.30	481.00	27.30	7.52	43.26	34.26	13.61	7.57	658.823	.534 1.298
.75	.50	46.0	35.0	44.25	958.00	52.68	12.54	58.92	32.86	13.48	7.65	1180.393	.527 1.125
1.50	.25	36.0	15.0	44.19	461.00	55.76	12.46	59.37	16.73	11.12	6.45	667.075	.678 1.399
1.50	.25	36.0	25.0	44.12	924.00	107.50	21.68	90.20	15.44	10.98	6.51	1220.439	.641 1.124
1.50	.25	46.0	15.0	44.02	309.00	38.50	8.55	46.89	14.11	10.81	6.58	478.461	.722 1.499
1.50	.25	46.0	25.0	43.91	482.00	57.34	11.58	59.25	12.68	10.59	6.64	684.009	.721 1.349
1.50	.25	46.0	35.0	43.79	958.00	110.41	20.00	91.79	11.09	10.35	6.70	1252.121	.685 1.064
1.50	.50	36.0	15.0	43.65	461.00	58.30	11.04	59.88	17.86	12.09	8.11	671.927	.616 1.361
1.50	.50	36.0	25.0	43.50	924.00	112.16	18.74	91.86	14.21	11.70	8.17	1224.337	.603 1.111
1.50	.50	46.0	15.0	43.33	310.00	40.09	7.13	45.55	10.14	11.26	8.24	475.740	.703 1.481
1.50	.50	46.0	25.0	43.14	483.00	59.60	9.26	59.20	5.55	10.75	8.30	678.803	.738 1.348
1.50	.50	46.0	35.0	42.94	959.00	114.55	15.32	94.04	.55	10.16	8.35	1244.919	.744 1.052

Table 6.9a: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section**

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : M-XYLENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.68
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 343.09
BOILING POINT DIFFERENCE (K) = 172.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				kJ/kg										
.75	.25	36.0	15.0	45.18	459.00	26.35	7.83	50.47	19.05	12.31	4.67	624.850	.654	1.430
.75	.25	36.0	25.0	44.72	923.00	48.74	13.22	56.84	20.69	11.93	4.57	1123.706	.638	1.207
.75	.25	46.0	15.0	44.56	309.00	18.43	5.69	36.73	21.46	11.77	4.65	452.283	.664	1.487
.75	.25	46.0	25.0	44.52	481.00	26.32	7.68	43.11	21.09	11.71	4.72	640.145	.662	1.367
.75	.25	46.0	35.0	44.48	958.00	48.44	12.96	57.95	20.68	11.65	4.79	1158.951	.645	1.150
.75	.50	36.0	15.0	44.44	460.00	28.38	7.83	43.61	37.62	13.90	4.86	640.639	.518	1.341
.75	.50	36.0	25.0	44.40	923.00	52.29	13.08	57.38	36.65	13.82	4.92	1145.544	.511	1.168
.75	.50	46.0	15.0	44.35	309.00	19.70	5.63	35.61	35.55	13.72	4.99	468.551	.531	1.391
.75	.50	46.0	25.0	44.30	481.00	28.04	7.53	43.29	34.28	13.61	5.05	657.097	.534	1.298
.75	.50	46.0	35.0	44.25	958.00	51.46	12.55	58.95	32.89	13.48	5.10	1176.680	.527	1.125
1.50	.25	36.0	15.0	44.19	461.00	60.10	12.49	59.39	16.75	11.12	5.16	670.186	.678	1.399
1.50	.25	36.0	25.0	44.12	924.00	110.45	21.73	90.21	15.47	10.98	5.21	1222.169	.641	1.124
1.50	.25	46.0	15.0	44.02	309.00	41.51	8.58	46.94	14.15	10.81	5.26	480.265	.722	1.499
1.50	.25	46.0	25.0	43.91	482.00	58.93	11.63	59.29	12.75	10.59	5.31	684.418	.720	1.349
1.50	.25	46.0	35.0	43.79	958.00	107.93	20.09	91.80	11.17	10.35	5.36	1248.488	.685	1.064
1.50	.50	36.0	15.0	43.65	461.00	62.87	11.11	59.97	18.04	12.09	5.40	674.144	.615	1.361
1.50	.50	36.0	25.0	43.50	924.00	115.34	18.89	91.91	14.45	11.70	5.45	1225.235	.602	1.111
1.50	.50	46.0	15.0	43.33	310.00	43.25	7.22	45.75	10.45	11.26	5.49	476.750	.702	1.480
1.50	.50	46.0	25.0	43.15	483.00	61.33	9.47	59.40	6.03	10.75	5.53	678.659	.736	1.348
1.50	.50	46.0	35.0	42.94	959.00	112.18	15.66	94.09	1.12	10.17	5.57	1240.740	.740	1.053

Table 6.9b: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section**

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : M-XYLENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.68
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 343.09
BOILING POINT DIFFERENCE (K) = 172.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES								***COPe***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				kJ/kg										
.75	.25	36.0	15.0	22.37	466.00	23.98	7.83	50.47	19.05	12.31	4.22	606.226	.660	1.435
.75	.25	36.0	25.0	22.10	927.00	44.60	13.22	56.84	20.69	11.93	4.14	1100.511	.642	1.211
.75	.25	46.0	15.0	22.00	316.00	16.95	5.69	36.73	21.46	11.77	4.23	434.829	.669	1.491
.75	.25	46.0	25.0	21.98	487.00	24.31	7.68	43.11	21.09	11.71	4.32	621.198	.666	1.371
.75	.25	46.0	35.0	21.96	960.00	44.95	12.96	57.95	20.68	11.65	4.40	1134.542	.649	1.154
.75	.50	36.0	15.0	21.94	467.00	26.43	7.83	43.61	37.62	13.90	4.48	622.813	.521	1.344
.75	.50	36.0	25.0	21.91	927.00	48.89	13.08	57.38	36.65	13.82	4.56	1123.293	.513	1.171
.75	.50	46.0	15.0	21.88	316.00	18.49	5.63	35.61	35.55	13.72	4.63	451.513	.534	1.394
.75	.50	46.0	25.0	21.85	487.00	26.40	7.53	43.29	34.28	13.61	4.71	638.664	.536	1.301
.75	.50	46.0	35.0	21.82	961.00	48.59	12.55	58.95	32.89	13.48	4.78	1154.056	.530	1.127
1.50	.25	36.0	15.0	21.78	467.00	56.91	12.49	59.39	16.75	11.12	4.84	650.278	.681	1.402
1.50	.25	36.0	25.0	21.74	927.00	104.87	21.73	90.21	15.47	10.98	4.91	1196.912	.644	1.127
1.50	.25	46.0	15.0	21.69	317.00	39.51	8.58	46.94	14.15	10.81	4.97	463.637	.725	1.502
1.50	.25	46.0	25.0	21.62	487.00	56.23	11.63	59.29	12.75	10.59	5.03	664.143	.723	1.351
1.50	.25	46.0	35.0	21.55	961.00	103.22	20.09	91.80	11.17	10.35	5.08	1224.262	.686	1.066
1.50	.50	36.0	15.0	21.47	468.00	60.25	11.11	59.97	18.04	12.09	5.14	656.074	.616	1.362
1.50	.50	36.0	25.0	21.38	928.00	110.77	18.89	91.91	14.45	11.70	5.19	1202.276	.603	1.112
1.50	.50	46.0	15.0	21.28	317.00	41.62	7.22	45.75	10.45	11.26	5.24	459.807	.702	1.480
1.50	.50	46.0	25.0	21.17	488.00	59.11	9.47	59.40	6.03	10.75	5.29	659.222	.735	1.347
1.50	.50	46.0	35.0	21.04	962.00	108.32	15.66	94.09	1.12	10.17	5.34	1217.744	.739	1.052

Table 6.10b: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : ETHYLBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.70
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 338.90
BOILING POINT DIFFERENCE (K) = 169.65

SYSTEMS		PARAMETERS		**********		IRREVERSIBILITIES						***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR kJ/kg	COPC	COPH
.75	.25	36.0	15.0	45.18	459.00	24.59	8.69	50.94	21.39	12.31	5.83	627.930	.651	1.432
.75	.25	36.0	25.0	44.73	923.00	47.72	14.55	56.15	23.18	11.93	5.72	1126.966	.634	1.211
.75	.25	46.0	15.0	44.57	309.00	17.20	6.36	37.31	23.90	11.78	5.81	455.924	.661	1.489
.75	.25	46.0	25.0	44.53	481.00	25.77	8.52	43.35	23.51	11.72	5.90	644.303	.658	1.370
.75	.25	46.0	35.0	44.50	958.00	49.88	14.27	57.29	23.06	11.66	5.99	1164.646	.642	1.155
.75	.50	36.0	15.0	44.46	460.00	26.48	8.72	44.05	41.26	13.92	7.29	646.171	.515	1.343
.75	.50	36.0	25.0	44.41	923.00	51.19	14.45	56.89	40.22	13.83	7.39	1151.373	.508	1.172
.75	.50	46.0	15.0	44.37	309.00	18.38	6.31	36.33	39.04	13.74	7.48	474.644	.527	1.392
.75	.50	46.0	25.0	44.32	481.00	27.44	8.40	43.72	37.72	13.63	7.57	663.790	.530	1.300
.75	.50	46.0	35.0	44.26	958.00	52.96	13.88	58.50	36.22	13.50	7.65	1184.975	.524	1.129
1.50	.25	36.0	15.0	44.20	461.00	56.06	13.76	58.66	18.79	11.14	6.45	670.055	.675	1.403
1.50	.25	36.0	25.0	44.13	924.00	108.07	23.80	87.91	17.42	11.00	6.51	1222.859	.639	1.129
1.50	.25	46.0	15.0	44.04	309.00	38.71	9.51	46.77	16.00	10.83	6.58	481.431	.718	1.502
1.50	.25	46.0	25.0	43.93	482.00	57.65	12.83	58.57	14.48	10.62	6.64	686.712	.717	1.353
1.50	.25	46.0	35.0	43.81	958.00	110.99	22.05	89.55	12.76	10.38	6.70	1254.227	.682	1.070
1.50	.50	36.0	15.0	43.67	461.00	58.61	12.30	59.42	20.21	12.12	8.11	675.447	.612	1.364
1.50	.50	36.0	25.0	43.52	924.00	112.75	20.78	89.84	16.31	11.74	8.17	1227.121	.600	1.117
1.50	.50	46.0	15.0	43.36	310.00	40.30	8.04	45.64	11.96	11.31	8.24	478.842	.697	1.483
1.50	.50	46.0	25.0	43.17	482.00	59.92	10.49	58.80	7.13	10.80	8.30	680.620	.732	1.353
1.50	.50	46.0	35.0	42.97	959.00	115.15	17.18	92.11	1.68	10.22	8.35	1246.675	.739	1.061

Table 11a: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section**

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : M-XYLENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.68
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 343.09
BOILING POINT DIFFERENCE (K) = 172.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES (kJ/kg)									COPs	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
.75	.25	36.0	15.0	22.37	466.00	22.26	7.83	50.47	19.05	12.31	5.27	605.559	.660	1.435
.75	.25	36.0	25.0	22.10	927.00	43.44	13.22	56.84	20.69	11.93	5.17	1100.383	.642	1.211
.75	.25	46.0	15.0	22.00	316.00	15.73	5.69	36.72	21.46	11.77	5.29	434.665	.668	1.491
.75	.25	46.0	25.0	21.98	487.00	23.68	7.67	43.10	21.09	11.71	5.39	621.637	.666	1.371
.75	.25	46.0	35.0	21.96	960.00	46.04	12.96	57.95	20.68	11.65	5.50	1136.730	.649	1.154
.75	.50	36.0	15.0	21.94	467.00	24.53	7.82	43.60	37.61	13.90	6.72	623.133	.521	1.344
.75	.50	36.0	25.0	21.91	927.00	47.61	13.08	57.37	36.64	13.82	6.84	1124.258	.513	1.171
.75	.50	46.0	15.0	21.88	316.00	17.16	5.62	35.58	35.54	13.72	6.95	452.454	.534	1.394
.75	.50	46.0	25.0	21.85	487.00	25.70	7.52	43.26	34.26	13.61	7.06	640.262	.536	1.301
.75	.50	46.0	35.0	21.82	961.00	49.74	12.54	58.92	32.86	13.48	7.16	1157.534	.530	1.127
1.50	.25	36.0	15.0	21.78	467.00	52.80	12.46	59.37	16.73	11.12	6.05	647.316	.681	1.402
1.50	.25	36.0	25.0	21.74	927.00	102.07	21.68	90.20	15.44	10.98	6.13	1195.249	.644	1.126
1.50	.25	46.0	15.0	21.69	317.00	36.65	8.55	46.89	14.11	10.81	6.21	461.903	.725	1.502
1.50	.25	46.0	25.0	21.62	487.00	54.71	11.58	59.25	12.68	10.59	6.28	663.732	.723	1.351
1.50	.25	46.0	35.0	21.55	961.00	105.58	20.00	91.79	11.09	10.35	6.35	1227.709	.687	1.066
1.50	.50	36.0	15.0	21.47	468.00	55.87	11.04	59.88	17.86	12.09	7.71	653.912	.617	1.362
1.50	.50	36.0	25.0	21.38	928.00	107.70	18.74	91.86	14.21	11.70	7.79	1201.368	.604	1.111
1.50	.50	46.0	15.0	21.28	317.00	38.57	7.13	45.55	10.14	11.26	7.86	458.790	.703	1.481
1.50	.50	46.0	25.0	21.17	488.00	57.44	9.26	59.20	5.55	10.75	7.93	659.303	.738	1.348
1.50	.50	46.0	35.0	21.04	962.00	110.59	15.32	94.04	.55	10.16	8.00	1221.713	.743	1.051

Table 6.10a: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : ETHYLBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.70
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 338.90
BOILING POINT DIFFERENCE (K) = 169.65

SYSTEMS SFR	PARAMETERS R	XST %	XWK %	IRREVERSIBILITIES EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR kJ/kg	COPc	COPh
.75	.25	36.0	15.0	45.18	459.00	26.35	8.69	50.94	21.39	12.31	4.67	628.524	.651	1.432
.75	.25	36.0	25.0	44.73	923.00	48.74	14.55	56.15	23.18	11.93	4.57	1126.846	.634	1.211
.75	.25	46.0	15.0	44.57	309.00	18.43	6.36	37.31	23.90	11.78	4.65	456.000	.661	1.489
.75	.25	46.0	25.0	44.53	481.00	26.32	8.53	43.36	23.51	11.72	4.72	643.682	.658	1.370
.75	.25	46.0	35.0	44.50	958.00	48.44	14.27	57.29	23.06	11.66	4.79	1162.020	.642	1.155
.75	.50	36.0	15.0	44.46	460.00	28.38	8.72	44.07	41.26	13.92	4.86	645.666	.515	1.343
.75	.50	36.0	25.0	44.41	923.00	52.29	14.46	56.90	40.23	13.83	4.92	1150.045	.508	1.172
.75	.50	46.0	15.0	44.37	309.00	19.70	6.32	36.36	39.06	13.74	4.99	473.530	.527	1.393
.75	.50	46.0	25.0	44.32	481.00	28.04	8.41	43.75	37.74	13.63	5.05	661.933	.530	1.300
.75	.50	46.0	35.0	44.26	958.00	51.46	13.90	58.53	36.25	13.50	5.10	1181.004	.524	1.129
1.50	.25	36.0	15.0	44.20	461.00	60.10	13.79	58.68	18.86	11.14	5.16	672.930	.675	1.403
1.50	.25	36.0	25.0	44.13	924.00	110.45	23.86	87.91	17.46	11.00	5.21	1224.036	.639	1.129
1.50	.25	46.0	15.0	44.04	309.00	41.51	9.54	46.82	16.06	10.83	5.26	483.060	.718	1.502
1.50	.25	46.0	25.0	43.93	482.00	58.93	12.89	58.61	14.56	10.62	5.31	686.851	.717	1.354
1.50	.25	46.0	35.0	43.81	958.00	107.93	22.16	89.55	12.87	10.38	5.36	1250.052	.682	1.071
1.50	.50	36.0	15.0	43.67	461.00	62.87	12.39	59.53	20.45	12.13	5.40	677.446	.611	1.364
1.50	.50	36.0	25.0	43.52	924.00	115.34	20.96	89.90	16.62	11.75	5.45	1227.540	.599	1.117
1.50	.50	46.0	15.0	43.36	310.00	43.25	8.14	45.88	12.36	11.31	5.49	479.791	.696	1.482
1.50	.50	46.0	25.0	43.17	482.00	61.33	10.67	59.02	7.66	10.81	5.53	680.188	.729	1.352
1.50	.50	46.0	35.0	42.97	959.00	112.18	17.60	92.18	2.39	10.23	5.57	1242.129	.735	1.062

Table 11b: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : ETHYLBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.70
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 338.90
BOILING POINT DIFFERENCE (K) = 169.65

SYSTEMS PARAMETERS				********** IRREVERSIBILITIES **********								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				========== kJ/kg ==========										
.75	.25	36.0	15.0	22.37	466.00	22.38	8.69	50.94	21.39	12.31	5.27	609.350	.657	1.438
.75	.25	36.0	25.0	22.10	927.00	43.66	14.55	56.15	23.18	11.93	5.17	1103.747	.639	1.216
.75	.25	46.0	15.0	22.01	316.00	15.82	6.36	37.31	23.90	11.78	5.29	438.459	.665	1.493
.75	.25	46.0	25.0	21.99	487.00	23.80	8.52	43.35	23.51	11.72	5.39	625.292	.662	1.374
.75	.25	46.0	35.0	21.97	960.00	46.28	14.27	57.29	23.06	11.66	5.50	1140.029	.646	1.159
.75	.50	36.0	15.0	21.94	467.00	24.66	8.72	44.05	41.26	13.92	6.72	628.280	.518	1.346
.75	.50	36.0	25.0	21.92	927.00	47.86	14.45	56.89	40.22	13.83	6.84	1129.004	.511	1.175
.75	.50	46.0	15.0	21.89	316.00	17.25	6.31	36.33	39.04	13.74	6.95	457.505	.530	1.395
.75	.50	46.0	25.0	21.86	487.00	25.83	8.40	43.72	37.72	13.63	7.06	645.215	.533	1.303
.75	.50	46.0	35.0	21.83	961.00	50.01	13.88	58.50	36.22	13.50	7.16	1162.095	.527	1.132
1.50	.25	36.0	15.0	21.79	467.00	53.08	13.76	58.66	18.79	11.14	6.05	650.274	.678	1.406
1.50	.25	36.0	25.0	21.75	927.00	102.61	23.80	87.91	17.42	11.00	6.13	1197.635	.641	1.132
1.50	.25	46.0	15.0	21.70	317.00	36.84	9.51	46.77	16.00	10.83	6.21	464.856	.721	1.505
1.50	.25	46.0	25.0	21.63	487.00	55.00	12.83	58.57	14.48	10.62	6.28	666.414	.719	1.356
1.50	.25	46.0	35.0	21.56	961.00	106.14	22.05	89.55	12.76	10.38	6.35	1229.782	.684	1.072
1.50	.50	36.0	15.0	21.48	468.00	56.16	12.30	59.42	20.21	12.12	7.71	657.411	.613	1.366
1.50	.50	36.0	25.0	21.39	928.00	108.27	20.78	89.84	16.31	11.74	7.79	1204.119	.601	1.118
1.50	.50	46.0	15.0	21.29	317.00	38.77	8.04	45.64	11.96	11.31	7.86	461.873	.698	1.484
1.50	.50	46.0	25.0	21.18	488.00	57.75	10.49	58.80	7.13	10.80	7.93	662.097	.732	1.353
1.50	.50	46.0	35.0	21.06	962.00	111.17	17.18	92.11	1.68	10.22	8.00	1223.435	.738	1.060

