A CALCULATION OF THE REFRIGERATION EFFICIENCY OF A CH4, C2H6, C3H8 AND N2 MIXTURE OVER THE TEMPERATURE RANGE 270-330K USING THE SECOND VIRIAL COEFFICIENT

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LIST OF SYMBOLS

P	Pressure (atm)
V	Volume (l)
T	Temperature (K)
$B(T)$	Second virial coefficient (cc/mol)
$C(T)$	Third virial coefficient (cc/mol)
C_p	Heat capacity (J/molK)
k	Boltzmann's constant (=$1.38*10^{-23}$ J/K)
R	Gas constant (=0.08206 dm^{3}atm/Kmol)
N	Avogadro constant (=$6.022*10^{23}$/mol)
r	Distance between two molecules (A)
μ	Joule-Thomson coefficient
α	Molecular structure parameter
β	Molecular structure parameter
l	Molecule length
ε	Depth of the potential well in the Lennard-Jones model
$\bar{\varepsilon}$	Average well depth in the Corner's four-center model
σ	The value of r at which $U(r) = 0$
X_i	Mole fraction of component i

CHAPTER I

INTRODUCTION

Current environmental concerns mandate the search for a Freon-113 replacement in the refrigerator industry.

New compounds, HFC-125 and HCFC-123, have been reported to function as substitutes for CFC-113. However, these compounds pose other chemical and ecological hazards. They are costly and contribute to the greenhouse effect(1). Brominated compounds are more damaging to the ozone layer than chlorinated compounds while little is known about the health effects of fluorinated alternatives. Some pure gases, such as Helium, Nitrogen, Hydrogen and Argon, have been used in refrigeration systems. However, refrigerator systems using single gases require high compression pressures or have a low thermodynamic cooling efficiency or pose other health hazards(2-8). Mixture gas systems, such as those which consist of 30% by volume Nitrogen, 30% of Methane, 20% of Ethane and 20% of Propane, afford a 10 to 12 fold improvement in cooling efficiency compared with pure Nitrogen(9,10). However, the composition of such mixtures has been empirically derived and leaves open the possibility of finding even better mixtures.

This work describes an effort to use Corner's four-center molecules model to calculate the second virial coefficient B(T) of mixture gas systems and pure gas systems, respectively. From this B(T) value, the Joule-Thomson coefficient μ_{JT} of mixture gases and pure gases may be obtained. In particular, the objective of this work has been to delineate the procedure for calculation of gas mixture cooling efficiencies from a tabulation of the second virial coefficient, B(T). Since B(T) is now calculable by quantum mechanical procedures(11,12), this work would then complete the process by which mixture gas cooling efficiency is calculated directly from quantum mechanical principles.

Background

The Equation of State - The Virial Coefficients

The virial equation for a real gas is expressed as follows:

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \ldots \qquad \text{I-1}$$

This equation can be used to describe gas behaviors over a very large range of temperature and pressure. The temperature dependent functions B(T), C(T),... are referred to as the second, third,... virial coefficients and are related to the intermolecular potential function. The second virial coefficient, B(T), is simply related to the intermolecular potential energy function, U(r), by the following equation(13):

$$B(T) = 2\Pi N\int_0^\infty (1-\exp(-U(r)/kT))r^2dr \qquad \text{I-2}$$

Intermolecular Potential Functions

There are various types of intermolecular forces which may arise between ions, atoms and molecules. Intermolecular forces, can be roughly divided into two types: short-range forces and long-range forces. The short-range forces are mainly referred valence forces or chemical forces and arise when the molecules come close enough together for their electron clouds to overlap. Such forces are beyond the scope of this work. The long-range forces which contribute to the interaction potential of molecules have three components: (i) the electrostatic contributions, (ii) the induction contribution, and (iii) the dispersion contribution(14,15). These long-range forces dominate the efficiency of Joule-Thomson cooling.

There are various empirical long range intermolecular potential functions which may be used to calculate the second virial and Joule-Thomson coefficient. Among these are the functions derived from the Rigid Impenetrable Spheres model, Point Centers of Repulsion model and the Square Well potential model(16). The Lennard-Jones(6-12) potential is another one which has been applied extensively. The Lennard-Jones potential is written as:

$$U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \qquad \text{I-3}$$

The term $(\sigma/r)^{12}$ represents the repulsive potential and the term $-(\sigma/r)^{6}$ the attractive potential, σ is that value of r for which U(r)=0, and ε is the maximum energy of attraction which occurs at $r=2^{1/6}\sigma$. Substitution of the Lennard-Jones potential into the integral for the second virial coefficient given in equation I-2, with the following reduced quantities also used(17):

$$r^* = r/\sigma \tag{I-4}$$

$$T^* = kT/\varepsilon \tag{I-5}$$

$$B^* = B/(2/3\Pi N\sigma^3) = B/b0 \tag{I-6}$$

$$B_k^* = T^{*k}(d^kB^*/dT^{*k}) \tag{I-7}$$

enables the reduced second virial coefficient to be written as:

$$B^*(T^*) = -\frac{4}{T^*}\int_0^\infty r^{*2}\left[-\frac{12}{r^{*12}}+\frac{6}{r^{*6}}\right]e^{-\frac{4}{T^*}\left(\frac{1}{r^{*12}}-\frac{1}{r^{*6}}\right)}dr^* \tag{I-8}$$

When $\exp[(4/T^*)r^{*-6}]$ is expanded in an infinite series, the integration may be performed analytically. Then the reduced second virial coefficient may be written as:

$$B^*(T^*) = \sum_{j=0} b^{(j)}T^{*-(2j+1)/4} \tag{I-9}$$

where the coefficients $b^{(j)}$ are given by:

$$b^{(j)} = -\frac{2^{j+\frac{1}{2}}}{4j!}\Gamma\left(\frac{2j-1}{4}\right) \tag{I-10}$$

So, the finial form of the second virial coefficient is given by:

$$B(T) = b0B^*(T^*) \tag{I-11}$$

However, the Lennard-Jones potential function is limited in application to spherical non-polar molecules. Corner has introduced a new molecular potential function which considers molecular structure in greater detail(18).

Corner's Four-Center Model for Long Molecules

In Corner's four-center model, a molecule is represented by four centers of force distributed evenly along a line of length $2^{5/6}$ l(see fig.1). The interaction energy for a pair of these four-center molecules is expressed by:

$$U(r) = \sum_{i=1}^{4}\sum_{j=1}^{4} 4\varepsilon c[(\sigma c/rij)^{12} - (\sigma c/rij)^{6}] \qquad \text{I-12}$$

In which rij is the distance between point center i in the first molecule and center j in the second. The subscript, c, on the above force-constants indicates that they apply to interactions between centers of force and not between the entire molecules. The summation is over all the sixteen possible interactions between centers of force.

Then the intermolecular potential may be expressed in the form:

$$U(r,\omega) = 4\varepsilon(\omega)[(\sigma(\omega)/r)^{12} - (\sigma(\omega)/r)^{6}] \qquad \text{I-13}$$

where the force constants now depend on the orientation, $\omega = \{\theta 1, \theta 2, \phi\}$.

Substitution of this angle-dependent potential given by equation I-13 into equation I-2, with the same reduced quantities used as in the Lennard-Jones potential case discussed before, gives a final form of B(T) which contains three parameters, σc, l and ε and is expressed as:

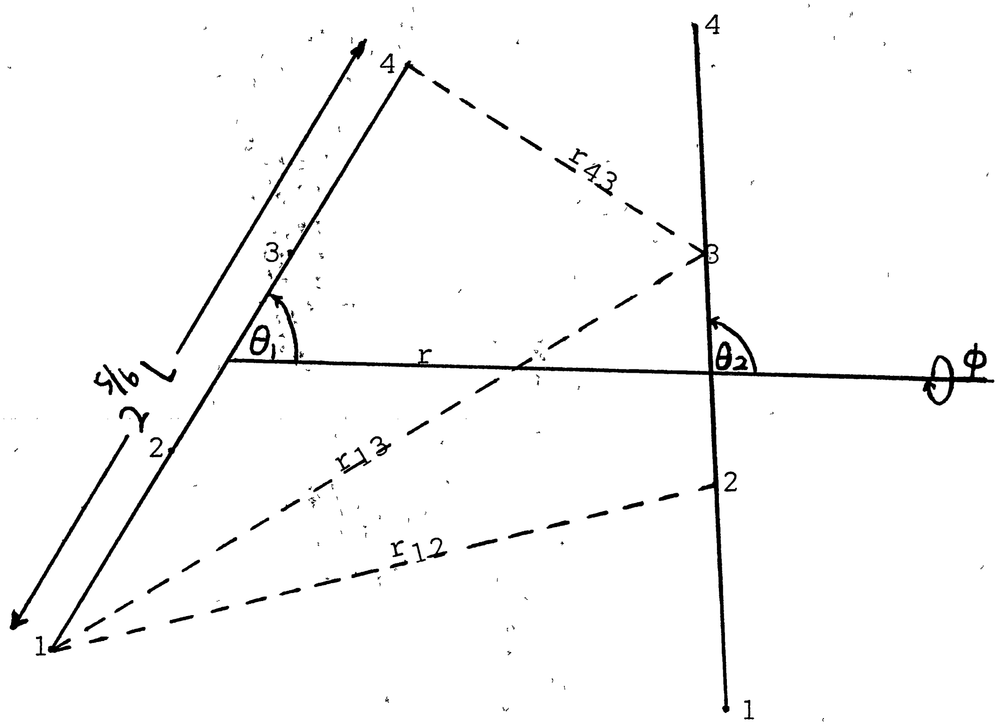

Figure 1. Pictorial Representation of Two Interacting "Four-Center" Molecules

$$B(T) = \frac{2\Pi N\sigma_c^3}{3}\alpha[B^*(\frac{kT}{\bar{\varepsilon}})+\beta(6B^*(\frac{kT}{\bar{\varepsilon}})+4B^*(\frac{kT}{\bar{\varepsilon}}))] \qquad \text{I-14}$$

In this equation, the quantities α and β are functions of $1/\sigma c$, with α given by:

$$\alpha = 1 + 29/15(1/\sigma c) + 53/15(1/\sigma c) \qquad \text{I-15}$$

The relation between β and $1/\sigma c$ is shown by figure 2.

The different component values of $1/\sigma c$, $\bar{\varepsilon}/k$, $B^*(kT/\bar{\varepsilon})$, $B_1^*(kT/\bar{\varepsilon})$ and $B_2^*(kT/\bar{\varepsilon})$ are given and tabulated in Molecular Theory of Gases and Liquids(13).

Joule-Thomson Coefficient

The purpose of this work is to outline the procedure for obtaining the Joule-Thomson coefficient for a gas mixture from knowledge of the second virial coefficient, B(T). For illustrative purposes, this work relies upon the Corner's four-center potential for derivation of B(T), although it is known that recently there have been quantum mechanical derivations of B(T)(19).

The Joule-Thomson coefficient is expressed by:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H \qquad \text{I-16}$$

$$\mu_{JT} = \frac{1}{Cp}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad \text{I-17}$$

Ignoring higher order terms, the virial equation of state is given by I-1:

$$\frac{PV}{RT} = 1+\frac{B}{V}$$

$$PV^2/RT - V - B = 0 \qquad \text{I-18}$$

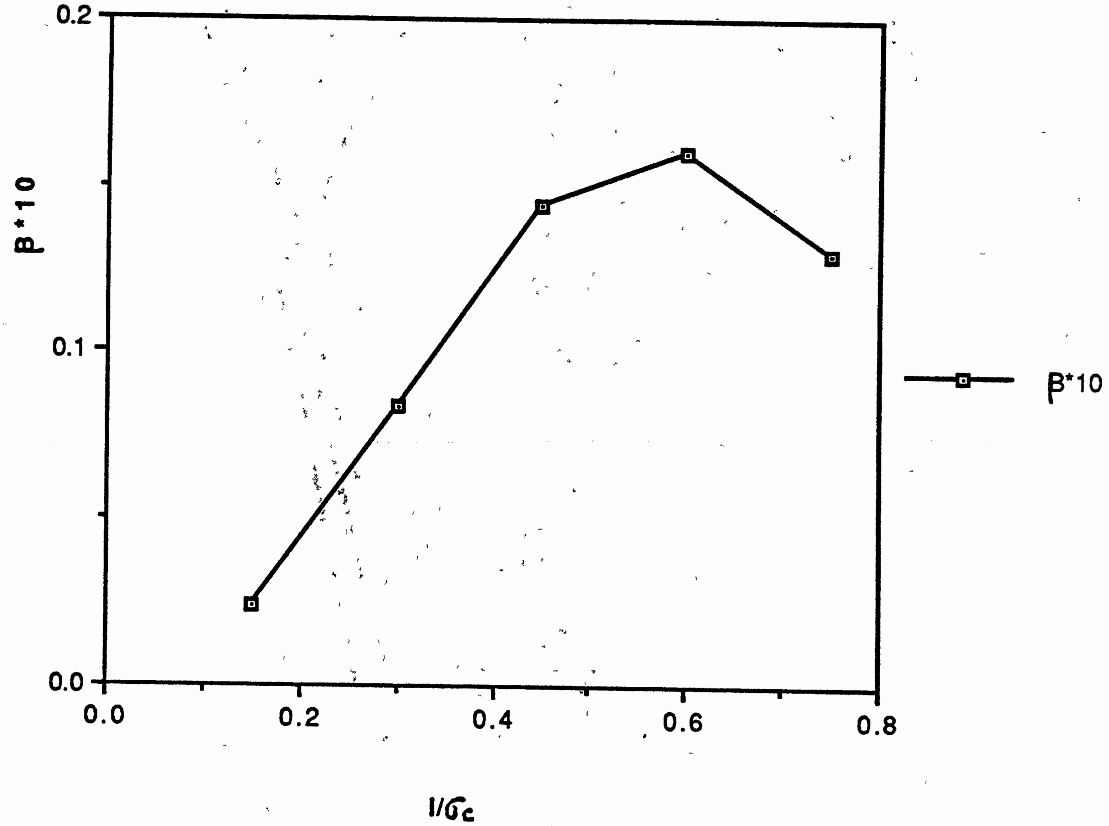

Figure 2. The Relation Between β and $1/\sigma_c$.

$$V = \frac{RT}{2P}\left[\ 1 + \sqrt{1 + \frac{4PB}{RT}}\ \right] \tag{I-19}$$

$$\frac{V}{T} = \frac{R}{2P}\left[\ 1 + \sqrt{1 + \frac{4PB}{RT}}\ \right] \tag{I-20}$$

$$\left[\frac{\partial(V/T)}{\partial T}\right]_P = \frac{R}{2P}\left[\frac{\partial[1 + \sqrt{1 + 4PB/RT}\ ]}{\partial T}\right]_P \tag{I-21}$$

$$\left[\frac{\partial(V/T)}{\partial T}\right]_P = \frac{1}{[1 + 4PB/RT]^{\frac{1}{2}}}\left[\frac{\partial(B/T)}{\partial T}\right]_P \tag{I-22}$$

also

$$T^2\left[\frac{\partial(V/T)}{\partial T}\right]_P = T^2\left[\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{V}{T^2}\right)\right]_P \tag{I-23}$$

$$\therefore \quad T^2\left[\frac{\partial(V/T)}{\partial T}\right]_P = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]_P \tag{I-24}$$

Therefore, combining the equations I-22, I-24 and I-17, the Joule-Thomson coefficient μ_{JT} may be expressed in terms relating to the second virial coefficient, B(T), by:

$$\mu_{JT} = \frac{T^2}{Cp[1 + 4PB/RT]^{\frac{1}{2}}}\left[\frac{\partial(B/T)}{\partial T}\right]_P \tag{I-25}$$

CHAPTER II

CALCULATION

The scope of this work was limited to pressure and temperature range found in a common household refrigerator. The temperature range was 270K-330K, while the pressure range was 1 atm-20 atm(20). All calculations were effected on a computer programmed in C. This program is contained in the appendix.

The calculation may be divided into four steps:

1. Use the equation I-14, the reduced quantities T^*, B^*, B_1^*, B_2^*, and the molecule structure parameter α, β, σ_c, $\bar{\varepsilon}/k$ from Molecular Theory of Gases and Liquids(13) to calculate B(T) of Nitrogen and mixture gas systems, respectively.
2. Use a cubic-spline to estimate the slope of the curve, (B/T) vs. T at each temperature point.
3. Calculate the heat capacity Cp of Nitrogen and mixture gas systems at different pressures.
4. Use all of the above data to calculate μ_{JT} for Nitrogen and the mixture gas systems.

In mixture gas systems, the second virial coefficient is given by(13):

$$B(T)_{mix} = \sum_{i=1}^{\nu}\sum_{j=1}^{\nu} B_{ij}(T) X_i X_j \qquad \text{II-1}$$

when i=j, Bij is the pure gas second virial coefficient;

when $i \neq j$, Bij represents the interaction between different gas molecules i and j.

So, for a three components system ($X1=XN2=0.4$, $X2=XCH4=0.4$, $X3=XC2H6=0.2$):

$$B(T)mix\text{-}3 = X1^2B11 + X2^2B22 + X3^2B33 + 2X1X2B12 + 2X1X3B13 + 2X2X3B23 \qquad \text{II-2}$$

For a four components system ($X1=XN2=0.3$, $X2=XCH4=0.3$, $X3=XC2H6=0.2$, $X4=XC3H6=0.2$):

$$B(T)mix\text{-}4 = X1^2B11 + X2^2B22 + X3^2B33 + X4^2B44 + 2X1X2B12 + 2X1X3B13 + 2X1X4B44 + 2X2X3B23 + 2X2X4B24 + 2X3X4B34 \qquad \text{II-3}$$

Also, the well depth $\vec{\varepsilon}$ of unlike molecules in the equation I-14, according to the empirical combining laws, is given by(16):

$$\vec{\varepsilon}ij = (\vec{\varepsilon}i\,\vec{\varepsilon}j)^{\frac{1}{2}} \qquad \text{II-4}$$

The value of σc between two molecules is given by:

$$\sigma ij = 1/2(\sigma i + \sigma j) \qquad \text{II-5}$$

Molecular Structure Parameter

Table I lists the molecular structure parameters, α, β, σc and $\bar{\varepsilon}/k$ for each component.

TABLE I

MOLECULAR STRUCTURE PARAMETER

COMPONENT	α	β	σc (A)	$\bar{\varepsilon}/k$ (K)
N2	1.30	0.0024	3.37	95
CH4	1.00	0.0000	3.79	148
C2H6	1.39	0.0040	4.50	206
C3H8	1.54	0.0062	4.90	228
N2-CH4	1.14	0.0010	3.58	118.6
N2-C2H6	1.35	0.0032	3.94	139.9
N2-C3H8	1.44	0.0044	4.13	147.2
CH4-C2H6	1.20	0.0018	4.14	174.6
CH4-C3H8	1.28	0.0022	4.34	183.7
C2H6-C3H8	1.46	0.0044	4.7	216.7

Source: Reference (13), Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., John Wiley & Sons, New York, 1954.