Table 12a: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : ETHYLBENZENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.70
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 338.90
BOILING POINT DIFFERENCE (K) = 169.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
				kJ/kg										
.75	.25	36.0	15.0	22.37	466.00	23.98	8.69	50.94	21.39	12.31	4.22	609.899	.657	1.438
.75	.25	36.0	25.0	22.10	927.00	44.60	14.55	56.15	23.18	11.93	4.14	1103.651	.639	1.216
.75	.25	46.0	15.0	22.01	316.00	16.95	6.36	37.31	23.90	11.78	4.23	438.541	.665	1.493
.75	.25	46.0	25.0	21.99	487.00	24.31	8.53	43.36	23.51	11.72	4.32	624.731	.662	1.374
.75	.25	46.0	35.0	21.97	960.00	44.95	14.27	57.29	23.06	11.66	4.40	1137.606	.646	1.159
.75	.50	36.0	15.0	21.94	467.00	26.43	8.72	44.07	41.26	13.92	4.48	627.834	.518	1.346
.75	.50	36.0	25.0	21.92	927.00	48.89	14.46	56.90	40.23	13.83	4.56	1127.789	.511	1.175
.75	.50	46.0	15.0	21.89	316.00	18.49	6.32	36.36	39.06	13.74	4.63	456.486	.530	1.395
.75	.50	46.0	25.0	21.86	487.00	26.40	8.41	43.75	37.74	13.63	4.71	643.493	.533	1.303
.75	.50	46.0	35.0	21.83	961.00	48.59	13.90	58.53	36.25	13.50	4.78	1158.374	.527	1.132
1.50	.25	36.0	15.0	21.79	467.00	56.91	13.79	58.68	18.86	11.14	4.84	653.016	.678	1.406
1.50	.25	36.0	25.0	21.75	927.00	104.87	23.86	87.91	17.46	11.00	4.91	1198.772	.641	1.132
1.50	.25	46.0	15.0	21.70	317.00	39.51	9.54	46.82	16.06	10.83	4.97	466.426	.721	1.505
1.50	.25	46.0	25.0	21.63	487.00	56.23	12.89	58.61	14.56	10.62	5.03	666.569	.719	1.356
1.50	.25	46.0	35.0	21.56	961.00	103.22	22.16	89.55	12.87	10.38	5.08	1225.818	.684	1.072
1.50	.50	36.0	15.0	21.48	468.00	60.25	12.39	59.53	20.45	12.13	5.14	659.368	.612	1.366
1.50	.50	36.0	25.0	21.39	928.00	110.77	20.96	89.90	16.62	11.75	5.19	1204.571	.600	1.118
1.50	.50	46.0	15.0	21.29	317.00	41.62	8.14	45.88	12.36	11.31	5.24	462.837	.696	1.483
1.50	.50	46.0	25.0	21.18	488.00	59.11	10.67	59.02	7.66	10.81	5.29	661.739	.729	1.352
1.50	.50	46.0	35.0	21.06	962.00	108.32	17.60	92.18	2.39	10.23	5.34	1219.121	.734	1.061

Table 12b: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : STYRENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.75
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 371.59
BOILING POINT DIFFERENCE (K) = 178.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR kJ/kg	COPC	COPH
.75	.25	36.0	15.0	45.18	459.00	24.21	17.38	56.18	37.25	12.31	5.83	657.340	.625	1.428
.75	.25	36.0	25.0	44.74	923.00	46.98	27.93	58.57	39.93	11.94	5.72	1158.806	.607	1.215
.75	.25	46.0	15.0	44.63	309.00	16.93	13.12	42.23	40.32	11.83	5.81	483.872	.631	1.479
.75	.25	46.0	25.0	44.60	481.00	25.37	17.16	47.70	39.78	11.78	5.90	673.280	.630	1.367
.75	.25	46.0	35.0	44.56	958.00	49.11	27.56	59.85	39.18	11.73	5.99	1195.976	.614	1.161
.75	.50	36.0	15.0	44.52	460.00	26.07	17.87	49.06	68.28	14.00	7.29	687.094	.485	1.335
.75	.50	36.0	25.0	44.48	923.00	50.39	28.40	60.23	66.92	13.92	7.39	1194.724	.478	1.175
.75	.50	46.0	15.0	44.44	309.00	18.10	13.39	41.60	65.37	13.83	7.48	513.195	.495	1.379
.75	.50	46.0	25.0	44.39	481.00	27.02	17.41	48.82	63.62	13.72	7.57	703.548	.498	1.294
.75	.50	46.0	35.0	44.34	958.00	52.14	27.64	62.13	61.63	13.61	7.65	1227.146	.493	1.133
1.50	.25	36.0	15.0	44.28	460.00	55.19	27.18	61.31	33.47	11.23	6.45	699.105	.643	1.396
1.50	.25	36.0	25.0	44.21	924.00	106.40	45.73	87.58	31.70	11.10	6.51	1257.243	.606	1.128
1.50	.25	46.0	15.0	44.13	309.00	38.11	19.56	50.60	29.83	10.94	6.58	508.744	.681	1.489
1.50	.25	46.0	25.0	44.02	482.00	56.75	25.96	61.45	27.81	10.75	6.64	715.388	.678	1.345
1.50	.25	46.0	35.0	43.91	958.00	109.27	43.57	89.55	25.53	10.52	6.70	1287.051	.641	1.070
1.50	.50	36.0	15.0	43.78	461.00	57.70	25.80	63.45	40.93	12.32	8.11	713.091	.563	1.346
1.50	.50	36.0	25.0	43.65	924.00	111.01	42.62	91.25	35.80	11.97	8.17	1268.478	.548	1.111
1.50	.50	46.0	15.0	43.49	310.00	39.68	17.95	50.64	30.06	11.57	8.24	511.628	.632	1.450
1.50	.50	46.0	25.0	43.32	482.00	58.99	23.18	63.33	23.37	11.10	8.30	713.584	.657	1.326
1.50	.50	46.0	35.0	43.13	959.00	113.37	37.93	94.36	16.13	10.56	8.35	1282.839	.653	1.053

Table 6.13a: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section

EVAPORATOR TEMPERATURE (K) = 268.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 3.58
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : STYRENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.75
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 371.59
BOILING POINT DIFFERENCE (K) = 178.65

SYSTEMS PARAMETERS				********** IRREVERSIBILITIES **********								***COPs***	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR kJ/kg	COPC	COPH
.75	.25	36.0	15.0	45.18	459.00	26.36	17.38	56.18	37.25	12.31	4.67	658.329	.625	1.428
.75	.25	36.0	25.0	44.74	923.00	48.76	27.93	58.57	39.93	11.94	4.57	1159.446	.607	1.215
.75	.25	46.0	15.0	44.63	309.00	18.44	13.12	42.23	40.32	11.83	4.65	484.227	.631	1.479
.75	.25	46.0	25.0	44.60	481.00	26.33	17.16	47.70	39.79	11.78	4.72	673.077	.630	1.367
.75	.25	46.0	35.0	44.56	958.00	48.47	27.57	59.86	39.19	11.73	4.79	1194.159	.614	1.161
.75	.50	36.0	15.0	44.52	460.00	28.39	17.88	49.08	68.30	14.00	4.86	687.032	.485	1.335
.75	.50	36.0	25.0	44.48	923.00	52.32	28.42	60.25	66.94	13.92	4.92	1194.245	.478	1.175
.75	.50	46.0	15.0	44.44	309.00	19.71	13.40	41.64	65.41	13.83	4.99	512.412	.495	1.379
.75	.50	46.0	25.0	44.39	481.00	28.05	17.43	48.86	63.67	13.72	5.05	702.179	.498	1.294
.75	.50	46.0	35.0	44.34	958.00	51.48	27.68	62.16	61.71	13.61	5.10	1224.083	.493	1.134
1.50	.25	36.0	15.0	44.28	460.00	60.13	27.23	61.33	33.53	11.23	5.16	702.887	.643	1.396
1.50	.25	36.0	25.0	44.21	924.00	110.51	45.83	87.58	31.79	11.10	5.21	1260.230	.606	1.128
1.50	.25	46.0	15.0	44.13	309.00	41.53	19.62	50.65	29.96	10.94	5.26	511.085	.681	1.489
1.50	.25	46.0	25.0	44.02	482.00	58.97	26.05	61.49	27.97	10.75	5.31	716.565	.678	1.346
1.50	.25	46.0	35.0	43.91	958.00	107.99	43.74	89.52	25.75	10.53	5.36	1284.788	.641	1.070
1.50	.50	36.0	15.0	43.79	461.00	62.91	25.95	63.56	41.37	12.32	5.40	716.302	.563	1.346
1.50	.50	36.0	25.0	43.65	924.00	115.41	42.92	91.28	36.38	11.97	5.45	1271.049	.548	1.112
1.50	.50	46.0	15.0	43.49	310.00	43.28	18.14	50.89	30.81	11.57	5.49	513.668	.630	1.449
1.50	.50	46.0	25.0	43.32	482.00	61.36	23.51	63.53	24.40	11.10	5.53	714.767	.654	1.326
1.50	.50	46.0	35.0	43.13	959.00	112.24	38.59	94.32	17.47	10.57	5.57	1280.889	.649	1.055

Table 6.13b: **Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section**

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : STYRENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.75
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 371.59
BOILING POINT DIFFERENCE (K) = 178.65

SYSTEMS		PARAMETERS		IRREVERSIBILITIES kJ/kg								COPs	
SFR	R	XST %	XWK %	EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR	COPC	COPH
.75	.25	36.0	15.0	22.37	466.00	22.03	17.38	56.18	37.25	12.31	5.27	638.794	.630	1.433
.75	.25	36.0	25.0	22.11	927.00	42.99	27.93	58.57	39.93	11.94	5.17	1135.643	.612	1.219
.75	.25	46.0	15.0	22.05	316.00	15.57	13.12	42.23	40.32	11.83	5.29	466.403	.635	1.483
.75	.25	46.0	25.0	22.03	486.00	23.43	17.16	47.70	39.78	11.78	5.39	653.273	.634	1.371
.75	.25	46.0	35.0	22.01	960.00	45.56	27.56	59.85	39.18	11.73	5.50	1171.388	.618	1.165
.75	.50	36.0	15.0	21.98	467.00	24.28	17.87	49.06	68.28	14.00	6.72	669.204	.488	1.338
.75	.50	36.0	25.0	21.96	927.00	47.12	28.40	60.23	66.92	13.92	6.84	1172.380	.481	1.177
.75	.50	46.0	15.0	21.93	316.00	16.98	13.39	41.60	65.37	13.83	6.95	496.046	.497	1.381
.75	.50	46.0	25.0	21.91	487.00	25.43	17.41	48.82	63.62	13.72	7.06	684.968	.500	1.296
.75	.50	46.0	35.0	21.87	960.00	49.23	27.64	62.13	61.63	13.61	7.16	1203.281	.495	1.136
1.50	.25	36.0	15.0	21.84	467.00	52.26	27.18	61.31	33.47	11.23	6.05	680.340	.646	1.399
1.50	.25	36.0	25.0	21.80	927.00	101.02	45.73	87.58	31.70	11.10	6.13	1232.071	.608	1.131
1.50	.25	46.0	15.0	21.75	316.00	36.27	19.56	50.60	29.83	10.94	6.21	491.164	.684	1.491
1.50	.25	46.0	25.0	21.69	487.00	54.15	25.96	61.45	27.81	10.75	6.28	695.092	.680	1.348
1.50	.25	46.0	35.0	21.62	961.00	104.49	43.57	89.55	25.53	10.52	6.35	1262.639	.643	1.072
1.50	.50	36.0	15.0	21.55	468.00	55.29	25.80	63.45	40.93	12.32	7.71	695.047	.565	1.348
1.50	.50	36.0	25.0	21.46	928.00	106.59	42.62	91.25	35.80	11.97	7.79	1245.495	.550	1.112
1.50	.50	46.0	15.0	21.37	317.00	38.17	17.95	50.64	30.06	11.57	7.86	494.628	.633	1.451
1.50	.50	46.0	25.0	21.27	488.00	56.85	23.18	63.33	23.37	11.10	7.93	695.035	.658	1.326
1.50	.50	46.0	35.0	21.16	962.00	109.45	37.93	94.36	16.13	10.56	8.00	1259.594	.653	1.053

Table 6.14a: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the Low Pressure Section

EVAPORATOR TEMPERATURE (K) = 273.15
ABSORBER TEMPERATURE (K) = 303.15
EVAPORATOR PRESSURE (BAR) = 4.32
CONDENSER PRESSURE (BAR) = 11.76
APPROACH TEMPT TO ABSORBER (K) = 10.00
EXTRACTING SOLVENT EMPLOYED : STYRENE
SOLV HEAT CAP-ca. 303K (kJ/kg.K) = 1.75
SOLV HEAT OF VAP-normal b. pt. (kJ/kg)= 371.59
BOILING POINT DIFFERENCE (K) = 178.65

SYSTEMS SFR	R	PARAMETERS XST %	XWK %	IRREVERSIBILITIES EVAPR	ABSOR	EXVA1	ECONO	VAPOR	RECTF	CONDS	EXVA2	T-IRR kJ/kg	***COPs*** COPC	COPH
.75	.25	36.0	15.0	22.37	466.00	23.99	17.38	56.18	37.25	12.31	4.22	639.703	.630	1.433
.75	.25	36.0	25.0	22.11	927.00	44.62	27.93	58.57	39.93	11.94	4.14	1136.241	.612	1.219
.75	.25	46.0	15.0	22.05	316.00	16.96	13.12	42.23	40.32	11.83	4.23	466.741	.635	1.483
.75	.25	46.0	25.0	22.03	486.00	24.33	17.16	47.70	39.79	11.78	4.32	653.098	.634	1.371
.75	.25	46.0	35.0	22.01	960.00	44.97	27.57	59.86	39.19	11.73	4.40	1169.717	.618	1.165
.75	.50	36.0	15.0	21.98	467.00	26.45	17.88	49.08	68.30	14.00	4.48	669.172	.488	1.338
.75	.50	36.0	25.0	21.96	927.00	48.92	28.42	60.25	66.94	13.92	4.56	1171.959	.481	1.177
.75	.50	46.0	15.0	21.93	316.00	18.50	13.40	41.64	65.41	13.83	4.63	495.339	.497	1.381
.75	.50	46.0	25.0	21.91	487.00	26.41	17.43	48.86	63.67	13.72	4.71	683.709	.500	1.297
.75	.50	46.0	35.0	21.87	960.00	48.61	27.68	62.16	61.71	13.61	4.78	1200.422	.495	1.136
1.50	.25	36.0	15.0	21.84	467.00	56.94	27.23	61.33	33.53	11.23	4.84	683.940	.646	1.399
1.50	.25	36.0	25.0	21.80	927.00	104.93	45.83	87.58	31.79	11.10	4.91	1234.931	.608	1.131
1.50	.25	46.0	15.0	21.75	316.00	39.53	19.62	50.65	29.96	10.94	4.97	493.415	.684	1.492
1.50	.25	46.0	25.0	21.69	487.00	56.26	26.05	61.49	27.97	10.75	5.03	696.243	.680	1.348
1.50	.25	46.0	35.0	21.62	961.00	103.27	43.74	89.52	25.75	10.53	5.08	1260.510	.643	1.072
1.50	.50	36.0	15.0	21.55	468.00	60.29	25.95	63.56	41.37	12.32	5.14	698.176	.564	1.348
1.50	.50	36.0	25.0	21.46	928.00	110.82	42.92	91.28	36.38	11.97	5.19	1248.027	.549	1.113
1.50	.50	46.0	15.0	21.37	317.00	41.64	18.14	50.89	30.81	11.57	5.24	496.657	.631	1.450
1.50	.50	46.0	25.0	21.27	488.00	59.14	23.51	63.53	24.40	11.10	5.29	696.256	.655	1.326
1.50	.50	46.0	35.0	21.16	962.00	108.37	38.59	94.32	17.47	10.57	5.34	1257.812	.649	1.054

Table 6.14b: Theoretical COP and Irreversibility in the Main Units of Ammonia-Water Absorption Heat Pump with Extraction Unit Attached in the High Pressure Section

6.3 Conclusions

From the discussions presented above, it is obvious that theoretically, replacing the non-isothermal separation processes in the conventional system with separation operations carried out isothermally reduces the quantity of HGE required as energy input into the system and thus reduces the irreversibility level in the systems. The COP of the system is increased correspondingly. It does not appear to make much difference, in term of the irreversibility and COP values, whether ammonia is extracted before pumping the fluid to higher pressure or it is extracted after the pumping operation has been carried out.

Based on thermodynamic evaluation, **m-xylene** and **ethylbenzene**, seem to have the best potential as extracting solvent for **ESA** systems. Of all the five solvents on which the thermodynamic simulation of the systems was based **nitrobenzene** gave the highest COP values and the lowest irreversibility values. However, its viscosity is rather too high (see Table 4.1) and it is doubtful if it will be useful as an extracting solvent This is because the relatively high viscosity may:

- encourage emulsification (which **retards phase separation** that is critically necessary in extraction process) of the ternary system.
- increase the viscosity of the ternary system thereby making thorough mixing of the system difficult.