Calculation of the Second Virial Coefficient

Using the data in Table I, the reduced quanties T^*, $B^*(T^*)$, $B_1^*(T^*)$ and $B_2^*(T^*)$ from reference(13) and equation I-14, the second virial coefficient, $B(T)$, for individual gases, for the three component system (Nitrogen, Methane and Ethane) and for the four component system (Nitrogen, Methane, Ethane and Propane) were calculated and tabulated as follows:

TABLE II

NITROGEN SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	2.42	-0.356835	1.265309	-2.914542	-22.6309
235	2.47	-0.325353	1.232124	-2.835607	-21.0141
240	2.53	-0.300993	1.200441	-2.760492	-19.4686
245	2.58	-0.277753	1.170259	-2.689197	-17.9944
250	2.63	-0.255496	1.141385	-2.621202	-16.5827
255	2.68	-0.234223	1.113818	-2.556507	-15.1084
260	2.74	-0.208931	1.081077	-2.479936	-13.6296
265	2.79	-0.189392	1.055799	-2.420971	-12.3907
270	2.84	-0.171005	1.032034	-2.365760	-11.2249
275	2.89	-0.150752	1.008772	-2.311800	-9.94239
280	2.95	-0.131868	0.981480	-2.248755	-8.74389
285	3.00	-0.115234	0.960003	-2.199200	-7.68949
290	3.05	-0.099823	0.940113	-2.153525	-6.71276
295	3.10	-0.082623	0.917914	-2.102571	-5.62267
300	3.16	-0.068310	0.897134	-2.055068	-4.71455
305	3.21	-0.052456	0.878977	-2.013613	-3.71096
310	3.26	-0.039132	0.861775	-1.974468	-2.86674
315	3.32	-0.026032	0.844860	-1.936010	-2.03670
320	3.37	-0.010495	0.824789	-1.890510	-1.05233
325	3.42	-0.001528	0.809249	-1.855350	-0.48241
330	3.47	-0.001314	0.794226	-1.821430	-0.46214

TABLE III

METHANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B(T)
230	1.55	-1.123518	-77.15200
235	1.58	-1.087715	-77.69338
240	1.62	-1.018682	-69.95292
245	1.65	-0.985453	-67.67107
250	1.69	-0.939075	-64.48631
255	1.72	-0.894779	-61.44450
260	1.75	-0.865943	-59.46428
265	1.79	-0.825510	-56.68780
270	1.82	-0.786785	-54.02854
275	1.85	-0.761537	-52.29476
280	1.89	-0.725994	-49.85406
285	1.92	-0.691868	-47.51063
290	1.96	-0.669590	-45.98076
295	1.99	-0.638116	-43.81946
300	2.02	-0.608377	-41.77726
305	2.06	-0.579505	-39.79460
310	2.09	-0.560257	-38.47284
315	2.12	-0.533402	-36.62873
320	2.16	-0.511863	-35.14968
325	2.19	-0.490325	-33.67063
330	2.23	-0.466201	-32.01407

TABLE IV

ETHANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.12	-2.064511	3.747804	-9.525542	-340.1029
235	1.14	-1.982649	3.622129	-9.161747	-326.5647
240	1.16	-1.909299	3.503841	-8.821637	-314.4198
245	1.19	-1.854286	3.392940	-8.505212	-305.2394
250	1.21	-1.802906	3.288212	-8.208292	-296.6659
255	1.24	-1.736821	3.189677	-7.930877	-285.7673
260	1.26	-1.673860	3.096356	-7.669695	-275.3897
265	1.28	-1.614023	3.008254	-7.424745	-265.5332
270	1.31	-1.556892	2.924598	-7.193432	-256.1274
275	1.33	-1.529680	2.884993	-7.084595	-251.6497
280	1.36	-1.450404	2.769992	-6.769632	-238.6090
285	1.38	-1.425552	2.734201	-6.672345	-234.5236
290	1.41	-1.364456	2.646373	-6.434028	-224.4816
295	1.43	-1.330282	2.597633	-6.302875	-218.8686
300	1.45	-1.274237	2.517832	-6.088575	-209.6650
305	1.48	-1.242799	2.473393	-5.970150	-204.5057
310	1.50	-1.200883	2.414140	-5.812250	-197.6267
315	1.53	-1.162200	2.359904	-5.669015	-191.2831
320	1.55	-1.123518	2.305668	-5.525780	-184.9395
325	1.58	-1.087714	2.255844	-5.395315	-179.0719
330	1.60	-1.051915	2.206021	-5.264850	-173.2044

TABLE V

PROPANE SECOND VIRIAL CONEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.01	-2.486116	4.345612	-11.29272	-588.6200
235	1.03	-2.434151	4.262963	-11.04559	-576.1868
240	1.05	-2.330220	4.097665	-10.55133	-551.3181
245	1.07	-2.238297	3.954154	-10.12938	-529.3850
250	1.10	-2.146374	3.810642	-9.707440	-507.4520
255	1.12	-2.064511	3.684967	-9.343645	-487.9696
260	1.14	-2.023580	3.622129	-9.161747	-478.2269
265	1.16	-1.945974	3.503841	-8.821637	-459.7761
270	1.18	-1.909299	3.448390	-8.663425	-451.0670
275	1.20	-1.835949	3.337489	-8.347000	-433.6488
280	1.23	-1.769863	3.238948	-8.069585	-417.9871
285	1.25	-1.703778	3.140407	-7.792170	-402.3254
290	1.27	-1.643941	3.052305	-7.547220	-388.1701
295	1.29	-1.614023	3.008254	-7.424745	-381.0924
300	1.32	-1.529680	2.884993	-7.084595	-361.1609
305	1.34	-1.502469	2.845388	-6.975757	-354.7339
310	1.36	-1.450404	2.769992	-6.769632	-342.4460
315	1.38	-1.425552	2.734201	-6.672345	-336.5850
320	1.40	-1.375847	2.662620	-6.477770	-324.8630
325	1.42	-1.330282	2.597633	-6.302910	-314.1314
330	1.45	-1.284716	2.532645	-6.128050	-303.3998

TABLE VI

NITROGEN-METHANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.94	-0.680729	1.700619	-3.975855	-45.2905
235	1.98	-0.648607	1.657711	-3.869175	-43.1600
240	2.02	-0.608377	1.604176	-3.736825	-40.4919
245	2.06	-0.579505	1.565860	-3.642482	-38.5771
250	2.10	-0.546325	1.521862	-3.534285	-36.3768
255	2.15	-0.516171	1.482086	-3.437305	-34.3774
260	2.19	-0.486017	1.442311	-3.340324	-32.3780
265	2.23	-0.458447	1.406100	-3.240400	-30.5469
270	2.28	-0.435185	1.375571	-3.178922	-29.0079
275	2.32	-0.405652	1.336889	-3.085807	-26.9075
280	2.36	-0.384613	1.309395	-3.019908	-25.6554
285	2.40	-0.363575	1.281901	-2.954010	-24.2608
290	2.45	-0.338394	1.248716	-2.875075	-22.5719
295	2.49	-0.318983	1.223828	-2.815873	-21.3052
300	2.53	-0.300993	1.200441	-2.760492	-20.1128
305	2.57	-0.277753	1.170259	-2.689197	-18.5726
310	2.61	-0.260815	1.148277	-2.637376	-17.4500
315	2.65	-0.242200	1.124156	-2.580768	-16.2164
320	2.70	-0.223586	1.100035	-2.524160	-14.9829
325	2.74	-0.208931	1.081077	-2.479936	-14.0118
330	2.78	-0.194276	1.062119	-2.435712	-13.0407

TABLE VII

NITROGEN-ETHANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.64	-0.993760	2.125657	-5.056101	-105.6032
235	1.68	-0.954534	2.071719	-4.916830	-101.4552
240	1.71	-0.909197	2.009578	-4.757002	-96.6621
245	1.75	-0.865942	1.950527	-4.605870	-92.0904
250	1.79	-0.825510	1.895628	-4.466317	-87.8188
255	1.82	-0.786785	1.843217	-4.333650	-83.7285
260	1.86	-0.755613	1.793172	-4.207507	-80.4259
265	1.89	-0.720071	1.753338	-4.107526	-76.6842
270	1.93	-0.691868	1.715536	-4.013080	-73.7076
275	1.96	-0.659099	1.671706	-3.903902	-70.2494
280	2.00	-0.627625	1.629720	-3.799720	-66.9286
285	2.04	-0.598753	1.591404	-3.705377	-63.8836
290	2.07	-0.569881	1.553088	-3.611035	-60.8385
295	2.11	-0.542017	1.516180	-3.520431	-57.9003
300	2.14	-0.520479	1.487769	-3.451159	-55.6299
305	2.18	-0.498940	1.459358	-3.381887	-53.3594
310	2.21	-0.473955	1.426453	-3.301878	-50.7260
315	2.25	-0.450693	1.395924	-3.228105	-48.2750
320	2.29	-0.427431	1.365395	-3.154331	-45.8237
325	2.32	-0.405652	1.336889	-3.085807	-43.5296
330	2.36	-0.384613	1.309395	-3.019908	-41.3137

TABLE VIII

NITROGEN-PROPANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.56	-1.105616	2.280756	-5.46054	-146.6041
235	1.60	-1.051911	2.206021	-5.26485	-139.5178
240	1.63	-1.018682	2.160099	-5.14556	-135.1363
245	1.66	-0.969994	2.092948	-4.97155	-128.7176
250	1.70	-0.923616	2.029262	-4.80738	-122.6061
255	1.73	-0.880361	1.970211	-4.65624	-116.9095
260	1.76	-0.852465	1.932227	-4.55935	-113.2366
265	1.80	-0.812033	1.877328	-4.41980	-107.9146
270	1.83	-0.774161	1.826161	-4.42351	-103.2325
275	1.87	-0.737842	1.777239	-4.16751	-98.1553
280	1.90	-0.714147	1.745372	-4.08753	-95.0394
285	1.94	-0.680729	1.700619	-3.97585	-90.6469
290	1.97	-0.648607	1.657711	-3.86917	-86.4259
295	2.00	-0.627625	1.629720	-3.79972	-83.6690
300	2.04	-0.598753	1.591404	-3.70537	-79.8776
305	2.07	-0.569881	1.553088	-3.61103	-76.0862
310	2.10	-0.550633	1.527544	-3.54814	-73.5586
315	2.14	-0.524786	1.493451	-3.46501	-70.1669
320	2.17	-0.498940	1.459358	-3.38188	-66.7752
325	2.21	-0.477832	1.431541	-3.31571	-64.0090
330	2.24	-0.454570	1.401012	-3.24040	-60.9548

TABLE IX

METHANE-ETHANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.31	-1.556892	2.924898	-7.19343	-170.0205
235	1.34	-1.475257	2.805782	-6.86692	-161.0959
240	1.37	-1.425552	2.734201	-6.67234	-155.6701
245	1.40	-1.375847	2.662620	-6.47777	-150.2442
250	1.43	-1.307499	2.565139	-6.21548	-142.7861
255	1.46	-1.263757	2.503019	-6.04910	-138.0140
260	1.49	-1.221841	2.443766	-5.89120	-133.4418
265	1.52	-1.171871	2.373463	-5.70482	-127.9923
270	1.54	-1.123518	2.305668	-5.52578	-122.7198
275	1.57	-1.087714	2.255844	-5.39531	-118.8169
280	1.60	-1.051911	2.206021	-5.26485	-114.9140
285	1.63	-1.010375	2.148618	-5.11574	-110.3875
290	1.66	-0.969994	2.092948	-4.97155	-105.9873
295	1.69	-0.939075	2.050490	-4.86210	-102.6188
300	1.72	-0.901988	1.999736	-4.73181	-98.5788
305	1.75	-0.865942	1.950527	-4.60587	-94.6526
310	1.77	-0.838987	1.913928	-4.51283	-91.7173
315	1.80	-0.812033	1.877328	-4.41980	-88.7819
320	1.83	-0.774161	1.826161	-4.29057	-84.6586
325	1.86	-0.749689	1.793172	-4.20750	-81.9945
330	1.89	-0.725994	1.761305	-4.12752	-79.4152

TABLE X

METHANE-PROPANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.25	-1.703778	3.140407	-7.79217	-229.2571
235	1.28	-1.643941	3.052305	-7.54722	-221.2003
240	1.30	-1.577301	2.944401	-7.24785	-212.2136
245	1.33	-1.529680	2.884993	-7.08459	-205.8198
250	1.36	-1.450404	2.769992	-6.76963	-195.1536
255	1.39	-1.400700	2.698411	-6.57505	-188.4686
260	1.41	-1.353064	2.630127	-6.39034	-182.0634
265	1.44	-1.296107	2.548892	-6.17176	-174.4066
270	1.47	-1.242799	2.473393	-5.97015	-167.2430
275	1.50	-1.200883	2.414140	-5.81225	-161.6107
280	1.52	-1.162200	2.359904	-5.66901	-156.4151
285	1.55	-1.123518	2.305668	-5.52578	-151.2195
290	1.58	-1.087714	2.255844	-5.39531	-146.4124
295	1.60	-1.043604	2.194541	-5.23502	-140.4903
300	1.63	-1.002067	2.137138	-5.08592	-134.9154
305	1.66	-0.969994	2.092948	-4.97155	-130.6111
310	1.69	-0.939075	2.050490	-4.86210	-126.4626
315	1.71	-0.909197	2.009578	-4.75700	-122.4543
320	1.74	-0.873151	1.960369	-4.63105	-117.6193
325	1.77	-0.845726	1.923078	-4.53609	-113.9413
330	1.80	-0.812033	1.877328	-4.41980	-109.4231

TABLE XI

ETHANE-PROPANE SECOND VIRIAL COEFFICIENT B(T) DATA

T(K)	T*	B*(T*)	B*(T*)	B*(T*)	B(T)
230	1.06	-2.284259	4.025910	-10.34035	-451.2726
235	1.08	-2.192335	3.882398	-9.918412	-432.9994
240	1.10	-2.125908	3.779223	-9.616491	-419.8019
245	1.13	-2.044046	3.653548	-9.252696	-403.5583
250	1.15	-1.982649	3.559292	-8.979850	-391.3755
255	1.18	-1.909299	3.448390	-8.663425	-376.8445
260	1.20	-1.835949	3.337489	-8.347000	-362.3134
265	1.22	-1.769863	3.238948	-8.069585	-349.2404
270	1.24	-1.703778	3.140407	-7.792170	-336.1674
275	1.27	-1.658900	3.074331	-7.608457	-327.3012
280	1.29	-1.599063	2.986229	-7.363507	-315.4795
285	1.31	-1.556892	2.924598	-7.193432	-307.1543
290	1.34	-1.529680	2.884993	-7.084595	-301.7845
295	1.36	-1.450404	2.769992	-6.769632	-290.8070
300	1.38	-1.400700	2.698411	-6.575057	-276.3479
305	1.41	-1.364456	2.646373	-6.434055	-269.2055
310	1.43	-1.318890	2.581386	-6.259195	-260.2320
315	1.45	-1.284716	2.532645	-6.128050	-253.5018
320	1.47	-1.242799	2.473393	-5.970150	-245.2543
325	1.50	-1.200883	2.414140	-5.812250	-237.0067
330	1.52	-1.162200	2.359904	-5.669015	-229.4016

TABLE XII

MIXTURE GAS SYSTEM SECOND VIRIAL COEFFICIENT B(T) DATA

B(T)mix-3	B(T)mix-4	T(K)
-88.162170	-168.561707	230
-84.195190	-161.924820	235
-80.214821	-155.512024	240
-77.034309	-149.548096	245
-73.375069	-143.122574	250
-70.158752	-137.429184	255
-67.290451	-132.636398	260
-64.197166	-127.106873	265
-61.396595	-122.303787	270
-58.884953	-117.900635	275
-56.224625	-113.389702	280
-53.869825	-109.317795	285
-51.325401	-105.413910	290
-49.166233	-101.709167	295
-46.934814	-97.025673	300
-44.766300	-93.729752	305
-42.894363	-90.378815	310
-40.956188	-87.355133	315
-38.861649	-83.752815	320
-37.195030	-80.701553	325
-35.614059	-77.619331	330

where B(T)mix-3 represents 3 component system;
B(T)mix-4 represents 4 component system.

Calculation of the Slope of (B/T) vs. T

$\partial(B/T)/\partial T$, by definition, represents the slope value of the curve of (B/T) vs. T. In this work, the cubic spline method(21) has been used to calculate this value.

In the cubic spline procedure with T representing the independent variable and (B/T) as the dependent variable, the point set $[T_1, (B/T)_1), (T_2, (B/T)_2) \ldots (T_n, (B/T)_n]$ is arranged in order of increasing T. The spline fit was accomplished by connecting each pair of adjacent points with a section of a third degree polynomial. This cubic function was forced to satisfy the following properties:

I. It passes through every data point.

II. It is continuous.

III. Its first derivative is continuous.

IV. Its second derivative is continuous.

and it may be written by:

$$\begin{aligned} S(T) = {} & [3/h_j^2(T_{j+1}-T)^2 - 2/h_j^3(T_{j+1}-T)^3](B/T)_j + \\ & [3/h_j^2(T-T_j)^2 - 2/h_j^3(T-T_j)^3](B/T)_{j+1} + \\ & h_j[1/h_j^2(T_{j+1}-T)^2 - 1/h_j^3(T_{j+1}-T)^3]M_j - \\ & h_j[1/h_j^2(T-T_j)^2 - 1/h_j^3(T-T_j)^3]M_{j+1} \end{aligned} \qquad \text{II-6}$$

Where $S(T_j)=(B/T)_j$, $S(T_{j+1})=(B/T)_{j+1}$, $M_j=S'(T_j)=[\partial(B/T)/\partial T]$; $j=0, 1, \ldots 20$; $h_j=T_{j+1}-T_j=5$.

Then the cubic function second derivative S"(T) can be expressed by:

$$\begin{aligned} S''(T) = {} & [6/h_j^2 - 12/h_j^3(T_{j+1}-T)](B/T)_j + \\ & [6/h_j^2 - 12/h_j^3(T-T_j)](B/T)_{j+1} + \end{aligned}$$

$$h_j[2/h_j^2 - 6/h_j^3(T_{j+1} - T)]M_j -$$

$$h_j[2/h_j^2 - 6/h_j^3(T-T_j)]M_{j+1}$$

$$S''(T_j) = -6/h_j^2(B/T)_j + 6/h_j^2(B/T)_{j+1} - 4M_j/h_j - 2M_{j+1}/h_j$$

$$S''(T_{j+1}) = 6/h_j^2(B/T)_j - 6/h_j^2(B/T)_{j+1} + 2M_j/h_j + 4M_{j+1}/h_j \qquad \text{II-7}$$

In equation II-7 all quantities are known except M_j and M_{j+1}. One condition which will define these values is condition IV above, that the second derivative be continuous. So, for the interval $[T_{j-1}, T_j]$, the second derivative $S''(T_j-)$ at the right end point T_j is written by:

$$S''(T_j-) = 6/h_{j-1}^2(B/T)_{j-1} - 6/h_{j-1}^2(B/T)_j + 2M_{j-1}/h_{j-1} + 4M_j/h_{j-1} \qquad \text{II-8}$$

similarly, the second derivative $S''(T_j+)$ at the left end point T_j is written by:

$$S''(T_j+) = -6/h_j^2(B/T)_j + 6/h_j^2(B/T)_{j+1} - 4M_j/h_j - 2M_{j+1}/h_j \qquad \text{II-9}$$

$$S''(T_j-) = S''(T_j+)$$

$$\therefore \quad 6/h_{j-1}^2(B/T)_{j-1} - 6/h_{j-1}^2(B/T)_j + 2M_{j-1}/h_{j-1} + 4M_j/h_{j-1} = -6/h_j^2(B/T)_j + 6/h_j^2(B/T)_{j+1} - 4M_j/h_j - 2M_{j+1}/h_j$$

$$(M_{j-1} + 2M_j)/h_{j-1} + (2M_j + M_{j+1})/h_j = 3\{[(B/T)_j - (B/T)_{j-1}]/h_{j-1}^2 + [(B/T)_{j+1} - (B/T)_j]/h_j^2\}$$

$$(1-\alpha_j)M_{j-1} + 2M_j + \alpha_j M_{j+1} = 3\{(1-\alpha_j)/h_{j-1}[(B/T)_j - (B/T)_{j-1}] + \alpha_j/h_j[(B/T)_{j+1} - (B/T)_j]\} \qquad \text{II-10}$$

where $\alpha_j = h_{j-1}/(h_{j-1} + h_j) = 5/10 = 1/2$. Also, it was assumed that the second derivative is zero at both end points of the data. so, $S''(T_0) = S''(T_n) = 0$. Then, in order to compute the value of M_j at each temperature, the following equations need to be solved:

$$2M_0 + M_1 = \beta_0$$

$$(1-\alpha_1)M_0 + 2M_1 + \alpha_1 M_2 = \beta_1$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$(1-\alpha_{n-1})M_{n-2} + 2M_{n-1} + \alpha_{n-1}M_n = \beta_{n-1}$$

$$M_{n-1} + 2M_n = \beta_n \tag{II-11}$$

Where $\beta_0 = 3/h_0(Y_1 - Y_0) = 3/5[(B/T)_1 - (B/T)_0)$;