6.4 Recommendations

1. There is the need to build some of the systems which this simulated work indicated to be promising and carry out experimental trials on such systems. This is necessary because a system may not perform in practice, the way it is envisaged from the result of simulation due partly to some network interaction effects which might not be easily obvious while carrying out the theoretical analyses.

2. Since as Linnhoff [1979] pointed out, "**Thermodynamic potential is not the same as cost**", higher COP and lower irreversibility, though thermodynamically desirable, are not the end in themselves. Ultimately, it is the cost factor that is the most important consideration in the selection or otherwise of a system. Therefore it will be necessary to carry out the cost benefit analysis on the system.

3. Pure component parameters as well as binary parameters of more organic solvents, especially those that can be identified as having adequate extracting characteristics, need to be obtained through more rigorous literature search and/or calculations. This would make the screening of more of these solvents for possible use as extracting solvents in the extraction-step-added absorption heat pump systems (ESA) realisable.

4. Experimental determination of some thermophysical properties of the streams consisting of water, ammonia and the identified organic solvents as well as derivation of high quality thermodynamic data such as entropy data of the streams which could then be rigorously extrapolated and interpolated using tested techniques like Chebyshev polynomial procedure are necessary. This will make a more rigorous second law analysis of the cycle of the ESA systems, which is desirable, possible.

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APPENDICES

APPENDIX A

UNIQUAC EQUATIONS

The modified **UNIQUAC** equation [Prausnitz et al., 1978,1980] for excess Gibbs free energy, g^E is given by Equation A.1 below.

$$\frac{g^E}{RT} = \sum x_i \ln\frac{\phi_i}{x_i} + \frac{z}{2}\sum q_i x_i \ln\frac{\theta_i}{\phi_i} - \sum q_i' x_i \ln\left(\sum \phi_j' \tau_{ji}\right) \quad \text{A.1}$$

where:

$$\phi_i = \frac{r_i x_i}{\sum r_j x_j} \quad \text{A.2}$$

$$\phi_i = \frac{q_i x_i}{\sum q_j x_j} \quad \text{A.3}$$

$$\phi_i' = \frac{q_i' x_i}{\sum q_j' x_j} \quad \text{A.4}$$

Activity coefficient for component i (γ_i), in a multi-component system is given by Equation A.5 below.

$$\ln\gamma_i = \ln\frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum x_j l_j - q_i' \ln\left(\sum \phi_j' \tau_{ji}\right) - q_i' \sum \frac{\phi_j' \tau_{ij}}{\sum \phi_k' \tau_{kj}} \quad \text{A.5}$$

where:

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1) \quad \text{A.6}$$

For binary system, activity coefficients for the components are given as follows:

$$\ln\gamma_1 = \ln\frac{\phi_1}{x_1} + (\frac{z}{2})q_1\ln\frac{\theta_1}{\phi_1} + \phi_2(l_1 - \frac{r_1}{r_2}l_2) - q_1'\ln(\theta_1' + \theta_2'\tau_{21})$$

$$+ \theta_2'q_1'(\frac{\tau_{21}}{\phi_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}}) \quad \text{A.7}$$

$$\ln\gamma_2 = \ln\frac{\phi_2}{x_2} + (\frac{z}{2})q_2\ln\frac{\theta_2}{\phi_2} + \phi_1(l_2 - \frac{r_2}{r_1}l_1) - q_2'\ln(\theta_2' + \theta_1'\tau_{12})$$

$$+ \theta_1'q_2'(\frac{\tau_{12}}{\phi_2' + \theta_1'\tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}}) \quad \text{A.8}$$

where:

$$\tau_{12} = \exp(\frac{-\Delta u_{12}}{RT}) \quad \text{A.9}$$

$$\tau_{21} = \exp(\frac{-\Delta u_{21}}{RT}) \quad \text{A.10}$$

APPENDIX B

EQUATIONS USED FOR UNIQUAC PARAMETERS' ESTIMATION

B1: Using mutual solubility data

For two compounds having limited mutual solubility, the following equations hold.

Phase equilibrium equations:

$$\gamma_1^{I} x_1^{I} \quad - \quad \gamma_1^{II} x_1^{II} \qquad \text{.....B.1}$$

$$\gamma_2^{I} x_2^{I} \quad - \quad \gamma_2^{II} x_2^{II} \qquad \text{.....B.2}$$

where the subscripted integers identify the components and the superscripts stand for the phases.

Mass balance:

$$x_1^{I} + x_2^{I} - 1 \qquad \text{.....B.3}$$

$$\rightarrow x_1^{I} - 1 - x_2^{I} \qquad \text{.....B.3a}$$

$$x_1^{II} + x_2^{II} - 1 \qquad \text{.....B.4}$$

$$\rightarrow x_2^{II} - 1 - x_1^{II} \qquad \text{.....B.4a}$$

Substituting into Equations B.1 and B.2 with Equations A.8 and A.9 and, Equations B.3a and B.4a we have:

$$(1-x_2^{\prime})\exp(\ln\frac{\phi_1^{\prime}}{(1-x_2^{\prime})}+\frac{z}{2}q_1\ln\frac{\theta_1^{\prime}}{\phi_1^{\prime}}+\phi_2^{\prime}(l_1-\frac{r_1}{r_2}l_2)-q_1^{\prime}\ln(\theta_1^{\prime}+\theta_2^{\prime}\tau_{21})+\theta_2^{\prime}q_1^{\prime}(\frac{\tau_{21}}{\theta_1^{\prime}+\theta_2^{\prime}\tau_{21}}-\frac{\tau_{12}}{\theta_2^{\prime}+\theta_1^{\prime}\tau_{12}}))\ =$$

$$x_1^{\prime\prime}\exp(\ln\frac{\phi_1^{\prime\prime}}{x_1^{\prime\prime}}+\frac{z}{2}q_1\ln\frac{\theta_1^{\prime\prime}}{\phi_1^{\prime\prime}}+\phi_2^{\prime\prime}(l_1-\frac{r_1}{r_2}l_2)-q_1^{\prime}\ln(\theta_1^{\prime\prime}+\theta_2^{\prime\prime}\tau_{21})+\theta_2^{\prime\prime}q_1^{\prime}(\frac{\tau_{21}}{\theta_1^{\prime\prime}+\theta_2^{\prime\prime}\tau_{21}}-\frac{\tau_{12}}{\theta_2^{\prime\prime}+\theta_1^{\prime\prime}\tau_{12}}))\quad\text{..B.5}$$

$$x_2^{\prime}\exp(\ln\frac{\phi_2^{\prime}}{x_2^{\prime}}+\frac{z}{2}q_2\ln\frac{\theta_2^{\prime}}{\phi_2^{\prime}}+\phi_1^{\prime}(l_2-\frac{r_2}{r_1}l_1)-q_2^{\prime}\ln(\theta_2^{\prime}+\theta_1^{\prime}\tau_{12})+\theta_1^{\prime}q_2^{\prime}(\frac{\tau_{12}}{\theta_2^{\prime}+\theta_1^{\prime}\tau_{12}}-\frac{\tau_{21}}{\theta_1^{\prime}+\theta_2^{\prime}\tau_{21}}))\ =$$

$$x_2^{\prime\prime}\exp(\ln\frac{\phi_2^{\prime\prime}}{x_2^{\prime\prime}}+\frac{z}{2}q_2\ln\frac{\theta_2^{\prime\prime}}{\phi_2^{\prime\prime}}+\phi_1^{\prime\prime}(l_2-\frac{r_2}{r_1}l_1)-q_2^{\prime}\ln(\theta_2^{\prime\prime}+\theta_1^{\prime\prime}\tau_{12})+\theta_1^{\prime\prime}q_2^{\prime}(\frac{\tau_{12}}{\theta_2^{\prime\prime}+\theta_1^{\prime\prime}\tau_{12}}-\frac{\tau_{21}}{\theta_1^{\prime\prime}+\theta_2^{\prime\prime}\tau_{21}}))\quad\text{..B.6}$$

Logarithmmising the two sides of the two equations above and rearranging we have:

$$\ln(\frac{\theta_1^{\prime\prime}+\theta_2^{\prime\prime}\tau_{21}}{\theta_1^{\prime}+\theta_2^{\prime}\tau_{21}})+\frac{\theta_2^{\prime}\tau_{21}}{\theta_1^{\prime}+\theta_2^{\prime}\tau_{21}}-\frac{\theta_2^{\prime}\tau_{12}}{\theta_2^{\prime}+\theta_1^{\prime}\tau_{12}}-\frac{\theta_2^{\prime\prime}\tau_{21}}{\theta_1^{\prime\prime}+\theta_2^{\prime\prime}\tau_{21}}+\frac{\theta_2^{\prime\prime}\tau_{12}}{\theta_2^{\prime\prime}+\theta_1^{\prime\prime}\tau_{12}}\ =\ k_1\text{.....B.7}$$

$$\ln(\frac{\theta_2^{\prime\prime}+\theta_1^{\prime\prime}\tau_{12}}{\theta_2^{\prime}+\theta_1^{\prime}\tau_{12}})+\frac{\theta_1^{\prime}\tau_{12}}{\theta_2^{\prime}+\theta_1^{\prime}\tau_{12}}-\frac{\theta_1^{\prime}\tau_{21}}{\theta_1^{\prime}+\theta_2^{\prime}\tau_{21}}-\frac{\theta_1^{\prime\prime}\tau_{12}}{\theta_2^{\prime\prime}+\theta_1^{\prime\prime}\tau_{12}}+\frac{\theta_1^{\prime\prime}\tau_{21}}{\theta_1^{\prime\prime}+\theta_2^{\prime\prime}\tau_{21}}\ =\ k_2\text{.....B.8}$$

where:

$$k_1 = \frac{1}{q_1'}\left(\ln\frac{\phi_1^{sII}}{\phi_1^{sI}} + \frac{z}{2}q_1\ln\left(\frac{\theta_1^{sII}\phi_1^{sI}}{\theta_1^{sI}\phi_1^{sII}}\right) + (\phi_2^{sII} - \phi_2^{sI})\left(l_1 - \frac{r_2}{r_1}l_2\right)\right) \quad \text{B.9}$$

$$k_2 = \frac{1}{q_2'}\left(\ln\frac{\phi_2^{sII}}{\phi_2^{sI}} + \frac{z}{2}q_2\ln\left(\frac{\theta_2^{sII}\phi_2^{sI}}{\theta_2^{sI}\phi_2^{sII}}\right) + (\phi_1^{sII} - \phi_1^{sI})\left(l_2 - \frac{r_1}{r_2}l_1\right)\right) \quad \text{B.10}$$

B2: Using Infinite Dilution Coefficient Data

Definitions:

For any binary solution at infinite dilution, the following conditions hold:

$$x_1 \rightarrow 0 \quad as \quad x_2 \rightarrow 1$$

$$x_2 \rightarrow 0 \quad as \quad x_1 \rightarrow 1$$

For the first condition, we have:

$$\frac{\Phi_1}{x_1} = \frac{r_1 x_1}{(r_1 x_1 + r_2 x_2) x_1} \qquad \text{B.11a}$$

$$\rightarrow \frac{\Phi_1}{x_1} = \frac{r_1}{r_2} \qquad \text{B.11}$$

$$\frac{\phi_1}{\theta_1} = \left(\frac{x_1 q_1}{x_1 q_1 + x_2 q_2}\right)\left(\frac{r_1 x_1 + r_2 x_2}{r_1 x_1}\right) \qquad \text{B.12a}$$

$$\rightarrow \frac{\theta_1}{\phi_1} = \frac{r_2 q_1}{r_1 q_2} \qquad \text{B.12}$$

$$\phi_2 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} \qquad \text{B.13a}$$

$$\rightarrow \phi_2 \; - \; 1 \qquad \text{B.13}$$

$$\theta_1' \; - \; \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'} \qquad \text{B.14a}$$

$$\rightarrow \theta_1' \; - \; 0 \qquad \text{B.14}$$

$$\theta_2' \; - \; \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'} \qquad \text{B.15a}$$

$$\rightarrow \theta_2' \; - \; 1 \qquad \text{B.15}$$

Note:

Corresponding equations with the LHS terms having the subscripts indicated in Equations B.11 - B.15 changed from 1 to 2 or 2 to 1, as the case may be, can be obtained in similar manner by substituting subscript 1 for subscript 2 or vice-versa, in those equations.

Substituting Equations B.11 - B.15 (and their corresponding equivalents derived by swapping subscripts 1 and 2) in Equations A.8 and A.9 we have :

$$\ln\gamma_1^{\infty} = \ln\frac{r_1}{r_2} + \frac{z}{2}q_1\ln\frac{r_2q_1}{r_1q_2} + (l_1 - \frac{r_1}{r_2}l_2) - q_1'\ln\tau_{21} + q_1'(1-\tau_{12}) \quad \text{B.16}$$

$$\ln\gamma_2^{\infty} = \ln\frac{r_2}{r_1} + \frac{z}{2}q_2\ln\frac{r_1q_2}{r_2q_1} + (l_2 - \frac{r_2}{r_1}l_1) - q_2'\ln\tau_{12} + q_2'(1-\tau_{21}) \quad \text{B.17}$$

By rearranging Equations B.16 and B.17 we have:

$$q_1'\ln\tau_{21} + q_1'(1-\tau_{12}) + k_1^{\infty} = 0 \quad \text{B.18}$$

$$q_2'\ln\tau_{12} + q_2'(1-\tau_{12}) + k_2^{\infty} = 0 \quad \text{B.19}$$

where:

$$k_1^{\infty} = \ln\gamma_1^{\infty} - \ln\frac{r_1}{r_2} - \frac{z}{2}q_1\ln\frac{r_2q_1}{r_1q_2} - (l_1 - \frac{r_1}{r_2}l_2) \quad \text{B.20}$$

$$k_2^{\infty} = \ln\gamma_2^{\infty} - \ln\frac{r_2}{r_1} - \frac{z}{2}q_2\ln\frac{r_1q_2}{r_2q_1} - (l_2 - \frac{r_2}{r_1}l_1) \quad \text{B.21}$$

B3: Using Binary Azeotropic Data

This method is useful if and only if:

$$0.25 \leq x_i \leq 0.75$$

where:

x_1 is the mole fraction of component i in the binary mixture

At equilibrium:

$$\varphi_i y_i P = \gamma_i x_i f_i^{OL} \quad \text{.....B.22}$$

For binary azeotrope:

$$y_i = x_i \quad \text{.....B.23}$$

$$\therefore \varphi_i P = \gamma_i f_i^{OL} \quad \text{.....B.24}$$

$$\rightarrow \gamma_i = \frac{\varphi_i P}{f_i^{OL}} \quad \text{.....B.25}$$

Taking the logarithm of the RHS of Equations A.8 and A.9 and, equating them in turn to the RHS of equation B.25, we have:

$$\frac{\varphi_1 P}{f_1^{OL}} = \exp\left(\ln\frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln\frac{\theta_1}{\phi_1} + \phi_2\left(l_1 - \frac{r_1}{r_2} l_2\right) - q_1' \ln(\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right)\right) \quad \text{.....B.26}$$

$$\rightarrow \ln(\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right) - k_1 = 0 \quad \text{.....B.27}$$

$$\frac{\varphi_2 P}{f_2^{OL}} = \exp\left(\ln\frac{\phi_2}{x_2} + \frac{z}{2}q_2\ln\frac{\theta_2}{\phi_2} + \phi_1\left(l_2 - \frac{r_2}{r_1}l_1\right) - q_2'\ln(\theta_2 + \theta_1\tau_{12}) + \theta_1 q_2\left(\frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}}\right)\right) \quad \text{.....B.28}$$

$$\rightarrow \ln(\theta_2 + \theta_1\tau_{12}) + \theta_1 q_2\left(\frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}}\right) - k_2 = 0 \quad \text{.....B.29}$$

In Equations B.27 and B.29 above:

$$k_i = \frac{1}{q_i'}\left(\ln\frac{\varphi_i P}{f_i^{OL}} - \ln\frac{\phi_i}{x_i} - \frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i} - \phi_j\left(l_i - \frac{r_i}{r_j}l_j\right)\right) \quad \text{.....B.30}$$

where:

φ_i *is fugacity coefficient of component i*

f_i^{OL} *is standard state fugacity coefficient of component i*

P *is pressure of the system*

i, j *are subscripts for components i, j*

APPENDIX C

LISTING OF PROGRAM FOR THE SIMULATION OF LIQUID-LIQUID EXTRACTION SCHEMES

```
c This program is an adaptation of the one due to Prausnitz et
c al [1980]. It is written to carry out a liquid-liquid equilib
c rium calculation for three component mixture- water, ammonia
c and solvent. The aim is to develop an ammonia-water-solvent ==
c extraction heat pump system.
      program dreli
      common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
     1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
     1,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)/
      real z(3),x(3),y(3),k(3)
      integer id(3),err,ir,ie
 100  call parin(3,er)
      if(er.gt.0)go to 900
 200  read(*,*)n,t,(id(i),i=1,n)
      if(n.eq.0)stop
      key=1
      write(6,11)n,t
 11   format(//30H LIQUID-LIQUID EQUILIBRIUM FOR,I3,23H
     1COMPONENT SYSTEM AT T=,F4.0)
      write(6,12)
 12   format(/1x,"INDEX",5X,"COMPONENT",15X,"FEED",6X,"R
     1PHASE",5X,"E PHASE"`8X,"K"/)
 210  read(*,*)ir,ie,(z(i),i=1,n)
      if(z(i).eq.0)stop
      sz=0.
      do 212 i=1,n
 212  sz=sz+z(i)
      if(sz.lt.0.999)go to 200
      call elip(n,id,key,ir,ie,z,t,v,x,y,k,ier)
      if(ier.gt.0)write(6,13) ier
 13   format(/9H ***ERROR,I2,3H***/)
 220  do 229 i=1,n
      ii=id(i)
      write(6,14)ii,nm1(ii),nm2(ii),z(i),x(i),y(i),k(i)
 14   format(2x,I3,2x,2A10,3F12.4,1PE14.2)
 229  continue
      write(6,15)v
 15   format(/3x,"E/R",1PE9.2////)
      go to 210
 900  write(6,19)
 19   format(/"ERROR IN PARAMETER INPUT DECK")
      stop
      end
      subroutine elips(n,id,key,ir,ie,z,t,a,xr,xe,k,err)
c elipe calculates conjugate phase compositions xr and xe for
c partially miscible n component liquid systems (n.le.20) of
c overall composition z at given temperature t(k).
      real

     z(n),xr(n),xe(n),k(n),gar(20),gae(20),ki(20),ks,kp,k2,
     1 rx(20),ex(20)
      integer id(n),err,erl
 100  err=0
      kee=key
```

```
      if(ir.eq.0.or.ie.eq.0)go to 101
      go to(101,130,130,130,130,130,130,130,101,130),key
c for new systems without ir, ie specified, find ir, ie as least
c soluble pair
 101  ks=1.
      kp=1.
 110  do 115 i=1,n
      xr(i)=0.
 115  xe(i)=0.
      j1=1
      if(ir.ne.0)go to 120
      if(ie.ne.0)go to 121
 116  do 119 j=2,n
      xr(j1) =0.
      xe(j1) =0.
      j1=j-1
      xr(j) =0.98
      xe(j) =0.02
      xr(j-1)=0.
      xe(j-1)=0.
      if(z(j)lt.0.10) go to 119
      do 118 i=1,j1
      xe(i)=0.98
      xr(i)=0.02
      if(i.gt.1)xe(i-1)=0.
      if(i.gt.1)xr(i-1)=0.
      if(z(i)lt.0.10) go to 118
      call lilik(n,id,kee,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1)go to 900
      kee=3
      if(k(i).le.ks)go to 117
      ks=k(i)
      is=i
 117  if(1./k(j).le.ks)go to 118
      ks=1./k(j)
      is=j
 118  continue
 119  continue
      xr(n)=0.
      xe(n)=0.
      xr(j1)=0.
      xe(j1)=0.
      go to 125
 120  if(ie.ne.0)go to 130
      is=ir
      go to 125
 121  is=ie
 125  xe(is)=0.98
      xr(is)=0.02
 126  do 129 j=1,n
      if(j.eq.is)go to 129
      xr(j)=0.98
      xe(j)=0.02
      if(j.eq.(is+1))go to 128
      if(j.gt.1)xr(j-1)=0.
      if(j.gt.1)xe(j-1)=0.
```

```
127   if(z(j).lt.0.10)go to 129
      call lilik(n,id,kee,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1)go to 900
      kee=3
      if(k(j).ge.kp)go to 129
      kp=k(j)
      ip=j
      go to 129
 128  if(j.gt.2)xr(j-2)=0.
      if(j.gt.2)xe(j-2)=0.
      go to 127
 129  continue
      ie=ip
      if(ir.ne.is)ie=is
      if(ie.ne.is)ir=ip
c initialize r and e phase compositions
 130  do 131 i=1,n
      xr(i)=0.
 131  xe(i)=0.
      xr(ir)=0.98
      xe(ir)=0.02
      xr(ie)=0.98
      xe(ie)=0.02
c get initial estimates v for k values
 135  call lilik(n,id,kee,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1)go to 900
      sz=0.
 136  do 137 i=1,n
      sz=sz+z(i)
 137  k1(i)=k(i)-1
      if(abs(sz-1.).gt.0.01)go to 903
c get initial estimate for a
      a=z(ie)/(z(ie)+z(ir))
      if(a.lt.0.)a=0.
      if(a.gt.1.)a=1.
      ao=a
      it=0
      kac=0
c conduct iteration over phase composition (outer loop)
 200  it=it+1
      if(it.gt.50)go to 900
      aa=ao
      ao=a
c conduct newton-raphson iteration for a at fixed k values
 300  do 319 m=1,10
      f=0.
      df=0.
 301  do 309 i=1,n
      k2=a*k1(i)+1.
      f=f+z(i)*k1(i)/k2
 309  df=df-z(i)*(k1(i)/k2)**2
      if(abs(f).lt.1.E-05)go to 210
      da=f/df
 310 an=a-da
c limit a to range 0-1 if it falls outside poles of f.
      if(an.lt.-1/kr(ir))go to 312
```

```
      an=a+(1./k1(ir)+a)/2.
      go to 319
 312  if(an.gt.-1./k1(ie))go to 319
      an=a+(1./k1(ie)+a)/2
 319  a=an
      sr=0.
      se=0.
c find new r and e phase compositions
 211  do 215 i=1,n
      xr(i)=z(i)/(a*k1(i)+1.)
      xe(i)=k(i)*xr(i)
      sr=sr+xr(i)
 215  se=se+xe(i)
 220  do 225 i=1,n
      xr(i)=xr(i)/sr
 225  xe(i)=xe(i)/se
c at alternate iterations after 3 accelerate phase composition
c by Wegstein method based on sum of deviations of component
c fugacities
 230  if(it.lt.3)go to 250
      if(it.le.5.and.(a.lt.0.or.a.gt.1.))go to 250
      if(kac.ge.1)go to 239
      if(ss.gt.s1)go to 250
      if(ss.gt.0.2)go to 250
      kac=1
      wg=ss/(s1-ss)
      wk=1.+wg
      sr=0.
      se=0.
      do 235 i=1,n
      xr(i)=wk*xr(i)-wg*rx(i)
c allow no negative mol fraction
      if(xr(i)lt.0.)xr(i)=0.
      xe(i)=wk*xe(i)-wg*ex(i)
      if(xe(i).lt.0.)xe(i)=0.
 235  se=se+xe(i)
c normalize accelerated compositions (to allow for xr(i) or xe(i)
c set to 0)
 236  do 237 i=1,n
      xr(i)=xr(i)/sr
 237  xe(i)=xe(i)/se
      go to 250
 239  kac=0
c get new k and gamma values
 250  call lilik(n,id,3,xr,xe,t,k,gar,gae,erl)
      if(erl.gt.1)go to 900
      ess=1.E-03
      if(it.le.5)go to 252
c check for vicinity of plait point
      ppi=k(ir)/k(ie)+k(ie)/k(ir)
      if(ppi.gt.10..or.ss.gt.0.05)go to 251
c exit if too near plait point
      if(it.ge.20)go to 290
      if(ppi.gt.7.)go to 251
c check if calculation near plait point is probably in single
c phase region--if so continue
```

```
      de=ao
      if(de.gt.0.5)de=ao-1.
      di=(aa-a)/de
      if(di.lt.0.1) go to 290
 251  if(ppi.lt.20)ess=2.E-04
 252  sl=ss
      ss=0.
 253  do 255 i=1,n
      kl(i)=k(i)-1.
c calculate objective function
 255  ss=ss+abs(gae(i)*xe(i)-gar(i)*xr(i))
c check convergence
      if(ss.le.ess)go to 190
      if(a.ge.0..and.a.le.1.)go to 260
      if(it.lt.3.or.ss.gt.0.20)go to 260
      if(it.lt.5.and.ss.gt.0.05)go to 260
c check if a moving away from 0-1 region
      if(abs(a)-abs(ao).gt.0.)go to 195
c save last phase compositions for use in acceleration
 260  do 265 i=1,n
      rx(i)=xr(i)
 265  ex(i)=xe(i)
      go to 200
c feed in vicinity of plait point--check if in two phase
c region
 290  if(a.ge.0..and.a.le.1.)go to 905
      go to 195
c do not allow convergence on accelerated iteration
 190  if(kac.eq.1)go to 260
c converged solution--check if in two phase region
 191  if(a.lt.0..or.a.gt.1.)go to 195
      err=erl
      return
c feed outside two phase region
 195  do 195 i=1,n
      xr(i)=z(i)
 196  xe(i)=z(i)
      if(a.lt.0.)a=0
      if(a.gt.1.)a=1
      err=erl
      return
c on failure to converge set a to -1 and er to 2
 900  err=2
      go to 910
c for bad input data set a to -1 and err to 5
 903  err=5
      go to 910
c for feed too near plait point set a to -1 and err to 7
 905  err=7
 910  do 911 i=1,n
      xr(i)=z(i)
 911  xe(i)=z(i)
      a=-1.
      return
      end
```

```
      subroutine gamma(n,id,key,x,t,gam,erg)
      real x(20),gam(20),pt(20),pts(20)
      integer id(20),erg
     common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
    1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
    1,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/gs/ier,rl(20),th(20),tp(20),gcl(20),tau(20,20)
      data z/10./
100   go to(110,120,120,130,130,120,130,120,110,120),key
110   erg=0
111   do 119 i=1,n
      ii=id(i)
119   rl(i)=z*(ru(ii)-qu(ii))/2.-ru(ii)+1.
120   sp=1.E-30
      st=1.E-30
      stp=1.E-30
      ss=0.
      sl=0.
121   do 125 i=1,n
      ii=id(i)
      th(i)=x(i)*qu(ii)
      tp(i)=x(i)*qp(ii)
      sp=sp+x(i)*ru(ii)
      st=st+th(i)
      stp=stp+tp(i)
      if(u(ii,ii).gt.1.E+19)go to 125
      ss=ss+x(i)
      sl=sl+x(i)*rl(i)
125   continue
126   do 129 i=1,n
      ii=id(i)
      th(i)=th(i)/st
      tp(i)=tp(i)/stp
      if(u(ii,ii).gt.1.E+19)go to 128
127   gcl(i)=rl(i)-ru(ii)*sl/sp+alog(ru(ii)*ss/sp)+z*qu(ii)*
     1 alog(qu(ii)*sp/(ru(ii)*st))/2
      go to 129
128   gcl(i)=0.
129   continue
      if(key.eq.3)go to 140
130   call taus(n,id,t,tau,ier)
140   do 141 i=1,n
141   pts(i)=0.
142   do 149 i=1,n
      pt(i)=1.E-30
      do 143 j=1,n
143   pt(i)=pt(i)+tp(j)*tau(j,i)
      do 145 j=1,n
145   pts(j)=pts(j)+tp(i)*tau(j,i)/pt(i)
149   continue
150   do 159 i=1,n
      ii=id(i)
      if(u(ii,ii).gt.1.E+19)go to 155
      grl=qp(ii)*(1.-alog(pt(i))-pts(i))
      go to 158
```

```
155   grl=0.
      do 156 j=1,n
      jj=id(j)
156   grl=grl+th(j)*(u(ii,jj)+u(jj,ii)/t)
158   gam(i)=exp(gcl(i)+grl)
159   continue
      if(iabs(ier).eq.1)erg=1
      return
      end
      subroutine taus(n,id,t,tau,ier)
      real tau(20,20)
      integer id(20)
      common/binary/eta(5050),u(100,100)
100   ier=0
110   do 119 i=1,n
      ii=id(i)
      if(u(ii,ii).gt.1.E+19)ier=isign(ier**2-2,-1)
      do 119 j=1,n
      if(j.eq.i)go to 115
      jj=id(j)
      if(u(ii,ii).gt.1.E+19.and.u(jj,jj).gt.1.E+19)go to
     1  115
      if(abs(u(ii,jj)).lt.1.E-19)go to 112
      if((u(ii,ii)+u(jj,jj)).gt.1.E+19)go to 115
      tau(i,j)=exp(-u(ii,jj)/t)
      go to 119
112   ier=isign(i,ier)
115   tau(i,j)=1
119   continue
      return
      end
      subroutine parin(m,erin)
      integer erin
      common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
     1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
     2,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/addp/wa(100),zc(100),vc(100)
100   erin=0
      if(m.gt.100)go to 900
      do 109 i=1,m
      read(*,01)j,nm1(j),nm2(j),nm3(j)
      read(*,*)j,tc(j),pc(j),a(j),rd(j),dm(j),ru(j),
     1qu(j),qp(j)
      if(j.ne.i)go to 900
 01   format(i3,A4,A4,A4)
      read(*,*)j,c1(j),c2(j),c3(j),c4(j),c5(j)
      if(j.ne.i)go to 900
      read(*,*)j,d1(j),d2(j),d3(j),d4(j),wa(j),zc(j),vc(j)
      if(j.ne.i)go to 900
109   continue
      read(*,*)j
      if(j.ne.0)go to 900
110   do 119 i=1,m
      i1=(i-1)*i/2+1
      i2=(i-1)*i/2+i
```

```
      read(*,*)(eta(ij),ij=i1,i2)
 119  continue
      read(*,*)e
      if(abs(e).gt.1.E-19)go to 900
 120  do 121 i=1,m
      do 121 j=1,m
 121  u(i,j)=0.
 125  read(*,*)i,j,uij,uji
      if(i.eq.0)go to 130
      u(i,j)=uij
      u(j,i)=uji
      go to 125
 130  do 139 i=1,m
      if(a(i).lt.1.E-19)u(i,i)=1.E+20
 139  continue
      return
 900  erin=5
      return
      end
      subroutine lilik(n,id,key,xr,xe,t,k,gar,gae,err)
c lilik calculates two phase effective liquid equilibrium ratios
c k for all n components (n.le.20) whose indices appear in vector
c id.
      real xr(n),xe(n),k(n),gar(n),gae(n),x(20),y(20),gx(20),
     1 gy(20)
      integer id(n),idf(20),err,erg
 100  err=0
c convert composition vectors to dimension 20 to match lower
c level subroutine
 101  do 102 i=1,n
      x(i)=xr(i)
      y(i)=xe(i)
 102  idf(i)=id(i)
c get r and e phase activity coefficients
      call gamma(n,idf,key,x,t,gx,erg)
      call gamma(n,3,y,t,gy,erg)
c convert activity coefficient vectors to dimension n
 110  do 119 i=1,n
      gar(i)=gx(i)
      gae(i)=gy(i)
      k(i)=gar(i)/gae(i)
      if(k(i).le.0..or.k(i).gt.1.E+19)go to 900
 119  continue
      err=erg
      return
c for a k value out of range set err to 2
 900  err=2
      do 905 i=1,n
 905  k(i)=0
      return
      end
```

APPENDIX D

LISTING OF PROGRAM FOR THE ESTIMATION OF BINARY PARAMETERS OF UNIQUAC EQUATION

D1: Listing of the program for the estimation of the UNIQUAC binary parameters using mutual solubility data

```
      program musop
c This program calculates the binary interaction parameters from
c mutual solubility data using UNIQUAC equation. The non-linear
c equations are solved by the Newton-Raphson iterative procedure
      dimension tau(4),tinc(4),v(4,4)
      common/mix/xo(2),xt(2),wo(2),wt(2),vo(2),vt(2)
      common/pure/qp(2),qu(2),ru(2),mw(2)
      realtpo(2),tpt(2),tuo(2),tut(2),pso(2),pst(2),el(2),mw(2)
     1 ,t
      integer idl,it,iprint
      data z/10./
      n=2
c read or write the title, control data and pure component data
      read(*,110)(nam(1,j),j=1,5),(nam(2,j),j=1,5),(mw(i),rho
     1 (i),i=1,2)
  110 format(2A15,4(F10.5))
      write(*,110)(nam(1,j),j=1,5),(nam(2,j),j=1,5),nam(1),mw
     1 (1),rho(1),mw(2),rho(2)
      read(*,*)it,idl,iprint,n,ivap,del1,del2,(tau(i),i=1,2)
      if(it.eq.0)go to 950
      write(*,225)it,iprint,v,del1,del2,(tau(i),i=1,2)
      read(*,*)(qp(i),qu(i),ru(i),i=1,2)
      if(idl.eq.1)go to 345
      if(idl.eq.2)go to 310
      read(*,*)wo(2),wt(1)
      wo(1)=1.-wo(2)
      wt(2)=1.-wt(1)
      go to 355
  310 read(*,*)vo(2),vt(1)
      vo(1)=1.-vo(2)
      vt(2)=1.-vt(1)
      go to 340
  345 read(*,*)xo(2),xt(1)
      xo(1)=1.-xo(2)
      xt(2)=1.-xt(1)
      go to 365
  340 do 350 i=1,2
      wo(i)=vo(i)*rho(i)
      wt(i)=vt(i)*rho(i)
  350 continue
      xo(1)=1./(1.+(mw(1)*wo(2))/mw(2)*wo(1))
      xo(2)=1./(1.+(mw(2)*wo(1))/mw(1)*wo(2))
      xt(1)=1./(1.+(mw(1)*wt(2))/mw(2)*wt(1))
      xt(2)=1./(1.+(mw(2)*wt(1))/mw(1)*wt(2))
  365 do 370 i=1,2
      do 370 j=1,2
      if(i.eq.j)go to 370
      tpo(i)=xo(i)*qp(i)/(xo(i)*qp(i)+xo(j)*qp(j))
      tpt(i)=xt(i)*qp(i)/(xt(i)*qp(i)+xt(j)*qp(j))
      tuo(i)=xo(i)*qu(i)/(xo(i)*qu(i)+xo(j)*qu(j))
      tut(i)=xt(i)*qp(i)/(xt(i)*qp(i)+xt(j)*qp(j))
      pso(i)=xo(i)*ru(i)/(xo(i)*ru(i)+xo(j)*ru(j))
```

```
      tpo(i)=xo(i)*ru(i)/(xo(i)*ru(i)+xo(j)*ru(j))
      el(i)=(z/2)*(ru(i)-qu(i))-(ru(i)-1.)
      const(i)=alog(pst(i)/pso(i))+z*qu(i)*alog(tut(i)
     1 *pso(i)/tuo(i)*pst(i)))/2+(el(i)-ru(i)*el(j)/ru(j)
     2 *(pst(j)-pso(j)))/qp(i)
 370  continue
c Newton-Raphson iteration
      do 155 m=1,it
c load partial derivatives array
      v(2,1)=tpt(1)/(tpt(2)+tpt(1)*tau(1))-tpo(1)/(tpo(2)+tpo(1)
     1*tau(1))+(tpo(2)*tpo(1)/(tpo(2)+tpo(1)*tau(1)))**2-tpt(2)
     2 *tpt(1)/(tpt(2)+tpt(1)*tau(1)))**2
      v(2,2)=(tpt(1)/(tpt(1)+tpt(2)*tau(2)))**2-(tpo(1)/(tpo(1)+
     1 tpo(2)*tau(2)))**2
      v(1,2)=tpt(2)/(tpt(1)+tpt(2)*tau(2))-tpo(2)/(tpo(1)+tpo(2)
     1*tau(2))+(tpo(1)*tpo(2)/(tpo(1)+tpo(2)*tau(2)))**2-tpt(1)
     2 *tpt(2)/(tpt(1)+tpt(2)*tau(2)))**2
      v(1,1)=(tpt(2)/(tpt(2)+tpt(1)*tau(1)))**2-(tpo(2)/(tpo(2)+
     1 tpo(1)*tau(1)))**2
      v(2,3)=const(2)-alog((tpt(2)+tpt(1)*tau(1))/(tpo(2)+tpo(1)
     1*tau(1)))-tpo(1)*tau(1)/(tpo(2)+tpo(1)*tau(1)+tpo(1)*tau(
     2 2)/(tpo(1)+tpo(2)*tau(2))+tpt(1)*tau(1)/(tpt(2)+tpt(1)*
     3 tau(1))+tpt(1)*tau(2)/(tpt(1)+tpt(2)*tau(2))
      v(1,3)=const(1)-alog((tpt(1)+tpt(2)*tau(2))/(tpo(1)+tpo(2)
     1*tau(2)))-tpo(2)*tau(2)/(tpo(1)+tpo(2)*tau(2)+tpo(2)*tau(
     2 2)/(tpo(2)+tpo(1)*tau(1))+tpt(2)*tau(2)/(tpt(1)+tpt(2)*
     3 tau(2))+tpt(2)*tau(1)/(tpt(2)+tpt(1)*tau(1))
c call simul to compute jacobian and correction in tinc
      deter=simul(2,v,tinc,del1,1,21)
      if(deter.ne.0)go to 300
      write(6,201)
      go to 65
c check for convergence and update tau values
 300  itcon=1
      do 500 i=1,2
      if(abs(tinc(i)).gt.del2)itcon=0
      if(iprint.eq.1)write(6,202)m,deter,tau(1),tau(2)
      if(itcon.eq.0)go to 155
      write(6,203)m,tau(1),tau(2),tinc(1),tinc(2)
 155  continue
      do 25 i=1,n
      u(i)=t*(alog(1./tau(i)))
      write(6,209)
      write(6,204)
 65   read(*,*)e
      if(e.ne.0)go to 200
 115  format(2F10.5,F10.2)
 201  format(38HOMATRIX IS ILL-CONDITIONED OR SINGULAR)
 202  format(6HOM   = ,I8/ 10HODETER =   ,E18.5/1X,"TAU(1)=
     1 ",F10.5,"TAU(2)= ",F10.5)
 201  format(38HOSUCCESSFUL CONVERGENCE /10HOIT   =   ,I3/1X,
     1 "TAU(1)= ",F10.5,"TAU(2)= ",F10.5/1X,"TINC(1)= ",1PE15.4
     2 ,2X,TINC(2)= ",1PE15.4)
 204  format(15HONO CONVERGENCE)
 205  format(1X,"PARAMETER ESTIMATION FROM MUTUAL SOLUBILITY
     DATA
```

```
     1 FOR",1X,3A4,"-"3A4,1X,"SYSTEM")
 206  format(1X,3A4,3X,F10.5,F10.2)
 209  format(1X,"U(1)= ", F10.5,5X,"U(2)= ",F10.5)
 225  format(8H1IT  =  ,I8/ 10H IPRINT = ,I8/10H N  =  ,I8/ 10H
     1 DEL1  =  ,E8.2/ 10H DEL2  =  ,E8.2/ 1X,"TAU(1) =",F12.5,
     2 8X,       "TAU(2) =",F12.5/)
      stop
      end

      function simul(n,b,x,eps,indic,nrc)
      real b(3,3),x(2),eps,simul
      dimension irow(2),jcol(2),jord(2)y(2),pivot(2)
      max=n
      if(indic.ge.0)max=n+1
c  is n larger than 50?
      if(n.le.50)go to 5
      write(*,200)
      simul=0
      return
c  begin elimination procedure
 5    deter=1.
      do 18 k=1,n
      kml=k-1
c search for pivot element
      pivot(k)=0.
      do 11 i=1,n
      do 11 j=1,n
c  scan irow and jcol arrays for invalid pivot subscripts
      if(k.eq.1)go to 9
      do 8 iscan=1,kml
      do 8 jscan=1,kml
      if(i.eq.irow(iscan))go to 11
      if(j.eq.jrow(jscan))go to 11
 8    continue
      if(abs(b(i,j)).le.abs(pivot(i))go to 11
      pivot(i)=b(i,j)
      irow(k)=i
      jrow(k)=j
 11   continue
c  insure that selected pivot is larger than eps
      if(abs(pivot(i).gt.eps)go to 13
      simul=0
      return
c  update the determinant value
 13   irowk=irow(k)
      jcolk=jcol(k)
      deter=deter*pivot(i)
c  normalize pivot row elements
      do 14 j=1,max
 14   b(irowk,j)=b(irowk,j)/pivot(i)
c  carry out summation and develop inverse
      b(irowk,jcolk)=1./pivot(i)
      do 18 i=1,n
      bijck=b(i,jcolk)
      if(i.eq.irowk)go to 18
```

```
      do 17 j=1,max
 17   if(j.ne.jcolk)b(i,j)=b(i,j)-bijck*b(irowk,j)
 18   continue
c order solution values(if any) and create jord array
      do 20 i=1,n
      irowi=irow(i)
      jcoli=jcol(i)
      jord(irowi)jcoli
 20   if(indic.ge.0)x(jcoli)=b(irowi,max)
c adjust sign of determinant
      intch=0
      nm1=n-1
      do 22 i=1,nm1
      ip1=i+1
      do 22 j=ip1,n
      if(jord(j).ge.jord(i))go to 22
      jtemp=jord(j)
      jord(j)=jord(i)
      jord(i)=jtemp
      intch=intch+1
 22   continue
      if(intch/2.ne.intch)deter=-deter
c  if intch is positive return with results
      if(indic.le.0)go to 26
      simul=deter
      return
c  if indic is negative or zero unscramble
c  the inverse first by rows
 26   do 28 j=1,n
      do 28 i=1,n
      irowi=irow(i)
      jcoli=jcol(i)
      y(jcoli)=b(irowi,j)
 28   b(i,j)=y(i)
      do 30 i=1,n
      do 30 j=1,n
      irowj=irow(j)
      jcolj=jcol(j)
      y(irowi)=b(i,irowj)
      y(jcolj)=b(i,jcolj)
 30   b(i,j)=y(j)
c  return for indic negative or zero
      simul=deter
      return
c  format for output statement
 200  format(10H0N TOO BIG)
      end
```

D2: Listing of the program for the estimation of the UNIQUAC binary parameters using infinite dilution coefficient data

```
      program infinite
c This program calculates the binary iteraction parameters from
c infinite dilution data using UNIQUAC equation. The non-linear
c equations are solved by the Newton-Raphson iterative procedure
```

```
      dimension tau(4),tinc(4),v(4,4)
      common/pure/qp(2),qu(2),ru(2)
      real mw(2),t,gamif(2)
      integer idl,it,iprint
      data z/10./
      n=2
c read or write the title, control data and pure component data
      read(*,110)(nam(1,j),j=1,5),(nam(2,j),j=1,5),(gamif(i),
     1 i=1,2),t
 110  format(2(3A4),3F10.5)
      write(*,110)(nam(1,j),j=1,5),(nam(2,j),j=1,5),(gamif(i),
     1 i=1,2),t
      read(*,*)it,idl,iprint,n,ivap,del1,del2,(tau(i),i=1,2)
      if(it.eq.0)go to 950
      write(*,225)it,iprint,v,del1,del2,(tau(i),i=1,2)
      read(*,*)(qp(i),qu(i),ru(i),i=1,2)
      do 370 i=1,2
      el(i)=(z/2)*(ru(i)-qu(i))-(ru(i)-1.)
      const(i)=alog(gamif(i)*ru(j)/ru(i))-(z/2)qu(i)*alog(ru(j)*
     1 *qu(i)/ru(i)*qu(j))-el(i)+ru(i)*el(j)/ru(j)
     2 *(pet(j)-pso(j)))/qp(i)
 370  continue
c Newton-Raphson iteration
      do 155 m=1,it
c load partial derivatives array
      v(2,1)=1./tau(1)
      v(2,2)=1.
      v(1,2)=1./tau(2)
      v(1,1)=1.
      v(2,3)=qp(2)*alogtau(1)-qp(2)*(1.-tau(2))+const(2)
      v(1,3)=qp(1)*alogtau(2)-qp(1)*(1.-tau(1))+const(1)
c call simul to compute jacobian and correction in tinc
      deter=simul(2,v,tinc,del1,1,21)
      if(deter.ne.0)go to 300
      write(6,201)
      go to 65
c check for convergence and update tau values
 300  itcon=1
      do 500 i=1,2
      if(abs(tinc(i)).gt.del2)itcon=0
      if(iprint.eq.1)write(6,202)m,deter,tau(1),tau(2)
      if(itcon.eq.0)go to 155
      write(6,203)m,tau(1),tau(2),tinc(1),tinc(2)
 155  continue
      do 25 i=1,n
      u(i)=t*(alog(1./tau(i)))
      write(6,209)
      write(6,204)
 65   read(*,*)e
      if(e.ne.0)go to 200
 125  format(3I10/10X,E7.2,13X,E7.2/20X,2F10.3)
 201  format(38H0MATRIX IS ILL-CONDITIONED OR SINGULAR)
 202  format(6H0M   = ,I8/ 10H0DETER =   ,E18.5/1X,"TAU(1)=
     1 ",F10.5,"TAU(2)= ",F10.5)
 201  format(38H0SUCCESSFUL CONVERGENCE /10H0IT   =   ,I3/1X,
     1 "TAU(1)= ",F10.5,"TAU(2)= ",F10.5/1X,"TINC(1)= ",1PE15.4
```

```
     2 ,2X,TINC(2)= ",1PE15.4)
 204  format(15HONO CONVERGENCE)
 205  format(1X,"PARAMETR ESTIMATION FROM INFINITE DILUTION ACTI
     1 VITY COEFFICIENT FOR",1X,3A4,"-"3A4,1X,"SYSTEM")
 206  format(1X,3A4,3X,F10.5,F10.2)
 209  format(1X,"U(1)= ", F10.5,5X,"U(2)= ",F10.5)
 225  format(8H1IT  =  ,I8/ 10H IPRINT = ,I8/10H N  =  ,I8/ 10H
     1 DEL1  =  ,E8.2/ 10H DEL2  =  ,E8.2/ 1X,"TAU(1) =",F12.5,
     2 8X,       "TAU(2) =",F12.5/)
      stop
      end
      function simul(n,b,x,eps,indic,nrc)
      real b(3,3),x(2),eps,simul
      dimension irow(2),jcol(2),jord(2)y(2),pivot(2)
      max=n
      if(indic.ge.0)max=n+1
c  is n larger than 50?
      if(n.le.50)go to 5
      write(*,200)
      simul=0
      return
c  begin elimination procedure
 5    deter=1.
      do 18 k=1,n
      km1=k-1
c seach for pivot element
      pivot(k)=0.
      do 11 i=1,n
      do 11 j=1,n
c  scan irow and jcol arrays for invalid pivot subscripts
      if(k.eq.1)go to 9
      do 8 iscan=1,km1
      do 8 jscan=1,km1
      if(i.eq.irow(iscan))go to 11
      if(j.eq.jrow(jscan))go to 11
 8    continue
      if(abs(b(i,j)).le.abs(pivot(i))go to 11
      pivot(i)=b(i,j)
      irow(k)=i
      jrow(k)=j
 11   continue
c  insure that selected pivot is larger than eps
      if(abs(pivot(i).gt.eps)go to 13
      simul=0
      return
c  update the determinant value
 13   irowk=irow(k)
      jcolk=jcol(k)
      deter=deter*pivot(i)
c  normalize pivot row elements
      do 14 j=1,max
 14   b(irowk,j)=b(irowk,j)/pivot(i)
c  carry out summation and develop inverse
      b(irowk,jcolk)=1./pivot(i)
      do 18 i=1,n
      bijck=b(i,jcolk)
```

```
      if(i.eq.irowk)go to 18
      b(i,jcolk)=-bijck/pivot(i)
      do 17 j=1,max
 17   if(j.ne.jcolk)b(i,j)=b(i,j)-bijck*b(irowk,j)
 18   continue
c  order solution values (if any) and create jord array
      do 20 i=1,n
      irowi=irow(i)
      jcoli=jcol(i)
      jord(irowi)jcoli
 20   if(indic.ge.0)x(jcoli)=b(irowi,max)
c  adjust sign of determinant
      intch=0
      nm1=n-1
      do 22 i=1,nm1
      ip1=i+1
      do 22 j=ip1,n
      if(jord(j).ge.jord(i))go to 22
      jtemp=jord(j)
      jord(j)=jord(i)
      jord(i)=jtemp
      intch=intch+1
 22   continue
      if(intch/2.ne.intch)deter=-deter
c  if intch is positive return with results
      if(indic.le.0)go to 26
      simul=deter
      return
c  if indic is negative or zero unscramble
c  the inverse first by rows
 26   do 28 j=1,n
      do 28 i=1,n
      irowi=irow(i)
      jcoli=jcol(i)
      y(jcoli)=b(irowi,j)
 28   b(i,j)=y(i)
      do 30 i=1,n
      do 30 j=1,n
      irowj=irow(j)
      jcolj=jcol(j)
      y(irowi)=b(i,irowj)
      y(jcolj)=b(i,jcolj)
 30   b(i,j)=y(j)
c  return for indic negative or zero
      simul=deter
      return
c  format for output statement
 200  format(10H0N TOO BIG)
      end
```