$\beta_j = 3[(1-\alpha_j)(Y_j - Y_{j-1})/h_{j-1} + \alpha_j(Y_{j+1} - Y_j)/h_j]$

$\beta_j = 3[1/10(Y_j - Y_{j-1}) + 1/10(Y_{j+1} - Y_j)]$

$\beta_j = 3/10(Y_{j+1} - Y_{j-1}) = 3/10[(B/T)_{j+1} - (B/T)_{j-1}]$;

$j = 1, 2, \ldots 19$;

$\beta_n = 3/h_{n-1}(Y_n - Y_{n-1}) = 3/5[(B/T)_n - (B/T)_{n-1}]$;

In essence, this results in the evaluation of the M(j) values by matrix solution of the following equation:

$$\begin{bmatrix} 2 & 1 & 0 & 0 & \ldots & 0 \\ 1/2 & 2 & 1/2 & 0 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & \ldots & 1/2 & 2 & 1/2 \\ 0 & 0 & \ldots & 0 & 1 & 2 \end{bmatrix} \begin{bmatrix} M_0 \\ M_1 \\ \ldots \\ M_{19} \\ M_{20} \end{bmatrix} = \begin{bmatrix} 3/5[(B/T)_1 - (B/T)_0] \\ 3/10[(B/T)_2 - (B/T)_0] \\ \ldots\ldots\ldots \\ 3/10[(B/T)_{20} - (B/T)_{18}] \\ 3/5[(B/T)_{20} - (B/T)_{19}] \end{bmatrix}$$

The M(j) values for Nitrogen and mixture gas systems are listed on Table XIII.

TABLE XIII

The VALUE OF ∂(B/T)/∂T OF NITROGEN AND MIXTURE GAS SYSTEMS

M(j)N2	M(j)mix-3	M(j)mix-4	T(K)
0.002289	0.006342	0.011159	230
0.001612	0.004675	0.007965	235
0.001629	0.004411	0.007929	240
0.001459	0.003993	0.007506	245
0.001410	0.004054	0.007333	250
0.001420	0.003368	0.006039	255
0.001257	0.003289	0.005921	260
0.001047	0.003202	0.005852	265
0.001065	0.002750	0.004968	270
0.001057	0.002675	0.004828	275
0.000917	0.002507	0.004529	280
0.000781	0.002384	0.004150	285
0.000807	0.002249	0.003752	290
0.000743	0.002010	0.004118	295
0.000682	0.002032	0.003820	300
0.000666	0.001796	0.003080	305
0.000533	0.001631	0.002986	310
0.000622	0.001731	0.002974	315
0.000555	0.001599	0.003009	320
0.000147	0.001215	0.002392	325
-0.00001	0.001654	0.003333	330

Calculation of the Heat Capacity

The heat capacity data for Nitrogen and Methane at different pressures are given by the IUPAC tables(22,23). However, the heat capacity data of Ethane and Propane at different pressures are not available. Fortunately, the following derivation(24,25) provides a mechanism by which to calculate the heat capacity of a gas at different pressures. The gas thermodynamic properties give:

$$dH = TdS + VdP \qquad \text{II-12}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \qquad \text{II-13}$$

According to the Maxwell relations:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{II-14}$$

$$\therefore \quad \left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \qquad \text{II-15}$$

$$\left[\frac{\partial(\partial H/\partial P)}{\partial T}\right]_P = -\left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P + \left(\frac{\partial V}{\partial T}\right)_P \qquad \text{II-16}$$

$$\left(\frac{\partial Cp}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad \text{II-17}$$

According to the virial equation of state:

$$PV^2 = RTV + BRT \qquad \text{II-18}$$

Therefore:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R(V + B)}{2PV - RT} \qquad \text{II-19}$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \frac{2R(\partial V/\partial T)}{2P + 2PV - RT} \qquad \text{II-20}$$

After substitution of equation II-19 into equation II-20, the second derivative of the volume may be expressed by:

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \frac{2R^2(V + B)}{(2P+2PV-RT)(2PV-RT)} \qquad \text{II-21}$$

$$\therefore \quad \left(\frac{\partial Cp}{\partial P}\right)_T = \frac{-2TR^2(V + B)}{(2P+2PV-RT)(2PV-RT)} \qquad \text{II-22}$$

$$dC_P = \frac{-2TR^2(V + B)}{(2P+2PV-RT)(2PV-RT)}\, dP \qquad \text{II-23}$$

According to the virial equation, and ignoring higher order terms:

$$P = \frac{RT}{V} + \frac{BRT}{V^2} \qquad \text{II-24}$$

So that:

$$dP = \frac{RT(V + 2B)}{V^3}\, dV \qquad \text{II-25}$$

Substitution of equation II-24 and II-25 into II-23 then yields:

$$dC_P = \frac{2R^2T(V + B)*RT(V + 2B)dV}{[2(RT/V+BRT/V^2)(1+V)-RT][2V(RT/V+BRT/V^2)-RT]V^3}$$

$$dCp = \frac{2R^3T^2(V + 2B)(V + B)dV}{[\frac{2RT(V+B)}{V^2} + RT + \frac{2BRT}{V}][RT + \frac{2BRT}{V}]V^3}$$

$$dCp = \frac{2R^3T^2(V + 2B)(V + B)dV}{\frac{RT[2(V + B) + V^2 + 2BV]}{V^2}\;\frac{RT(V + 2B)V^3}{V}} \qquad \text{II-26}$$

$$\therefore \quad dC_P = \frac{2R(V + B)}{V^2 + 2(B + 1)V + 2B}\, dV \qquad \text{II-27}$$

However, equation II-27 cannot be integrated analytically. A numerical approximation can be used to perform the integration.

The detailed procedure is , first, to choose P = 1 atm as the reference condition and use the following equations (25) to calculate the heat capacity of Ethane and Propane over the temperature range 270-330K at P = 1 atm, respectively:

$$Cp = 2.247 + 0.0382T - 11.049*10^{-6}T^{2} \text{ cal/molK} \qquad \text{II-28}$$

$$Cp = 2.410 + 0.0572T - 17.533*10^{-6}T^{2} \text{ cal/molK} \qquad \text{II-29}$$

Then the values of the heat capacity Cpx at different pressures can be obtained from:

$$C_{px} = C_{p} + \frac{2R(V + B)}{V + 2(B + 1)V + 2B} \Delta V \qquad \text{II-30}$$

The applicable temperature range for equation II-28 and II-29 is from 298K to 1500K. In this calculation, the low temperature limit was extended down to 270K. In order to verify that this procedure was reliable, the equivalent equation for Nitrogen (II-31) was used to calculate the heat capacity of Nitrogen over the temperature range 270-330K. This data compared well with the IUPAC data.

$$Cp = 6.83 + 0.90*10^{-3}T - 0.12*10^{5}T^{-2} \text{ cal/molK} \qquad \text{II-31}$$

The heat capacity of the mixture gas systems can then be calculated by using the following equation:

$$Cpmix = \Sigma XiCpi \qquad \text{II-32}$$

and is tabulated in the following Tables.

Table XIV shows that the Cp values calculated according to equation II-32 are within 3% error of those tabulated in the IUPAC listing, verifying the reliability of the software applied to calculation of the heat capacity values.

TABLE XIV

THE HEAT CAPACITY OF NITROGEN AND METHANE AT P=1 atm

Cp(N2)	Cp*(N2)	Cp(CH4)	T(K)
29.2	28.50	34.1	230
29.2	28.5	34.15	235
29.2	28.61	34.2	240
29.2	28.66	34.3	245
29.2	28.71	34.4	250
29.2	28.76	34.5	255
29.2	28.81	34.6	260
29.2	28.86	34.75	265
29.2	28.90	34.9	270
29.2	28.95	35.05	275
29.2	28.99	35.2	280
29.2	29.03	35.35	285
29.2	29.07	35.5	290
29.2	29.11	35.7	295
29.2	29.15	35.9	300
29.2	29.18	36.05	305
29.2	29.22	36.2	310
29.2	29.25	36.45	315
29.2	29.29	36.7	320
29.2	29.32	36.9	325
29.2	29.35	37.1	330

Source: Reference(21,22). IUPAC table.
Cp*(N2) was calculated by equation II-31.

TABLE XV

THE HEAT CAPACITY OF NITROGEN AND METHANE AT DIFFERENT PRESSURES

Cp(N2)	Cp(CH4)	Cp(N2)	Cp(CH4)	T(K)
P=5	P=5	P=10	P=10	
29.50	34.80	29.60	35.80	230
29.50	34.85	29.60	35.80	235
29.50	34.90	29.60	35.80	240
29.50	34.95	29.60	35.80	245
29.50	35.00	29.60	35.80	250
29.50	35.10	29.60	35.90	255
29.50	35.20	29.60	35.90	260
29.50	35.30	29.60	35.95	265
29.50	35.40	29.60	36.00	270
29.50	35.50	29.60	36.10	275
29.50	35.60	29.60	36.20	280
29.50	35.75	29.60	36.30	285
29.50	35.90	29.60	36.40	290
29.50	36.05	29.60	36.55	295
29.50	36.20	29.60	36.70	300
29.50	36.40	29.60	36.85	305
29.50	36.60	29.60	37.00	310
29.50	36.80	29.60	37.15	315
29.50	37.00	29.60	37.30	320
29.50	37.20	29.60	37.50	325
29.50	37.40	29.60	37.70	330

TABLE XV (Continued)

Cp(N2)	Cp(CH4)	Cp(N2)	Cp(CH4)	T(K)
P=15	P=15	P=20	P=20	
30.00	37.10	30.50	38.4	230
30.00	36.95	30.50	38.15	235
30.00	36.80	30.50	37.90	240
30.00	36.75	30.50	37.75	245
30.00	36.70	30.50	37.60	250
30.00	36.65	30.50	37.50	255
30.00	36.60	30.50	37.40	260
30.00	36.65	30.50	37.40	265
30.00	36.70	30.50	37.40	270
30.00	36.75	30.50	37.40	275
30.00	36.80	30.50	37.40	280
30.00	36.85	30.50	37.45	285
30.00	36.90	30.50	37.50	290
30.00	37.05	30.50	37.60	295
30.00	37.20	30.50	37.70	300
30.00	37.30	30.50	37.80	305
30.00	37.40	30.50	37.90	310
30.00	37.55	30.50	38.05	315
30.00	37.70	30.50	38.20	320
30.00	37.90	30.50	38.35	325
30.00	38.10	30.50	38.50	330

Source: Reference(21,22), IUPAC table.