APPENDIX E

LISTINGS OF PROGRAMS FOR FIRST AND SECOND LAWS' ANALYSES

E1: Listing of Driver Program for First and Second Laws of Thermodynamics' Analyses for "ESA" Absorption Heat Pump Systems

```
      program thermo
      real ieva,icon,ige,iab,ieco,iva1,iva2,iext,irec,ist,
     1it,mw(3),k(10),nbp(10)
      common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
     1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
     2,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/addp/wa(100),zc(100),vc(100)
      dimension hbv(10),wfc(10),x(10),y(10),id(10),xf(10),cp(10),
     1 yf(10),gam(10),xx(10),yy(10),xm(10),xw(10),wf(10),hv(10)
100   call parin(3,er)
      if(er.gt.0)go to 900
      read(*,*)n,ice,(id(i),i=1,n)
      do 111 i=1,n
      read(*,*)nbp(i),mw(i),cp(i),hv(i)
111   continue
      read(*,*)tev,tab
      read(*,*)fs,rr,(xw(i),i=2,3)
      dbp=abs(nbp(3)-nbp(2))
      if(ice.eq.1)then
          write(*,1500)
      else
          write(*,2000)
      endif
1500  format(18x,'THEORECTICAL COP AND IRREVERSIBILITY IN THE
     1MAIN UNITS OF'/19X,'AMMONIA-WATER ABSORPTION HEAT PUMP WITH
     2EXTRACTION UNIT'/30X,'ATTACHED IN THE LOW PRESSURE
     1SECTION'/)
2000  format(18x,'THEORETICAL COP AND IRREVERSIBILITY IN THE
     1MAIN UNITS OF'/19X,'AMMONIA-WATER ABSORPTION HEAT PUMP WITH
     2EXTRACTION UNIT'/30X,'ATTACHED IN THE HIGH PRESSURE
     1SECTION'/)
      tco=tab
      call vap(tco,tc(2),pc(2),nbp(2),pst)
      pco=pst
      call vap(tev,tc(2),pc(2),nbp(2),pev)
      pab=pev
      write(*,4000)tev,tab,pev,pco,nm1(3),nm2(3),nm3(3),cp(3)
     1,hv(3),dbp
4000  format(21x,'EVAPORATOR TEMPERATURE (K)          =  ',F6.2/
     121x,'ABSORBER TEMPERATURE (K)             =  ',F6.2/
     121X,'EVAPORATOR PRESSURE (BAR)            =  ',F6.2/
     221X,'CONDENSER  PRESSURE (BAR)            =  ',F6.2/
     317x,'APPROACH TEMPT TO ABSORBER (K)        =   10.00'/
     417X,'EXTRACTING  SOLVENT  EMPLOYED         : ',A4,A4,A4/
     517X,'SOLV HEAT CAP-ca. 303K (kJ/KG.K)      =  ',F6.2/
     617X,'SOLV HEAT OF VAP-normal b. pt. (kJ/KG)=  ',F6.2/
     717X,'BOILING POINT DIFFERENCE (K)          =  ',F6.2/)
      do 52 kk=1,2
      sfr=float(kk)*fs
      sf=sfr/(1.+sfr)
```

```
      do 54 jj=1,2
      r=float(jj)*rr
      do 55 ll=1,2
      cst1=float(ll-1)*10.+36.
      cst=cst1/100.
      dma=cst/mw(2)
      dmw=(1.-cst)/mw(1)
      fma=dma/(dma+dmw)
      fmw=1.-fma
      do 56 mm=1,3
      cwk1=float(mm-1)*10.+15.
      cwk=cwk1/100.
      wma=cwk/mw(2)
      wmw=(1.-cwk)/mw(1)
      fwa=wma/(wma+wmw)
      fww=1.-fwa
      if((cst1-cwk1).lt.10.)go to 56
      fm1=r+1.0
      fm2a=1.0
      fm3=1.0
      fm5=1.0/(cst-cwk)
      fm4=fm5-1.0
      fm10=r
      if(ice.eq.1)then
          fm2=fm1
          t4=tab
      else
          fm6=fm5
          fm4a=fm4
          fm2=1.0
          t4=tab+10.
          t4a=t4
          t7a=tab
      endif
      t0=293.15
      t1=278.15
      te=298.15
c ********laws analysee*******
c ========evaporator========
      wfc(1)=0.0
      wfc(2)=1.0
      call enth(2,id,1,0,wfc,tco,pco,h2a,ere)
      call enth(2,id,1,2,wfc,tev,pev,h3,ere)
      h2a=h2a/mw(2)
      h3=h3/mw(2)
      qev=fm3*h3-fm2a*h2a
      ieva=qev*((t0/tev)-(t0/t1))
c ========expansion valve to evaporator (EXVA2)=====
      nvt=2
      call rho((tev+tco)/2,ice,nvt,pco,pev,(pco+pev)/2,pc,tc,
     1zc,mw,vc,wa,rh)
      iva2=fm2*(pco-pev)*rh*1.01325
c =========condenser=========
      h2=h2a
      if(abs(nbp(3)-nbp(2)).lt.200.)then
          t1=tco
```

```
else
     t1=tco+10.
     fm8=sfr/(cst-cwk)
     fm8a=fm8
     fm8b=fm8
     fm7=fm8+fm1
endif
call enth(2,id,1,2,wfc,t1,pco,h1,ere)
h1=h1/mw(2)
qcon=fm1*(h2-h1)
wf(1)=1.0
wf(2)=0.0
call enth(2,id,1,2,wf,t0,1.01325,hi,ere)
call enth(2,id,1,2,wf,ts,1.01325,ho,ere)
qcono=(ho-hi)/mw(1)
r2=abs(qcon/qcono)
tlm=(ts-t0)/alog(ts/t0)
acon=qcon*(1.-ts/tco)
acono=qcono*(1.-t0/tlm)
icon=-(acon+r2*acono)
text=tab
t5=tab
t6=text
t10=tco
     if(abs(nbp(3)-nbp(2)).lt.200.)then
c **compute if nbp tempt diff between solvent and ammonia not
c **large enough
c =========rectifier==========
          faw=xw(2)*mw(2)/(xw(2)*mw(2)+xw(3)*mw(3))
          fsw=1.-faw
          saw=sfr*faw/fsw
          fm8=(sfr+saw)/(cst-cwk)
          fm8a=fm8
          fm8b=fm8
          fm7=fm8+fm1
          ap=(r+1.)*(cst-cwk)+sfr+saw
          sm=sfr/ap
          fm=1.-sm
          xfm=fm/mw(2)
          xsm=sm/mw(3)
          xm(2)=xfm/(xfm+xsm)
          xm(3)=1.-xm(2)
          y(2)=.950
          y(3)=.050
          call budet(1,3,id,1,xw,y,t,pst,k,err)
          tst=t
          pco=pst
          camv=y(2)*mw(2)/(y(2)*mw(2)+y(3)*mw(3))
          rf=(camv-faw)/(1.+r)
          fm9=(fm-faw)*fm7/rf
          fm9a=fm9-fm1
          t8=tst
          t9=t8
          t8a=text+10.
          t8b=t8
          t9a=tco
```

```
            call enth(3,id,1,2,y,tst,pco,h9,ere)
            h9=h9/(y(2)*mw(2)+y(3)*mw(3))
            x(2)=0.0
            x(3)=1.0
            call enth(3,id,1,0,xw,tco,pco,h9a,ere)
            h9a=h9a/(xw(2)*mw(2)+xw(3)*mw(3))
            qrec=fm9a*h9a+fm1*h1-fm9*h9
            qreco=acono
            tlm=(ts-t0)/alog(ts/t0)
            areco=qreco*(1.-t0/tlm)
            tlm=(tst-tco)/alog(tst/tco)
            arec=qrec*(1.-t0/tlm)
            rrec=abs(qrec/qreco)
            irec=-(arec+rrec*areco)
c ===========vaporiser==========
            if(ice.eq.1)then
                 fm6=fm7
                 fm5a=fm6
                 t5a=fm8*(t8-t8a)/fm6+t6
                 t7=t5a
            else
                 fm7a=fm7
                 t7=fm8*(t8-t8a)/fm7+t6
            endif
            call enth(3,id,1,0,xw,t8,pco,h8,ere)
            h8=h8/(xw(2)*mw(2)+xw(3)*mw(3))
            call enth(3,id,1,0,xm,t7,pco,h7,ere)
            h7=h7/(xm(2)*mw(2)+xm(3)*mw(3))
            qst=(fm8*h8+fm9*h9)-(fm9a*h9a+fm7*h7)
            call enth(3,id,1,0,x,tst,pco,h9s,ere)
            h9s=h9s/(x(2)*mw(2)+x(3)*mw(3))
            qsts=fm9*h9s-fm7*h7
            tlm=(tst-t7)/alog(tst/t7)
            asts=qsts*(1.-t0/tlm)
            astv=(qst-qsts)*(1.-t0/tst)
            ast=asts+astv
            astq=qst*(1.-t0/tst)
            ist=astq-ast
       else
c **compute if nbp tempt diff between solvent and ammonia is
c **large enough,ammonia heated 10 deg C. above boiling point
c ========vaporiser==========
            xw(2)=0.0
            xw(3)=0.0
            tst=tco+10.
            t1=tst
            t8=tst
            t8a=t8
            t8b=t8
            if(ice.eq.1)then
                 fm6=fm7
                 fm5a=fm6
                 t5a=text
                 t7=t5a
            else
                 fm7a=fm7
```

```
                t7=text
              endif
              xw(2)=0.0
              xw(3)=1.0
              call enth(3,id,1,0,xw,t8,pco,h8,ere)
              h8=h8/mw(3)
              ap=(r+1.)*(cst-cwk)+sfr
              sm=sfr/ap
              fm=1.-sm
              xfm=fm/mw(2)
              xsm=sm/mw(3)
              xf(2)=xfm/(xfm+xsm)
              xf(3)=1.-xf(2)
              call enth(3,id,1,0,xf,t7,pco,h7,ere)
              h7=h7/(xf(2)*mw(2)+xf(3)*mw(3))
              tlm=(tst-t7)/alog(tst/t7)
              call enth(2,id,1,2,wfc,t7,pco,hlv,ere)
              call enth(2,id,1,0,wfc,t7,pco,hls,ere)
              h7a=(hlv-hls)/mw(2)
              qst=(fml*hl+fm8*h8)-(fm7*h7+fml*h7a)
              ist=qst*((t0/tlm)-(t0/tst))
            endif
c*****extraction at lower pressures*****
            if(ice.eq.1)then
c ==========economiser==========
              if(t8.eq.t8a.or.t5a.eq.t6)go to 299
              call enth(3,id,1,0,xw,t8,pev,h8b,ere)
              h8b=h8b/(xw(2)*mw(2)+xw(3)*mw(3))
              call enth(3,id,1,0,xw,t8a,pev,h8a,ere)
              h8a=h8a/(xw(2)*mw(2)+xw(3)*mw(3))
              qecoi=fm8a*h8a-fm8b*h8b
              tlm=(t8-t8a)/(alog(t8/t8a))
              aecon1=qecoi*(1.-t0/tlm)
              tlm=(t5a-t6)/(alog(t5a/t6))
              aecon2=-qecoi*(1.-t0/tlm)
              ieco=-(aecon1+aecon2)
c ========expansion valve to extractor (EXVA1)=====
 299          nvt=2
              call vap(tab,tc(2),pc(2),nbp(2),pvp3)
              call rho(tab,ice,nvt,pco,pev,pvp1,pc,tc,zc,mw,vc,
     1        wa,rh3)
              call vap(tab,tc(3),pc(3),nbp(3),pvp4)
              call rho(tab,ice,3,pco,pev,(pco+pev)/2,pc,tc,zc,mw,
     1        vc,wa,rh4)
              x(2)=xw(2)*mw(2)/(xw(2)*mw(2)+xw(3)*mw(3))
              x(3)=1.-x(2)
              rhx=rh3*x(2)+rh4*x(3)
              iva1=fm8*(pco-pev)*rhx*1.01325
c ===========extractor===========
              x(1)=0.0
              x(2)=1.0
              x(3)=0.0
              call enth(3,id,1,0,x,t10,pev,h10,ere)
              h10=h10/mw(2)
              x(1)=fww
              x(2)=fwa
```

```
      call enth(2,id,1,0,x,text,pev,h4,ere)
      h4=h4/(x(1)*mw(1)+x(2)*mw(2))
      x(1)=fmw
      x(2)=fma
      call enth(2,id,1,0,x,tab,pev,h5,ere)
      h5=h5/(x(1)*mw(1)+x(2)*mw(2))
      an=r+fm8+1.
      ef1=fm8/an
      af1=1.-ef1
      am=af1/mw(2)
      em=ef1/mw(3)
      tm=em+am
      x(2)=am/tm
      x(3)=em/tm
      call gamma(3,id,1,x,text,gam,erg)
      est=0.
      do 230 i=2,3
230   est=est+x(i)*alog((x(i))*(gam(i)))
      rc1=8.314
      esta=rc1*t0*(1.0+fm10+fm8a)*est
      esta=esta/(x(2)*mw(2)+x(3)*mw(3))
      imix=-esta
      epa=(cst-cwk)/mw(2)
      epw=(fmw*epa)/fma
      x(1)=epw/(epa+epw)
      x(2)=1.-x(1)
      call gamma(2,id,1,x,text,gam,erg)
      est1=0.
      do 232 i=1,2
232   est1=est1+x(i)*alog((x(i))*(gam(i)))
      rtm=1.+(1.-cst)/cst
      esta1=rc1*t0*rtm*est1
      esta1=esta1/(x(1)*mw(1)+x(2)*mw(2))
c     iext=imix+esta1
      else
c **extraction at higher pressure
c ==========economiser===========
      if(t8.eq.t8a.or.t7.eq.t6)go to 499
      call enth(3,id,1,0,xw,t8a,pco,h8a,ere)
      h8a=h8a/(xw(2)*mw(2)+xw(3)*mw(3))
      call enth(3,id,1,0,xw,t8,pco,h8,ere)
      h8=h8/(xw(2)*mw(2)+xw(3)*mw(3))
      qecoi=fm8a*h8a-fm8*h8
      tlm=(t8a-t8)/(alog(t8a/t8))
      aecon1=qecoi*(1.-t0/tlm)
      tlm=(t7-t6)/(alog(t7/t6))
      aecon2=-qecoi*(1.-t0/tlm)
      ieco=-(aecon1+aecon2)
c ========expansion valve to absorber (EXVA1)=====
499   nvt=1
      x(1)=1.-fwa
      x(2)=fwa
      call vap(t4,tc(1),pc(1),nbp(1),pvp1)
      call rho(t4,ice,nvt,pco,pev,pvp1,pc,tc,zc,mw,vc,
     1  wa,rh1)
      call vap(t4,tc(2),pc(2),nbp(2),pvp2)
```

```
      call gamma(2,id,1,x,tab,gam,erg)
      est=0.
      do 237 i=1,2
  237 est=est+x(i)*alog((x(i))*(gam(i)))
      rc1=8.314
      esta=rc1*t0*(fm3+fm4)*est
      esta=esta/(x(1)*mw(1)+x(2)*mw(2))
      imix=-esta
      tlm=(tab-tev)/(alog(tab/tev))
      iht=qab*((t0/tlm)-(ts/tab))
      iab=imix+iht
      copflc=qev/qst
      copelc=copflc*(t0/tev-1.)/(1.-t0/tst)
      copflh=abs(qab+qcon+qrec)/qst
      copelh=copflh*(t0/tev-1.)/(1.-t0/tst)
      tq=qev+qcon+qrec+qeco+qext+qab+qst
      it=ieva+icon+irec+ieco+iext+iab+ist+iva1+iva2
      tcmtv=tab-tev
      cr=pco/pab
      cdf=cst-cwk
      if(kk.eq.1.and.jj.eq.1.and.ll.eq.1.and.mm.eq.1)then
          write(*,6700)
          write(*,6800)sfr,r,cst1,cwk1,ieva,iab,iva1,ieco,ist,
     1    irec,icon,iva2,it,copflc,copflh
      else
           write(*,6800)sfr,r,cst1,cwk1,ieva,iab,iva1,ieco,ist,
     1    irec,icon,iva2,it,copflc,copflh
      endif
   56 continue
   55 continue
   54 continue
   52 continue
c============format ridge============
 6700 FORMAT(1X,'SYSTEMS  PARAMETERS'1X,25('*'),
     1'IRREVERSIBILITIES' ,22('*'),1X,3('*'),'COPs',3('*')/
     21X,' SFR   R  CST  CWK   EVAPR  ABSOR  EXVA1  ECONO  VAPOR
     4RECTF  CONDS  EXVA2  T-IRR   COPC  COPH'/12X,'%    %    ',31
     5('='),' kJ/KG ',26('='))
 6800 FORMAT(1X,2(F4.2,1x),2(F4.1,1x),8(F6.2,1x),F8.3,1x,F5.3,
      1x,
     1F5.3)
c====================**************************============
  900 stop
      end
```

E2: Listing of Driver Program For First and Second Laws of Thermodynamics´ Analyses for Conventional Absorption Heat Pump Systems

```
      program thermo
      real ieva,icon,ige,iab,ieco,iva1,iva2,iext,irec,ist,
     1it,mw(3),k,nbp(10)
      common/pure/nm1(100),nm2(100),tc(100),pc(100),rd(100),
     1 dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100),
     2 ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/addp/wa(100),zc(100),vc(100)
      dimensidhbv(10),wfc(10),x(10),y(10),id(10),xf(10),cp(10),
     1  yf(10),gam(10),xx(10),xm(10),yy(10),hv(10)
100   call parin(3,er)
      if(er.gt.0)go to 900
      read(*,*)n,ice,kc,(id(i),i=1,n)
      do 111 i=1,n
      read(*,*)nbp(i),mw(i),cp(i),hv(i)
111   continue
      read(*,*)tev,tab
      dbp=abs(nbp(1)-nbp(2))
      write(*,1500)
1500  format(18x,´THEORECTICAL COP AND IRREVERSIBILITY IN THE
     1MAIN UNITS OF´/28X,´CONVENTIONAL AMMONIA-WATER HEAT
     2PUMP´/)
      tco=tab
      call vap(tco,tc(2),pc(2),nbp(2),pco)
      pge=pco
      call vap(tev,tc(2),pc(2),nbp(2),pev)
      pab=pev
      write(*,4000)tev,tab,pev,pco,cp(1),hv(1),dbp
4000  format(21x,´EVAPORATOR TEMPERATURE (K)          = ´,F6.2/
     121x,´ABSORBER TEMPERATURE (K)              = ´,F6.2/
     121X,´EVAPORATOR PRESSURE (BAR)             = ´,F6.2,/
     221X,´CONDENSER  PRESSURE (BAR)             = ´,F6.2/
     317X,´WATER HEAT CAP.-ca. 303K (kJ/kg.K)    = ´,F6.2/
     417X,´WATER HEAT OF VAP.-normal b.pt. (kJ/kg.)= ´,F7.2/
     517X,´BOILING POINTS DIFFERENCE (K)         = ´,F6.2/)
      do 54 kk=1,2
      r=float(kk)*0.25
      do 55 ll=1,2
      cst1=float(ll-1)*10.+36.
      cst=cst1/100.
      dma=cst/mw(2)
      dmw=(1.-cst)/mw(1)
      fma=dma/(dma+dmw)
      fmw=1.-fma
      do 56 mm=1,3
      cwk1=float(mm-1)*10.+15.
      cwk=cwk1/100.
      wma=cwk/mw(2)
      wmw=(1.-cwk)/mw(1)
      fwa=wma/(wma+wmw)
      fww=1.-fwa
```

```
      if((cst1-cwk1).lt.10.)go to 55
      t=0.
      x(1)=fww
      x(2)=fwa
      y(1)=0.1
      y(2)=0.9
      call budet(1,2,id,1,x,y,t,pge,k,err)
      tge=t
      pco=pge
      camv=y(2)*mw(2)/(mw(1)*y(1)+mw(2)*y(2))
      fm1=1.0+r
      fm2=1.0
      fm2a=1.0
      fm3=1.0
      fm7=1.0/(cst-cwk)
      fm6=fm7
      fm8=fm7-1.0
      fm9=((cst-cwk)/(camv-cwk))*fm6
      fm10=fm9-1.0
      fm4=fm8
      fm4a=fm8
      fm5=fm7
      t0=293.15
      t1=278.15
      ts=298.15
c **======lawe analyses=====**
c ========evaporator=======
      wfc(1)=0.0
      wfc(2)=1.0
      call enth(2,id,1,0,wfc,tco,pco,h2a,ere)
      call enth(2,id,1,2,wfc,tev,pev,h3,ere)
      h2a=h2a/mw(2)
      h3=h3/mw(2)
      qev=(fm3*h3-fm2*h2a)
      ieva=qev*((t0/tev)-(t0/t1))
c ========expansion valve to evaporator (EXVA2)=====
      nvt=0
      call rho((tev+tco)/2,ice,nvt,pco,pev,(pco+pev)/2,pc,tc,
     1zc,mw,vc,wa,wfc,rh)
      iva2=fm2*(pco-pev)*rh*1.01325
c =========condenser=========
      h2=h2a
      call enth(2,id,1,2,wfc,tco,pco,h1,ere)
      h1=h1/mw(2)
      qcon=(fm2*h2-fm1*h1)
      wfc(1)=1.0
      wfc(2)=0.0
      call enth(2,id,1,2,wfc,t0,1.01325,hi,ere)
      call enth(2,id,1,2,wfc,ts,1.01325,ho,ere)
      qcono=(ho-hi)/mw(1)
      r2=abs(qcon/qcono)
      tlm=(ts-t0)/alog(ts/t0)
      acon=qcon*(1.-ts/tco)
      acono=qcono*(1.-t0/tlm)
      icon=-(acon+r2*acono)
c =========rectifier==========
```

```
      t1=tco
      t9=tge
      t10=t1
      x(1)=fww
      x(2)=fwa
      call enth(2,id,1,0,x,tco,pco,h10,ere)
      h10=h10/(fww*mw(1)+fwa*mw(2))
      call enth(2,id,1,2,y,tge,pco,h9,ere)
      h9=h9/(y(1)*mw(1)+y(2)*mw(2))
      qrec=(fm1*h1+fm10*h10)-(fm9*h9+r*h2)
      qreco=acono
      tlm=(ts-t0)/alog(ts/t0)
      areco=qreco*(1.-t0/tlm)
      tlm=(tge-tc0)/alog(tge/tco)
      arec=qrec*(1.-t0/tlm)
      rrec=abs(qrec/qreco)
      irec=-(arec+rrec*areco)
c ==========generator==========
      t4=tab+10.
      t6=tab
      t8=t9
      x(1)=fww
      x(2)=fwa
      call enth(2,id,1,0,x,t4,pge,h4,ere)
      h4=h4/(x(1)*mw(1)+x(2)*mw(2))
      call enth(2,id,1,0,x,t8,pge,h8,ere)
      h8=h8/(x(1)*mw(1)+x(2)*mw(2))
      xx(1)=fmw
      xx(2)=fma
      call enth(2,id,1,0,xx,t6,pge,h6,ere)
      h6=h6/(xx(1)*mw(1)+xx(2)*mw(2))
      h7=(fm6*h6+fm8*h8-fm4*h4)/fm7
      qge=(fm8*h8+fm9*h9)-(fm10*h10+fm7*h7)
c **calculate t7 assuming only sensible heat around economiser
c **& neglecting approach tempt in the pipes
      t7=fm8*(t8-t4)/fm7+t6
      tlm=(tge-t7)/alog(tge/t7)
      call enth(2,id,1,0,xx,tge,pge,h9s,ere)
      h9s=h9s/(xx(1)*mw(1)+xx(2)*mw(2))
      qges=fm9*h9s-fm7*h7
      ages=qges*(1.-t0/tlm)
      agev=(qge-qges)*(1.-t0/tge)
      age=ages+agev
      ageq=qge*(1.-t0/tge)
      ige=ageq-age
c =============economiser==========
      qecoi=(fm4*h4-fm8*h8)
      tlm=(t4-t8)/(alog(t4/t8))
      aecon1=qecoi*(1.-t0/tlm)
      tlm=(t7-t6)/(alog(t7/t6))
      aecon2=-qecoi*(1.-t0/tlm)
      ieco=-(aecon1+aecon2)
c ========expansion valve to absorber (EXVA1)=====
      nvt=1
      x(1)=1.-fwa
      x(2)=fwa
```

```
      pvp1=0.
      pvp2=0.
      rh1=0.
      rh2=0.
      call vap(t4,tc(1),pc(1),nbp(1),pvp1)
      call vap(t4,tc(2),pc(2),nbp(2),pvp2)
      call rho(t4,ice,nvt,pco,pev,pvp1,pc,tc,zc,mw,vc,wa,x,rh1)
      call rho(t4,ice,0,pco,pev,pvp2,pc,tc,zc,mw,vc,wa,x,rh2)
      x(1)=x(1)*mw(1)/(x(1)*mw(1)+x(2)*mw(2))
      x(2)=x(2)*mw(2)/(x(1)*mw(1)+x(2)*mw(2))
      rhs=x(1)*rh1+x(2)*rh2
      iva1=fm8*(pco-pev)*rhs*1.01325
c ============absorber==============
      h5=h6
      h4a=h4
      t5=t6
      t4a=t4
      xm(1)=fmw
      xm(2)=fma
      call gamma(2,id,1,xm,tab,gam,erg)
      call enth(2,id,1,1,xm,tab,pev,h4d,ere)
      h4d=h4d/(x(1)*mw(1)+x(2)*mw(2))
      hmx=fm5*(h4d-h5)
      qab=fm5*h5-(fm3*h3+fm4*h4+hmx)
      entmix=qab
      est=0.
      do 230 i=1,2
  230 est=est+xm(i)*alog((xm(i))*(gam(i)))
      rc=8.314
      esta=rc*t0*(fm3+fm4)*est
      esta=(esta/(xm(1)*mw(1)+xm(2)*mw(2)))
      imix=-esta
      tlm=(tab-tev)/alog(tab/tev)
      iht=qab*((t0/tlm)-(ts/tab))
      iab=imix+iht
      copflc=qev/qge
      copslc=copflc*(t0/tev-1.)/(1.-t0/tge)
      copflh=abs(qab+qcon+qrec)/qge
      copslh=copflh*(t0/tev-1.)/(1.-t0/tge)
      tq=qev+qcon+qrec+qeco+qge+qab
      it=ieva+icon+irec+ieco+ige+iab+iva1+iva2
      tcmtv=tab-tev
      cr=pge/pab
      cdf=cst-cwk
      if(mm.le.1.and.ll.le.1.and.kk.le.1)then
          write(*,6750)
          write(*,6800)r,cst1,cwk1,ieva,iab,ige,iva1,ieco,irec,
     1     icon,iva2,it,copflc,copflh
      else
          write(*,6800)r,cst1,cwk1,ieva,iab,ige,iva1,ieco,irec,
     1     icon,iva2,it,copflc,copflh
      endif
   56 continue
   55 continue
   54 continue
c============format ridge============
```

```
6750 FORMAT(1X,'***PARAMETERS***  ',23('*'),'IRREVERSIBILITIES'
    1,25('*'),2X,'***COPs***'/1X,'  R    CST   CWK  EVAPR  ABSOR
    1GENER   EXVA   ECONO   RECTF  CONDS   EXVA2   T-IRR   COPC
    1COPH'/7X,'  %      %   ',1X,27('='),'kJ/KG',33('='))
6800 FORMAT(1X,F4.2,2X,2(F4.1,2X),3(F6.2,1X),2(F6.2,1X),1X,
    1 F7.2,1x,2(F6.2,1X),F8.3,1X,2(F5.3,2X))
 900 stop
     end
```