TABLE XVI

THE HEAT CAPACITY OF ETHANE AND PROPANE AT P=1 atm

Cp(C2H6)	Cp(C3H8)	T(K)
43.716335	61.248165	230
44.407986	62.274261	235
45.097328	63.296692	240
45.784355	64.315453	245
46.469074	65.330544	250
47.151478	66.341972	255
47.831573	67.349731	260
48.509354	68.353821	265
49.184822	69.354248	270
49.857983	70.351006	275
50.528828	71.344093	280
51.197365	72.333519	285
51.863586	73.319275	290
52.527500	74.301361	295
53.189098	75.279785	300
53.848389	76.254539	305
54.505367	77.225624	310
55.160030	78.193047	315
55.812386	79.156792	320
56.462425	80.116882	325
57.110157	81.073296	330

TABLE XVII

THE HEAT CAPACITY OF ETHANE AND PROPANE AT DIFFERENT PRESSURES

Cp(C2H6)	Cp(C3H8)	Cp(C2H6)	Cp(C3H8)	T(K)
P=5 atm	P=5 atm	P=10 atm	P=10 atm	
44.211113	61.827007	44.651840	63.309082	230
44.901798	62.847706	45.332611	64.171982	235
45.590660	63.860600	46.014725	65.015610	240
46.277943	64.872078	46.698566	65.929047	245
46.963085	65.880798	47.381340	66.730087	250
47.645439	66.887306	48.060440	67.575119	255
48.325653	67.893494	48.738323	68.537193	260
49.003666	68.893723	49.414650	69.490005	265
49.679482	69.893242	50.089371	70.471176	270
50.353939	70.886971	50.765350	71.438881	275
51.024464	71.877708	51.433491	72.411201	280
51.694340	72.864998	52.105247	73.383667	285
52.360794	73.849113	52.771011	74.356674	290
53.025738	74.831223	53.437283	75.334892	295
53.687729	75.806999	54.099186	76.298111	300
54.348103	76.782028	54.761158	77.271233	305
55.005844	77.752228	55.419823	78.236107	310
55.661335	78.720070	56.076450	79.203041	315
56.314518	79.683144	56.730827	80.162102	320
56.965435	80.642792	57.383091	81.118729	325
57.614040	81.598785	58.033077	82.071991	330

TABLE XVII (Continued)

Cp(C2H6)	Cp(C2H6)	T(K)
P=15 atm	P=20 atm	
45.271507	46.079811	230
45.926159	46.469353	235
46.441143	47.007320	240
47.078346	47.619217	245
47.735905	48.255928	250
48.394573	48.894592	255
49.058891	49.546570	260
49.725594	50.089333	265
50.393406	50.694340	270
51.067982	51.350586	275
51.728821	51.984089	280
52.400650	52.649975	285
53.062916	53.300972	290
53.728962	53.962921	295
54.388882	54.616726	300
55.051384	55.277485	305
55.709808	55.933418	310
56.366611	56.588608	315
57.021339	57.242188	320
57.674236	57.894470	325
58.324978	58.544891	330

TABLE XVIII

THE HEAT CAPACITY OF MIXTURE GAS SYSTEMS AT DIFFERENT PRESSURES

Cpmix-3	Cpmix-4	Cpmix-3	Cpmix-4	T(K)
P=5 atm	P=5 atm	P=10 atm	P=10 atm	
34.562222	40.497623	35.170368	41.272182	230
34.720360	40.854900	35.306522	41.580917	235
34.878132	41.210251	35.442944	41.886066	240
35.035587	41.565006	35.579712	42.205521	245
35.192616	41.918777	35.716267	42.502285	250
35.369087	42.286549	35.812088	42.777111	255
35.545132	42.653831	35.947666	43.105103	260
35.720734	43.019478	36.102932	43.445930	265
35.895897	43.384544	36.257874	43.792110	270
36.070789	43.748180	36.433071	44.150845	275
36.244892	44.110435	36.606697	44.508938	280
36.438869	44.486866	36.781048	44.867783	285
36.632160	44.861980	36.954205	45.225536	290
36.825146	45.236393	37.147457	45.599434	295
37.017548	45.608948	37.017548	45.969460	300
37.229622	45.996025	37.532230	46.341476	305
37.441170	46.381615	37.723965	46.711185	310
37.652267	46.766281	37.915291	47.080898	315
37.862904	47.149532	38.106167	47.448586	320
38.073086	47.531647	38.316620	47.830364	325
38.282810	47.912567	38.526615	48.211014	330

TABLE XVIII (Continued)

Cpmix-3 P=15 atm	Cpmix-3 P=20 atm	T(K)
35.894302	36.775963	230
35.965233	36.753872	235
36.008228	36.761463	240
36.115669	36.823845	245
36.227180	36.891186	250
36.338917	36.978920	255
36.451778	37.069313	260
36.605118	37.177868	265
36.758682	37.298870	270
36.913597	37.430119	275
37.065765	37.556820	280
37.220131	37.709995	285
37.372585	37.860195	290
37.565792	38.032585	295
37.757778	38.203346	300
37.930275	38.375496	305
38.101963	38.546684	310
38.293324	38.737720	315
38.484268	38.928436	320
38.694847	39.118893	325
38.904995	39.308979	330

Calculation of the μ_{JT}

The final step is to calculate μ_{JT} data of pure gas and mixture gas systems respectively by use of the following equation:

$$\mu_{JT} = \frac{T^2}{Cp[1 + 4PB/(RT)]^{\frac{1}{2}}} \left[\frac{\partial(B/T)}{\partial T}\right]_P \qquad \text{I-25}$$

The calculated μ_{JT} data are listed in the following Tables.

TABLE XIX

THE μJT DATA OF NITROGEN AT DIFFERENT PRESSURES

μJT1	μJT2	μJT3	μJT4	μJT5	T(K)
P=1	P=5	P=10	P=15	P=20 atm	
0.419845	0.419640	0.423457	0.420372	0.421721	230
0.325123	0.324403	0.326618	0.323475	0.323713	235
0.308588	0.308159	0.310598	0.307956	0.308546	240
0.303375	0.302471	0.304235	0.300997	0.300896	245
0.305338	0.304213	0.305707	0.302168	0.301771	250
0.319735	0.318333	0.319608	0.315614	0.314895	255
0.294329	0.292841	0.293758	0.289828	0.288903	260
0.254542	0.253113	0.253724	0.250146	0.249160	265
0.268731	0.267085	0.267555	0.263606	0.262388	270
0.276615	0.274773	0.275071	0.270823	0.269381	275
0.248750	0.246975	0.247090	0.243122	0.241674	280
0.219613	0.217955	0.217941	0.214326	0.212933	285
0.234932	0.233070	0.232944	0.228970	0.227372	290
0.223646	0.221785	0.221553	0.217662	0.216031	295
0.212279	0.210444	0.210137	0.206361	0.204728	300
0.214504	0.212575	0.212173	0.208268	0.206529	305
0.213458	0.211421	0.210873	0.206847	0.204975	310
0.177253	0.175609	0.175214	0.171928	0.170430	315
0.196553	0.194616	0.194037	0.190258	0.188462	320
0.053859	0.053319	0.053148	0.052102	0.051598	325
-0.004397	-0.004353	-0.004339	-0.004254	-0.004210	330

TABLE XX

THE μJT DATA OF THREE COMPONENT SYSTEM AT DIFFERENT PRESSURES

μJT1	μJT2	μJT3	μJT4	μJT5	T(K)
P=1	P=5	P=10	P=15	P=20 atm	
1.004183	1.029673	1.068415	1.112737	1.164247	230
0.768713	0.786132	0.812948	0.843950	0.879508	235
0.752573	0.767677	0.791348	0.819836	0.850170	240
0.742099	0.754658	0.774008	0.797086	0.821020	245
0.705947	0.719045	0.739396	0.763807	0.789425	250
0.637899	0.647474	0.663764	0.681043	0.699248	255
0.644097	0.652680	0.668258	0.684172	0.700579	260
0.647534	0.655434	0.669852	0.683954	0.698960	265
0.573925	0.580387	0.592230	0.603264	0.615331	270
0.575793	0.581827	0.592587	0.602696	0.613667	275
0.556221	0.561618	0.570952	0.579827	0.589400	280
0.544888	0.549531	0.558057	0.566019	0.574221	285
0.529234	0.533113	0.540797	0.547830	0.554691	290
0.505529	0.508770	0.514684	0.519829	0.525197	295
0.486464	0.489803	0.496171	0.501865	0.507585	300
0.459322	0.461582	0.466598	0.470861	0.475013	305
0.428598	0.430129	0.434555	0.438241	0.441547	310
0.466664	0.468210	0.472762	0.476221	0.479223	315
0.442046	0.443384	0.447430	0.450172	0.452445	320
0.344480	0.348131	0.349935	0.351534	0.345294	325
0.480739	0.481581	0.485131	0.487223	0.489252	330