E3: Listing of Subroutines for First and Second Laws' Analyses

```
      subroutine enth(n,id,key,lev,zf,t,p,h,ere)
      real z(20),phi(20),zf(n)
      integer id(20),ere
     common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
     1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
     2,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/ge/ier,rl(20),th(20),tp(20),gcl(20),tau(20,20)
      common/virial/kv,b(210),bd(210),db(210),dbd(210),bm
      common/pe/phl(20),zi(20),c(210),vnt,tl,pl
      data r,cj/8.31439,0.0988075/,tr,tr2,trf/300.,90000.,1411./
      ere=0
      bu=0.
  100 do 104 i=1,n
  104 z(i)=zf(i)
      if(key.lt.9)go to 120
      if(lev.lt.2)go to 110
      call bijs(n,id,key,t,ere)
      if(ere.gt.1)go to 900
      if(kv.eq.0)go to 110
      call phis(n,id,8,z,t,p,phi,err)
      if(err.gt.1)go to 900
      go to 120
  110 if(lev.eq.0)go to 120
      call taus(n,id,t,tau,ier)
      if(iabs(ier).eq.1)ere=1
      st=0.
      stp=0.
  111 do 115 i=1,n
      ii=id(i)
      th(i)=z(i)*qu(ii)
      tp(i)=z(i)*qp(ii)
      stp=stp+tp(i)
  115 st=st+th(i)
  116 do 119 i=1,n
      th(i)=th(i)/st
  119 tp(i)=tp(i)/stp
  120 tm1=t-tr
      tm2=alog(t/tr)
      tm3=(t**2-tr2)/2
      tlt=t*alog(t)-t-trf
      hig=0.
  125 do 129 i=1,n
      ii=id(i)
  129 hig=hig+z(i)*(d1(ii)*tm1+d2(ii)*tm2+d3(ii)*tm3+d4(ii)*tlt)
      if(lev.lt.2)go to 150
  130 if(kv.eq.1)go to 140
      hv=0.
  131 do 135 i=1,n
      li=(i-1)*i/2
      do 135 j=1,i
      cmt=2.
      if(j.eq.i)cmt=1.
```

```
135   hv=hv+cmt*z(i)*z(j)*(b(li+j)-db(li+j))
139   hv=hig+cj*p*hv
      h=hv
      return
140   sd=0.
      so=0.
      s1=0.
141   do 145 i=1,n
      li=(i-1)*i/2
      so=so+zi(i)*(b(li+i)-db(li+i))
      do 143 j=1,i
      zij=zi(i)*zi(j)*c(li+j)
      sd=sd+zij*(1.-dbd(li+j)/bd(li+j))
143   s1=s1+zij*(b(li+j)-db(li+j))
145   continue
      hv= hig+vnt*(cj*p*(so+s1)-r*t*sd)
      h=hv
      return
150   tmr=t**2
      tms=2.*t*tmr
      h1=0.
151   do 155 i=1,n
      ii=id(i)
155   h1=h1+z(i)*(-c2(ii)+c3(ii)*tmr+c4(ii)*t+c5(ii)*tms)
      h=hig-r*h1
160   if(lev.eq.0)return
      he=0.
      hc=0.
161   do 169 i=1,n
      ii=id(i)
      tm1=0.
      tm2=0.
      if(u(ii,ii).gt.1.E+19)go to 166
      do 165 j=1,n
      jj=id(j)
      tm3=tp(j)*tau(j,i)
      tm1=tm1+tm3
165   tm2=tm2+tm3*(u(jj,ii)-2.*bu/t)
      he=he+qp(ii)*z(i)*tm2/tm1
      go to 169
166   do 168 j=1,n
      jj=id(j)
168   tm1=tm1+th(j)*u(jj,ii)
      hc=hc+z(i)*tm1
169   continue
      h=h+r*(he+hc)
      return
900   ere=2
      h=0.
      return
      end
      subroutine phis(n,id,key,y,t,p,phi,err)
      real y(20),si(20),zo(20),phi(20),ss(20)
      integer id(20),err,ere
      common/virial/kv,b(210),bd(210),db(210),dbd(210),bm
      common/ps/phl(20),zi(20),c(210),vnt,tl,pl
```

```
      data r/83.1473/
100   err=0
      prt=p/(r*t)
      go to(110,101,120,101,101,101,101,120,110,101),key
101   if(abs(t-t1).lt.0.02)go to 103
      go to 110
103   if(abs(p-p1).lt.0.01)go to 105
      go to 110
105   if(key.eq.4.or.key.eq.7)return
      go to 120
110   call bijs(n,id,key,t,erb)
      if(erb.gt.1)go to 900
120   if(kv.eq.1)go to 200
      bm=0.
130   do 139 i=1,n
      ss(i)=0.
      li=(i-1)*i/2
      do 133 j=1,i
133   i1=i+1
      if(i1.gt.n)go to 136
      do 135 j=i1,n
      lj=(j-1)*j/2
135   ss(i)=ss(i)+y(j)*b(lj+i)
136   bm=bm+y(i)*ss(i)
139   continue
140   do 149 i=1,n
      phi(i)=exp(prt*(2.*ss(i)-bm))
      phl(i)=phi(i)
149   continue
      t1=t
      p1=p
      return
200   ko=0
      go to(203,201,201,201,201,201,201,203,203,201),key
201   do 202 i=1,n
      li=(i-1)*i/2
202   zi(i)=phl(i)*y(i)*exp(-prt*b(li+i))
      if(key.eq.3)go to 208
      ko=1
203   do 207 i=1,n
      if(ko.eq.0)zi(i)=y(i)
      li=(i-1)*i/2
      do 206 j=1,i
      lj=(j-1)*j/2
     c(li+j)=-2.*prt*bd(li+j)*exp(prt*(b(li+i)+b(lj+j)-b(li+j)))
      if(c(li+j).lt.0.)go to 900
      if(j.eq.i)go to 205
      if(ko.eq.1)go to 206
      if(c(li+j).le.0.5)go to 206
      if(y(j).lt.y(i))go to 204
      zt=y(i)/(c(li+j)*y(j)+1.)
      zj=y(j)/(c(li+j)*zt+1.)
      if(zt.lt.zi(i))zi(i)=zt
      if(zj.lt.zi(j))zi(j)=zj
      go to 206
204   zj=y(j)/(c(li+j)*y(i)+1.)
```

```
      common/binary/eta(5050),u(100,100)
      common/virial/kv,b(210),bd(210),db(210),dbd(210),bm
      common/bs/g(210),ts(210),s(210),z(210),h(210),e(210)
     1,w(210),et(210)
      data b1,b2,b3/1.2618,7243.8,1.7941E07/cn1,cn2,cn3,cn4/0.94
     1 ,-1.47,-0.85,1.015/cp1,cp2,cp3,cp4/-0.75,3.,-2.1,-2.1/
     2 ca1,ca2,ch1,ch2/-0.3,-0.05,1.99,0.2/cw1,cw2,cw3/0.006026
     3,0.02096,-0.001366/,cs1,ck1,ck2,ce1,ce2,ce3,ce4,ce5/2.4507
     4,0.7,0.6,650.,300.,4.27,42800.,22400./,co1,co2,co3/0.748,
     5 0.91,0.4/,e3/0.3333333/
100   erb=0
      go to (109,200,200,200,200,200,200,200,109,200),key
109   kv=0
110   do 119 i=1,n
      ii=id(i)
      l=(i+1)*i/2
      w(l)=cw1*rd(ii)+cw2*rd(ii)**2+cw3*rd(ii)**3
      s(l)=(cs1-w(l))**3*tc(ii)/pc(ii)
      if(s(l).lt.0.)go to 900
      iii=(ii+1)*ii/2
      et(l)=eta(iii)
      if(et(l).ge.4.4999)kv=1
      ts(l)=tc(ii)*(co1+co2*w(l)-co3*et(l)/(2.+20.*w(l)))
      if(ts(l).lt.0.)go to 900
      if(dm(ii).lt.1.45)go to 117
      h(l)=16.+400.*w(l)
      t1=h(l)/(h(l)-6.)
      t2=3./(h(l)-6.)
      tk=2.882-(1.882*w(l)/(0.03+w(l)))
      z(l)=b3*dm(ii)**4/(ts(l)*s(l)**2*tc(ii)*tk)
      if(z(l).lt.-1.)go to 900
      s(l)=s(l)*(1.+t2*z(l))
      ts(l)=ts(l)*(1.-t1*z(l)+t1*(t1+1.)*z(l)**2/2.)
117   g(l)=b2*dm(ii)**2/(ts(l)*s(l))
119   continue
      if(n.eq.1)go to 130
120   do 129 i=2,n
      ii=id(i)
      li=(i+1)*i/2
      i1=i-1
      do 129 j=1,i1
      jj=id(j)
      lj=(j+1)*j/2
      l=(i-1)*i/2+j
      w(l)=(w(li)+w(lj))/2.
      s(l)=sqrt(s(li)*s(lj))
      ts(l)=ck1*sqrt(ts(li)*ts(lj))+ck2/(1./ts(li)+1./ts(lj))
      if(dm(ii).lt.1.E-19)go to 123
      if(dm(jj).gt.1.E-19)go to 124
      if(dm(ii).lt.2.5)go to 124
      z(l)=dm(ii)**2*(ts(lj)**2*s(lj))**e3/(ts(l)*s(li))
      go to 125
123   if(dm(jj).lt.2.5)go to 124
      z(l)=dm(jj)**2*(ts(li)**2*s(li))**e3/(ts(l)*s(lj))
      go to 125
124   z(l)=0.
```

```
      go to 126
125   h(l)=16.+400.*w(l)
      t1=h(l)/(h(l)-6.)
      t2=3./(h(l)-6.)
      s(l)=s(l)*(1.-t2*z(l))
      ts(l)=ts(l)*(1.+t1*z(l))
126   g(l)=b2*dm(ii)*dm(jj)/(ts(l)*s(l))
      ij=(ii-1)*ii/2+jj
      if(jj.gt.ii)ij=(jj-1)*jj/2+ii
      if(abs(eta(ij)).lt.1.E-19)go to 127
      et(l)=eta(ij)
      if(et(l).ge.4.4999)kv=1
      go to 129
127   et(l)=0.
      if(abs(et(li)-et(lj)).lt.1.E-19)et(l)=et(li)
129   continue
130   do 139 i=1,n
      do 139 j=1,i
      l=(i-1)*i/2+j
      s(l)=b1*s(l)
      h(l)=ch1+ch2*g(l)**2
      z(l)=ca1+ca2*g(l)
      if(g(l).lt.0.04)go to 135
      if(g(l).ge.0.25)go to 134
      g(l)=0.
      go to 135
134   g(l)=g(l)-0.25
135   if(et(l).ge.4.5)go to 137
      if(et(l).lt.1.E-19)go to 139
      e(l)=ce1/(ts(l)+ce2)-ce3
      go to 139
137   e(l)=ce4/(ts(l)+ce5)-ce3
139   continue
200   do 209 i=1,n
      do 209 j=1,i
      l=(i-1)*i/2+j
      ta=t/ts(l)
      t1=1./(1./ta-1.6*w(l))
      t2=t1*t1
      t3=t2*t1
      bn=cn1+cn2/t1+cn3/t2+cn4/t3
      if(g(l).gt.1.E-19)go to 201
      bp=0.
      go to 202
201   bp=(cp1+cp2/t1+cp3/t2+cp4/t3)*g(l)
202   b(l)=s(l)*(bn+bp)
      bn=z(l)*exp(h(l)/ta)
      if(et(l).lt.1.E-19)go to 204
      bp=exp(et(l)*e(l))-exp(et(l)*(1500./t+e(l)))
      go to 205
204   bp=0.
205   bd(l)=s(l)*(bn+bp)
      if(key.gt.1.and.key.le.5)go to 208
      dbn=-cn2-2.*cn3/t1-3.*cn4/t2
      dbp=(-cp2-2.*cp3/t1-3*cp4/t2)*g(l)
      db(l)=s(l)*(dbn+dbp)/ta
```

```
      dbn=-h(l)*bn/ta
      if(et(l).lt.1.E-19)go to 206
      dbp=1500.*et(l)*exp(et(l)*(1500./t+e(l)))/t
      go to 207
206   dbp=0.
207   dbd(l)=e(l)*(dbn+dbp)
      if(kv.eq.0)db(l)=db(l)+dbd(l)
208   if(kv.eq.0)b(l)=b(l)+bd(l)
209   continue
      return
900   erb=2
      nl=(n+1)*n/2
      do 902 l=1,nl
      b(l)=0.
902   bd(l)=0.
      return
      end
      subroutine valik(n,id,key,x,y,t,p,k,err)
      real x(n),y(n),k(n),phi(20),gam(20),xf(20),yf(20)
      integer id(n),err,er,erg,idf(20)
      common/val/fip(20)
100   err=0
101   do 102 i=1,n
      xf(i)=x(i)
      yf(i)=y(i)
102   idf(i)=id(i)
110   call phis(n,idf,key,yf,t,p,phi,er)
      if(er.gt.1)go to 900
      go to(120,120,130,120,120,120,120,120,120,120),key
120   call purf(n,idf,t,p,fip)
130   call gamma(n,idf,key,xf,t,gam,erg)
140   do 149 i=1,n
      k(i)=gam(i)*fip(i)/(phi(i)*p)
      if(k(i).le.0..or.k(i).gt.1.E19)go to 900
149   continue
      err=erg
      return
900   err=er
905   do 906 i=1,n
906   k(i)=0.
      return
      end
      subroutine purf(n,id,t,p,fip)
      real fip(20),fo(20),vip(20)
      integer id(20)
     common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
    1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
    2,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      data,ca,cb,cc,e/83.1473,1.60,0.655,0.00693026,0.28571429/
100   rt=r*t
      at=alog(t)
      t2=t*t
101   do 109 i=1,n
      ii=id(i)
      fo(i)=exp(c1(ii)+c2(ii)/t+c3(ii)*t+c4(ii)*at+c5(ii)*t2)
      tr=t/tc(ii)
```

```
      if(tr.gt.0.75)go to 105
      tau=1.+(1.-tr)**e
      go to 107
105   tau=ca+cc/(tr-cb)
107   vip(i)=r*tc(ii)*a(ii)**tau/pc(ii)
109   continue
110   do 119 i=1,n
      fip(i)=fo(i)*exp(vip(i)*p/rt)
119   continue
      return
      end
      subroutine budet(type,n,id,key,x,y,t,p,k,err)
      real x(n),y(n),k(n),cn(20)
      integer id(n),type,err,er
      data eps/0.001/
100   err=0
      if(p.lt.1.E-6.or.p.gt.100.)go to 903
      kee=key
      s=0.
      ss=0.
101   do 109 i=1,n
      s=s+x(i)
109   ss=ss+y(i)
      if(type.eq.1.and.abs(s-1.).gt.0.01)go to 903
      if(type.eq.2.and.abs(ss-1.).gt.0.01)go to 903
      if(type.eq.1.and.abs(ss-1.).gt.0.01)go to 114
      if(type.eq.2.and.abs(s-1.).gt.0.01)go to 118
      go to 120
114   do 115 i=1,n
115   y(i)=x(i)
      go to 120
118   do 119 i=1,n
119   x(i)=y(i)
120   it=0
200   if(t.lt.200..or.t.gt.600.)t=400.
210   it=it+1
      if(it.gt.10)go to 900
220   call valik(n,id,kee,x,y,t,p,k,er)
      if(er.gt.1)go to 900
      s=0.
221   do 229 i=1,n
      if(type.eq.2)go to 225
      cn(i)=k(i)*x(i)
      go to 229
225   cn(i)=y(i)/k(i)
229   s=s+cn(i)
230   fo=alog(s)
      if(abs(fo).le.eps)go to 290
      call valik(n,id,4,x,y,t+1.,p,k,er)
      if(er.gt.1)go to 900
      ss=0.
      if(type.eq.2)go to 235
231   do 234 i=1,n
      y(i)=cn(i)/s
234   ss=ss+k(i)*x(i)
      go to 240
```

```
235   do 239 i=1,n
      x(i)=cn(i)/s
239   ss=ss+y(i)/k(i)
240   f1=alog(ss)
      t=(f1-fo)*t/(f1-t*fo/(t+1.))
      if(t.gt.700.)go to 900
      if(t.gt.100.)go to 245
      if(er.lt.0)go to 901
      go to 900
245   kee=2
      if(type.eq.1)kee=5
      go to 210
290   do 299 i=1,n
      if(type.eq.2)go to 295
      y(i)=cn(i)/s
      go to 299
295   x(i)=cn(i)/s
299   continue
      if(t.gt.600.)go to 903
      if(t.gt.200.)go to 199
      if(er.lt.0)go to 901
      go to 903
199   if(iabs(er).eq.1)err=1
      return
900   err=2
      go to 905
901   err=-5
      go to 905
903   err=5
905   t=0.
      return
      end
      subroutine gamma(n,id,key,x,t,gam,erg)
      real x(20),gam(20),pt(20),pts(20)
      integer id(20),erg
     common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
    1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
     1,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/gs/ier,rl(20),th(20),tp(20),gcl(20),tau(20,20)
      data z/10./
100   go to(110,120,120,130,130,120,130,120,110,120),key
110   erg=0
111   do 119 i=1,n
      ii=id(i)
119   rl(i)=z*(ru(ii)-qu(ii))/2.-ru(ii)+1.
120   sp=1.E-30
      st=1.E-30
      stp=1.E-30
      ss=0.
      sl=0.
121   do 125 i=1,n
      ii=id(i)
      th(i)=x(i)*qu(ii)
      tp(i)=x(i)*qp(ii)
      sp=sp+x(i)*ru(ii)
```

```
      st=st+th(i)
      stp=stp+tp(i)
      if(u(ii,ii).gt.1.E+19)go to 125
      ss=ss+x(i)
      sl=sl+x(i)*rl(i)
  125 continue
  126 do 129 i=1,n
      ii=id(i)
      th(i)=th(i)/st
      tp(i)=tp(i)/stp
      if(u(ii,ii).gt.1.E+19)go to 128
  127 gcl(i)=rl(i)-ru(ii)*sl/sp+alog(ru(ii)*ss/sp)+z*qu(ii)*
     1 alog(qu(ii)*sp/(ru(ii)*st))/2
      go to 129
  128 gcl(i)=0.
  129 continue
      if(key.eq.3)go to 140
  130 call taus(n,id,t,tau,ier)
  140 do 141 i=1,n
  141 pts(i)=0.
  142 do 149 i=1,n
      pt(i)=1.E-30
      do 143 j=1,n
  143 pt(i)=pt(i)+tp(j)*tau(j,i)
      do 145 j=1,n
  145 pts(j)=pts(j)+tp(i)*tau(j,i)/pt(i)
  149 continue
  150 do 159 i=1,n
      ii=id(i)
      if(u(ii,ii).gt.1.E+19)go to 155
      grl=qp(ii)*(1.-alog(pt(i))-pts(i))
      go to 158
  155 grl=0.
      do 156 j=1,n
      jj=id(j)
  156 grl=grl+th(j)*(u(ii,jj)+u(jj,ii)/t)
  158 gam(i)=exp(gcl(i)+grl)
  159 continue
      if(iabs(ier).eq.1)erg=1
      return
      end
      subroutine taus(n,id,t,tau,ier)
      real tau(20,20)
      integer id(20)
      common/binary/eta(5050),u(100,100)
  100 ier=0
  110 do 119 i=1,n
      ii=id(i)
      if(u(ii,ii).gt.1.E+19)ier=isign(ier**2-2,-1)
      do 119 j=1,n
      if(j.eq.i)go to 115
      jj=id(j)
      if(u(ii,ii).gt.1.E+19.and.u(jj,jj).gt.1.E+19)go to
     1  115
      if(abs(u(ii,jj)).lt.1.E-19)go to 112
      if((u(ii,ii)+u(jj,jj)).gt.1.E+19)go to 115
```

```
      tau(i,j)=exp(-u(ii,jj)/t)
      go to 119
112   ier=isign(i,ier)
115   tau(i,j)=1
119   continue
      return
      end
      subroutine parin(m,erin)
      integer erin
     common/pure/nm1(100),nm2(100),nm3(100),tc(100),pc(100),rd(
    1100),dm(100),a(100),c1(100),c2(100),c3(100),c4(100),c5(100)
    2,ru(100),qu(100),qp(100),d1(100),d2(100),d3(100),d4(100)
      common/binary/eta(5050),u(100,100)
      common/addp/wa(100),zc(100),vc(100)
100   erin=0
      if(m.gt.100)go to 900
      do 109 i=1,m
      read(*,01)j,nm1(j),nm2(j),nm3(j)
      read(*,*)j,tc(j),pc(j),a(j),rd(j),dm(j),ru(j),
     1qu(j),qp(j)
      if(j.ne.i)go to 900
 01   format(i3,A4,A4,A4)
      read(*,*)j,c1(j),c2(j),c3(j),c4(j),c5(j)
      if(j.ne.i)go to 900
      read(*,*)j,d1(j),d2(j),d3(j),d4(j),wa(j),zc(j),vc(j)
      if(j.ne.i)go to 900
109   continue
      read(*,*)j
      if(j.ne.0)go to 900
110   do 119 i=1,m
      i1=(i-1)*i/2+1
      i2=(i-1)*i/2+i
      read(*,*)(eta(ij),ij=i1,i2)
119   continue
      read(*,*)e
      if(abs(e).gt.1.E-19)go to 900
120   do 121 i=1,m
      do 121 j=1,m
121   u(i,j)=0.
125   read(*,*)i,j,uij,uji
      if(i.eq.0)go to 130
      u(i,j)=uij
      u(j,i)=uji
      go to 125
130   do 139 i=1,m
      if(a(i).lt.1.E-19)u(i,i)=1.E+20
139   continue
      return
900   erin=5
      return
      end
      subroutine vap(t,tc,pc,tb,p)
      pc=pc/1.01325
      tr=t/tc
      tbr=tb/tc
      r=1.987
```

```
      hvb=r*tc*tbr*((0.4343*alog(pc)-0.68859+0.89584*tbr)/
     1   (0.37691-0.37306*tbr+0.14878*pc**(-1.)*tbr**(-2.)))
      a=hvb/(r*tc*((1.-tbr)**0.375))
      h=tbr*alog(pc)/(1.-tbr)
      dv=5.2691+2.0753*a-3.1738*h
      el=(tbr**dv-1.)/dv+0.040*(1./tbr-1.)
      er=alog(1./pc)-a*(1.14893-1./tbr-0.11719*tbr-0.03174*
     1    tbr**2.-0.375*alog(tbr))
      alphac=(er/el+0.46284*a)/1.042
      elt=(1.042*alphac-0.46284*a)*((tr**dv-1.)/dv+0.040*
     1 (1/tr-1.))
      ert=a*(1.14893-1./tr-0.11719*tr-0.03174*tr**2-0.375*
     1 alog(tr))
      p=pc*exp(elt+ert)
      p=p*1.01325
      return
      end
      subroutine rho(t,ice,nvt,p1,p2,pvp,pc,tc,zc,mw,vc,wa,rhd)
      real mw(3)
      dimension a(3),b(3),c(3),d(3),e(3),f(3),vr(3,3),vc(3),
     1 zc(3),pc(3),wa(3),tc(3),tr(3),rh(3),rhs(3),en(3)
      data a(1),a(2),a(3)/0.11917,0.98465,-0.55314/,b(1),
     1 b(2),b(3)/0.009513,-1.60378,-0.15793/,c(1),c(2),c(3)/
     @.21091,1.82484,-1.01601/,d(1),d(2),d(3)/-0.06922,-0.61432
     3 ,0.34095/,e(1),e(2),e(3)/0.07480,-0.34546,0.46795/,f(1),
     4 f(2),f(3)/-0.084476, 0.087037,-0.239938/
      p1=p1/1.01325
      p2=p2/1.01325
      pvp=pvp/1.01325
      do 10 j=1,3
      do 10 i=1,3
      pc(i)=pc(i)/1.01325
      tr(i)=t/tc(i)
      vr(j,i)=a(j)+b(j)*tr(i)+c(j)*tr(i)**2+d(j)*tr(i)**3+e(j)
     1/tr(i)+f(j)*alog(1.-tr(i))
10    continue
      p=(p1+p2)/2
      do 230 j=1,3
      rhs(j)=((vc(j)/mw(j))*(vr(1,j)+wa(j)*vr(2,j)+(wa(j)**2)
     1*vr(3,j)))**(-1.)
      en(j)=(1.0-0.89*wa(j))*exp(6.9547-76.2853*tr(j)+191.3060
     1*(tr(j)**2)-203.5472*(tr(j)**3)+82.7631*(tr(j)**4))
      rh(j)=rhs(j)*(1.+(9.*zc(j)*en(j)*(p-pvp))/pc(j))**0.11111
230   continue
      if(nvt.eq.1)rhd=rh(1)
      if(nvt.eq.2)rhd=rh(2)
      if(nvt.eq.3)rhd=rh(3)
      return
      end
```