TABLE XXI

THE µJT DATA OF FOUR COMPONENT SYSTEM AT DIFFERENT PRESSURES

µJT1	µJT2	µJT3	T(k)
P=1	P=5	P=10 atm	
1.518544	1.624429	1.801857	230
1.151728	1.192121	1.331426	235
1.120237	1.219780	1.311061	240
1.124856	1.186617	1.286417	245
1.132948	1.190437	1.282688	250
0.961349	1.006335	1.079778	255
0.970651	1.012828	1.081977	260
0.986909	1.026710	1.091436	265
0.861468	0.893920	0.946261	270
0.860367	0.890757	0.939122	275
0.828975	0.856374	0.899379	280
0.779835	0.803785	0.841534	285
0.814156	0.836033	0.870255	290
0.723476	0.744124	0.776865	295
0.773947	0.793243	0.823022	300
0.639479	0.654119	0.677237	305
0.635044	0.648327	0.669882	310
0.647206	0.660005	0.680731	315
0.669764	0.682149	0.702194	320
0.544565	0.553889	0.569064	325
0.775802	0.788051	0.808130	330

CHAPTER III

CONCLUSIONS AND RECOMMENDATIONS

Curves of μ_{JT} vs. T for pure Nitrogen, the three component system and the four component system are shown on figure 3, figure 4 and figure 5, respectively. The μ_{JT} vs. T for Pure Methane, Ethane and Propane at P=1 atm are shown in figure 4. On figure 3, the data for μ_{JT} for Nitrogen(26) is shown for comparison. Other than the disjointed character of the data calculated for this work, the literature values are very similar to those calculated for this work. This demonstrates that the calculational procedures and programs appear to be reliable. From this calculated information the following conclusions may be drawn:

I. The cooling efficiency of mixture gas systems are much higher than that of any pure gas system. A three component system has a 2.5 fold higher cooling efficiency compared with pure Nitrogen, while a four component system has a 4 fold higher cooling efficiency than pure Nitrogen.

II. In pure gas systems, μ_{JT} is relatively insensitive to increasing pressure. However, in mixture gas systems, μ_{JT} significantly increases with increasing pressure. This phenomenon indicates that cooling efficiency of gas mixtures may be improved by operating at the highest pressures permitted by the refrigerant device.

The μ_{JT} curves are not smooth, against expectations. The jitter in the data may come from either errors in the second virial coefficient B(T) data obtained by using Corner's four-center molecular model or from errors in the heat capacity data. Better calculation results may be achieved in future work by using the following improvements:

I. Calculate the second virial coefficient by quantum mechanical procedures.

II. Use more accurate methods to calculate the heat capacity of mixture gas systems at different pressures.

III. Expand the calculation to include analysis of the third virial coefficient.

IV. Incorporate procedures to accommodate liquefaction. Propane has a large component in the liquid state at 15 atm and 27 C(27). Since pressures up to this value would exist in a useful refrigerator, clearly liquefaction has to be considered for practical systems.

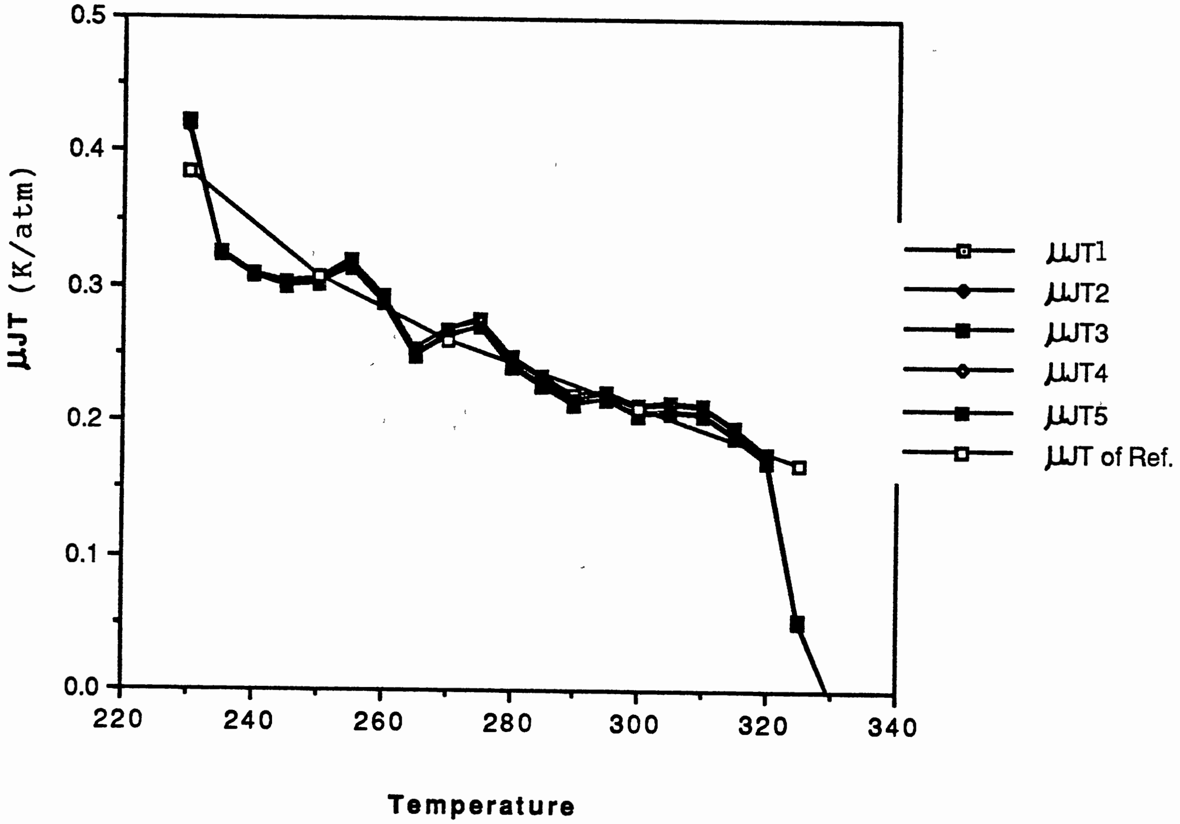

Figure 3. μ_{JT} for Pure Nitrogen vs. Temperature at Different Pressures. ($\mu_{JT}1$ at P=1 atm, $\mu_{JT}2$ at P=5 atm, $\mu_{JT}3$ at P=10 atm, $\mu_{JT}4$ at P=15 atm, $\mu_{JT}5$ at P=20 atm.)

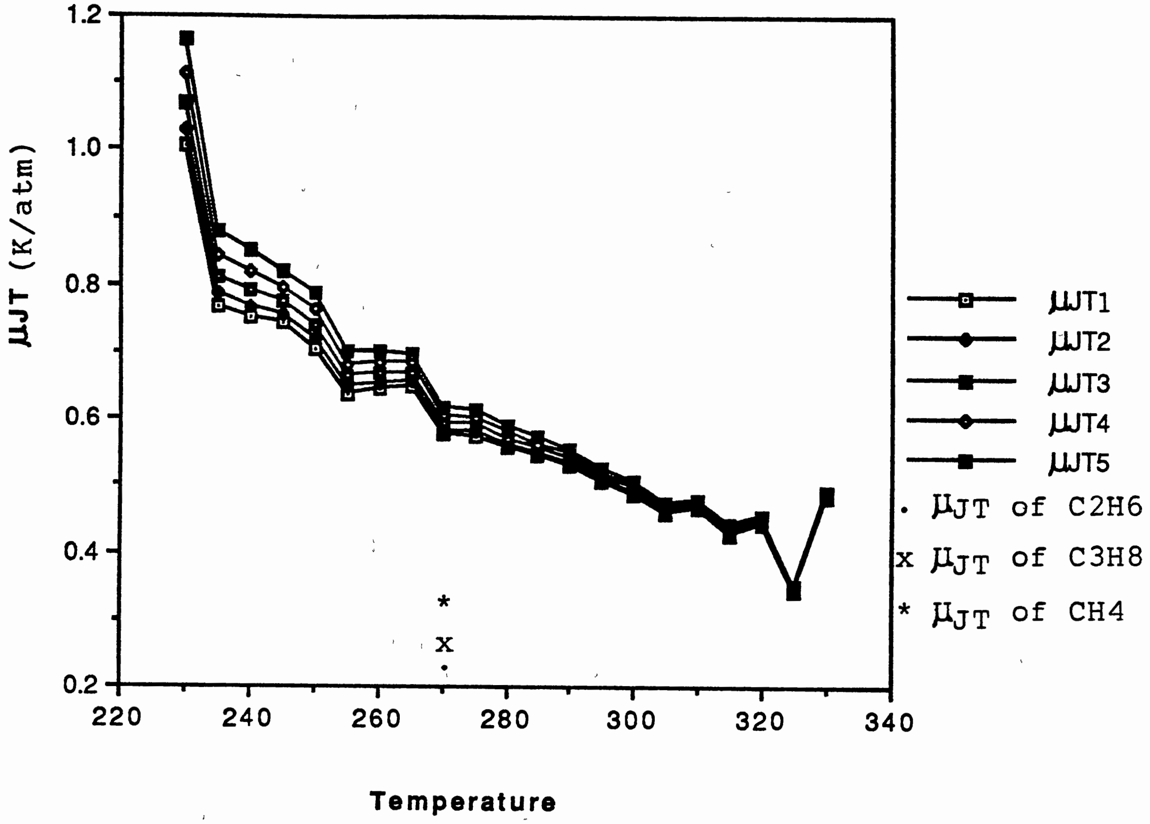

Figure 4. μ_{JT} for Three Component System vs. Temperature at Different Pressures. ($\mu_{JT}1$ at P=1 atm, $\mu_{JT}2$ at P=5 atm, $\mu_{JT}3$ at P=10 atm, $\mu_{JT}4$ at P=15 atm, $\mu_{JT}5$ at P=20 atm.)