APPENDIX F

NOTES ON SEPARATION PROCESSES

Introduction

Pratt [1967] classified separation processes into two broad groups,viz: "Mechanical Separation Processes" and "Molecular Separation Processes". The processes in the latter group are those used for separating homogenous mixtures into their constituent compounds. They are equilibrium ,semi-equilibrium or non-equilibrium processes.

More energy degradation occur in the non-equilibrium processes and so they are used only for mixtures which are very difficult or impossible to separate by equilibrium or semi-equilibrium processes. Equilibrium (or semi-equilibrium) processes are therefore to be preferred for the separation of common mixtures in order to prevent as much energy degradation as possible in the process. In these preferred groups are distillation, chemical exchange, extractive, azeotropic and molecular distillations, gas centrifuge,absorption,stripping, adsorption and liquid-liquid extraction.

In the processes such as liquid-liquid extraction, stripping and absorption additional materials have to be introduced into the mixture to effect separation into pure constituents. This extra component is called the mass separation agent and its function in these processes is similar to that of heat (energy) in the evaporation/distillation processes. Since mass separating agents are used in these processes secondary separation would be required to recover the separating agent and the solute.

Stripping Processes

The stripping separation process involves the desorption of the solute from its solution by changes in the physical and/or chemical conditions of the solution to be separated into its constituents and subsequent sweeping off of the desorbed solute by the stripping gas(es). The solute is thereafter recovered from the mass separating agent (stripping gas).

The physical conditions that may be changed to effect separation include temperature, pressure and pH of the solution. This change in condition leads to change in the vapour-liquid equilibrium of the system. The solute component present in the vapour phase is removed from the vapour phase of the solution by stripping gas(es) that has/have affinity for the solute but little or no affinity for the vapour of the remaining constituents of the solution.

For instance, ammonia can be stripped from aqueous ammonia solution using any of the inert gases such as hydrogen, nitrogen and air that practically have no affinity for water or its vapour [Perry and Green, 1984]. The stripping gas(es) bubble(s) through the solution and sweep(s) off ammonia vapour present in the vapour phase to leaves behind excess water vapour. This leads to the desorption of more ammonia in order to reestablish the vapour-liquid-equilibrium of the system, and the process continues for as long as the column configuration allows or until virtually all ammonia in the solution is desorbed. A good example of the application of stripping process is the removal of ammonia from waste-water.

Adsorption Process

Adsorption process achieves separation of a mixture through the preferential removal of one of the components of the mixture by the adsorbent. Activated charcoal and many molecular sieves have been used to remove ammonia from aqueous ammonia solution (Breck,1974). The process is however not strictly isothermal. Secondary separation called regeneration is necessary to recover the adsorbent and the adsorbed solute. If thermal regeneration of the adsorbent is employed the process becomes non-isothermal Wet regeneration on the other hand requires additional separation step to recover the adsorbent and the solute of the original mixture.

Liquid-Liquid Extraction Process

Liquid-liquid extraction separation depends on the non-ideal distribution behaviour of the components in the two immiscible liquid phases formed after the extracting solvent and the mixture to be separated have been shaken together and allowed to equilibrate. In a ternary system, for example, the extracting solvent must have high selectivity for one of the raffinate mixture's constituents and at the same time the second component must have high activity coefficient in the solvent (so as to be excluded from the solvent) for good separation to be achieved.

In selecting solvents for extraction separation process,the concept of solubility parameter [Helpinstill and van Winkle,1968; Hildebrand,1948; Hanson,1971], selectivity and capacity [Deal and Derr,1964; Pierotti et al.,1959] and consolute solution temperature-CST- [Francis,1969] could be employed.

Solubility parameter and selectivity (separation factor) are respectively defined as:

$$\delta = \left(\frac{\Delta Ev}{V}\right)^{0.5} = \left(\frac{\Delta H - RT}{V}\right)^{0.5} \quad \text{.....F.1}$$

$$\alpha_2^1 = \frac{x_1'' x_2'}{x_1' x_2''} = \frac{\gamma_1' \gamma_2''}{\gamma_1'' \gamma_2'} \quad \text{.....F.2}$$

where:

δ is the solubility parameter,

ΔE is the energy of vaporisation,

V is the molar volume,

α is the separation factor,

x_1 and x_2 are the mole fractions of the feed solvent and the solute respectively,

γ_1 and γ_2 are the activity coefficients of the feed solvent and the solute respectively,

$'$ and $''$ represent the raffinate and extract phase respectively.

Ammonia and water are miscible in all proportions largely because of the high degree of similarity of the intermolecular forces and molar volumes of the two compounds as well as the existence of hydrogen bond between the molecules of the two compounds. This high degree of mutual solubility makes the separation of the mixture seemingly impossible. However, the greater dispersion forces in ammonia molecules render covalent compounds such as organic solvents more soluble in ammonia while the greater effect of polar forces makes electrolytes more soluble in water [Nicholls, 1979; Lagowski, 1967]. Thus

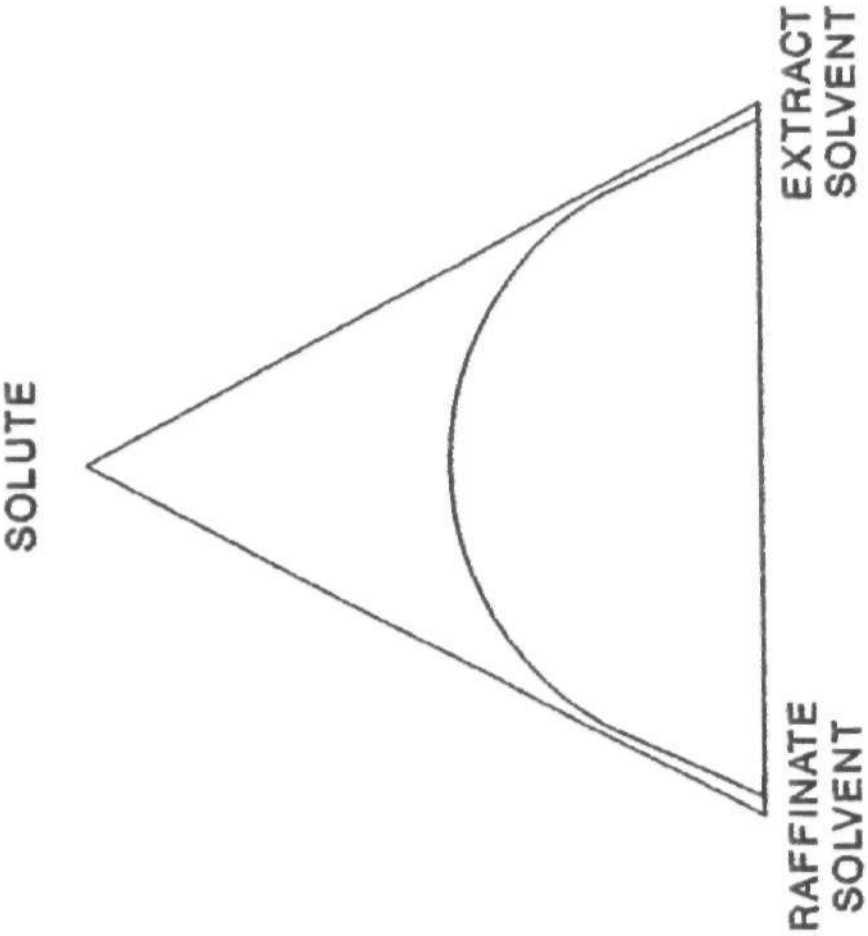


Figure F.1: Binodal Curves Of Type I System