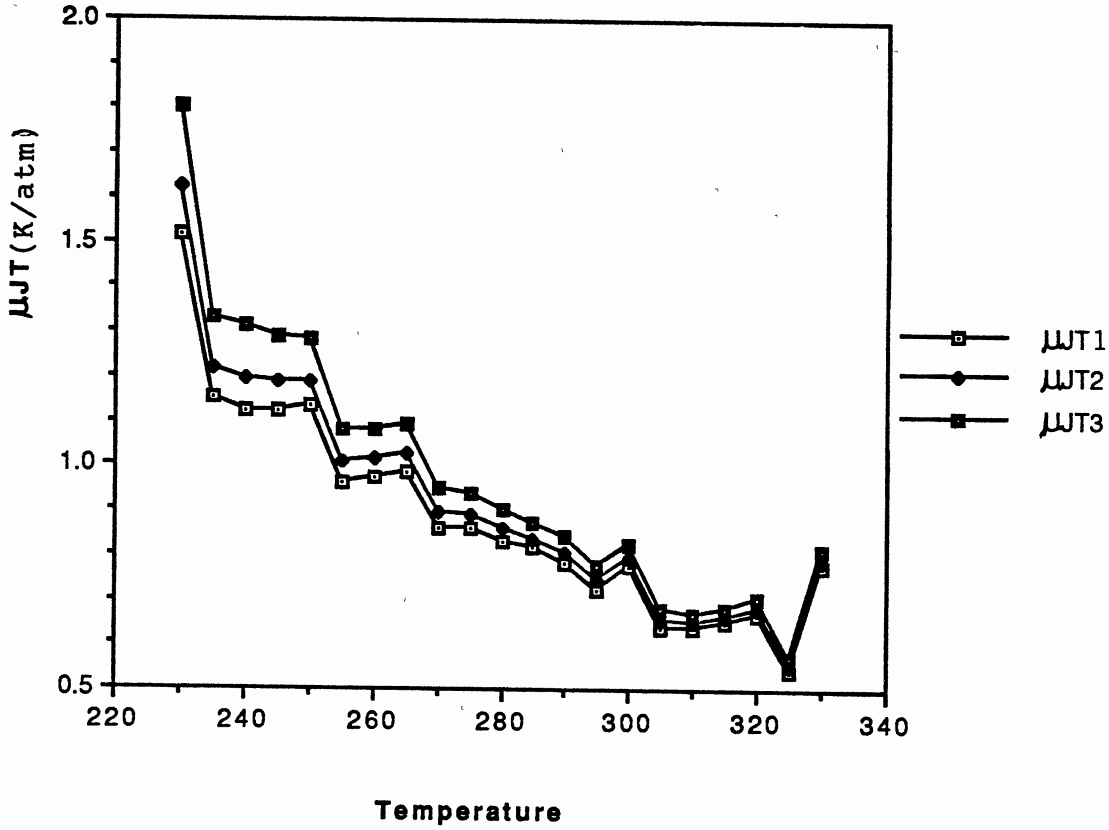

Figure 5. μ_{JT} for Four Component System vs. Temperature at Different Pressures. (μ_{JT}1 at P=1 atm, μ_{JT}2 at P=5 atm, μ_{JT}3 at P=10 atm.)

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APPENDIX

COMPUTER PROGRAMS

PROGRAM TO CALCULATE μ_{JT} DATA OF NITROGEN

```
#include <stdio.h>
#include <conio.h>
#include <math.h>
#include <io.h>

#define   R  0.08206

FILE *store;
FILE *output;
FILE *result;
FILE *store1;

int i, j, k;
int p1,p2,p3,p4,p5,p6,p7;
p1=1;
p2=5;
p3=10;
p4=15;
p5=20;
p6=25;
p7=30;

float sum;
float B[22], Y[22], M[22], S[22], C[22], Cnew[22], T[22];
float UJT1[22],UJT2[22],UJT3[22],UJT4[22],UJT5[22],UJT6[22],UJT7[22];
float A[22][22];
float Anew[22][22];

main()
{
char query;
printf("This is a test program.\n");
printf("if you want to create a NEW file data type --y--\n");
query=getche();
if((query=='y')|(query=='Y'))
      take_raw();
else
      take_calculate();
}

take_raw()
{
store=fopen("pgasdata","w+");
fprintf(store, "\tB[i]                T[i]\n");

for(i=0;i<21;++i)
        {
        printf("\ninput #%d\n", i);
        scanf("%f %f\n", &B[i], &T[i]);
        fprintf(store, "\t%f         %f\n", B[i], T[i]);
        }
}
```

```
take_calculate()
{
store=fopen("pgasdata","r");

for(i=0;i<21;++i)
        {
        fscanf(store,"%f %f\n", &B[i], &T[i]);
        }

output=fopen("poutdata","w+");
fprintf(output,"This is a table of N2 B[i]/T[i] Vs T[i]\n");

for(i=0;i<21;++i)
        {
        Y[i]=B[i]/T[i];
        printf("\t%f         %f\n", Y[i], T[i]);
        fprintf(output,"\t%f          %f\n",Y[i], T[i]);
        }

/* The following program use cubic spline method to calculate the slope
   value Mj of curve (B/T) vs T at each T point.  The name pgas_spline
   is used to account pure gas system.
   In cubic spline:  H[j]=T[j+1]-T[j]=5;
                     a[j]=H[j-1]/(H[j-1]+H[j])=1/2, (1-a[j])=1/2;
                     C[0]=3/5*(Y[1]-Y[0]);
                     C[20]=3/5*(Y[20]-Y[19]);
                     C[j]=3/10*(Y[j+1]-Y[j-1]), for j=1,19;
   The Mj value can be get by solving a tridiagonal matrix.          */

        C[0]=0.6*(Y[1]-Y[0]);
        C[20]=0.6*(Y[20]-Y[19]);
i=0;
for(i=i+1;i<20; ++i)
        {
        C[i]=0.3*(Y[i+1]-Y[i-1]);
        }

printf("This is array C data\n");

for(i=0; i<21; ++i)
        {
        printf("\t%f\n", C[i]);
        }

/* set up matrix A data.         */
```

```
for(i=0; i<21; ++i)
        for(j=0; j<21; ++j)
                {
                if(j==i)
                        A[i][j]=2.0;
                else
                        if(j==(i-1)||j==(i+1))
                                {
                                if(i!=0||i!=20)
                                        A[i][j]=0.5;
                                else
                                        A[i][j]=1.0;
                                }
                else
                        A[i][j]=0.0;
                }

printf("The follow data is about array A\n");

for (i=0;i<21;++i)
        {
        for(j=0;j<21;++j)
                {
                printf("%2.1f ", A[i][j]);
                }
        printf("\n");
        }

for(j=0;j<21;++j)
        {
        i=j+1;
        Cnew[i]=C[i]-A[i][j]*C[j]/A[j][j];
        C[i]=Cnew[i];

        for(k=j;k<21;++k)
                {
                Anew[i][k]=A[i][k]-A[i][j]*A[j][k]/A[j][j];
                }

        for(k=j;k<21;++k)
                {
                A[i][k]=Anew[i][k];
                }
        }

getch();

printf("The follow data is diagonal matrix.\n");
```

```
for(i=0; i<21; ++i)
        {
        for(j=0; j<21; ++j)
                {
                printf("%2.1f ", A[i][j]);
                }
        printf(" %f\n", C[i]);
        }

/*  Now calculate the slope value M[j].     */

M[20]=C[20]/A[20][20];
for(i=19;i>=0;--i)
        {
        sum=0.0;
        for(j=20; j>=(i+1); --j)
                {
                sum=sum+A[i][j]*M[j];
                }
        M[i]=(C[i]-sum)/A[i][i];
        }

store1=fopen("slope.N","w+");
fprintf(store1, "\t Table of M[i] Vs T[i]\n");
for(i=0;i<=20;++i)
        {
        fprintf(store1, "\t%f   %f\n", M[i],T[i]);
        printf("\t%f  %f\n", M[i], T[i]);
        }

/* The final step is to calculate Joule-Thomson coefficent UJT
   by equation: UJT[i]=T[i]*T[i]*M[i]/(Cp*sqrt(1+4*P*B[i]/(R*T[i]))  */

result=fopen("UJTdata","w+");
fprintf(result,"This is UJT data table.\n");
printf(" P=1      P=5      P=10     P=15      P=20      P=25     P=30\n");

for(i=0;i<21;++i)
        {
        UJT1[i]=T[i]*T[i]*M[i]/(29.2*sqrt(1+4*p1*0.001*B[i]/(R*T[i])));
        UJT2[i]=T[i]*T[i]*M[i]/(29.5*sqrt(1+4*p2*0.001*B[i]/(R*T[i])));
        UJT3[i]=T[i]*T[i]*M[i]/(29.6*sqrt(1+4*p3*0.001*B[i]/(R*T[i])));
        UJT4[i]=T[i]*T[i]*M[i]/(30.2*sqrt(1+4*p4*0.001*B[i]/(R*T[i])));
        UJT5[i]=T[i]*T[i]*M[i]/(30.5*sqrt(1+4*p5*0.001*B[i]/(R*T[i])));
        UJT6[i]=T[i]*T[i]*M[i]/(30.9*sqrt(1+4*p6*0.001*B[i]/(R*T[i])));
        UJT7[i]=T[i]*T[i]*M[i]/(31.3*sqrt(1+4*p7*0.001*B[i]/(R*T[i])));
        printf("%f %f %f %f %f %f %f %f\n",
            UJT1[i],UJT2[i],UJT3[i],UJT4[i],UJT5[i],UJT6[i],UJT7[i],T[i]);
        fprintf(result,"%f  %f  %f  %f  %f  %f  %f  %f\n",
            UJT1[i],UJT2[i],UJT3[i],UJT4[i],UJT5[i],UJT6[i],UJT7[i],T[i]);
        }

        fcloseall();
}
```

PROGRAM TO CALCULATE $\partial(B/T)/\partial T$ OF MIXTURE GAS SYSTEM

```
#include <stdio.h>
#include <conio.h>
#include <math.h>
#include <io.h>

#define R     0.08206
#define X1    0.30
#define X2    0.30
#define X3    0.20
#define X4    0.20
#define X11   0.40
#define X22   0.40
#define Y1    (0.30 * 0.30)
#define Y2    (0.30 * 0.30)
#define Y3    (0.20 * 0.20)
#define Y4    (0.20 * 0.20)
#define Y11   (0.40 * 0.40)
#define Y22   (0.40 * 0.40)

FILE *store;
FILE *output;
FILE *output1;
FILE *output2;

float T[22], VM[22], VE[22], VP[22], VN[22];
float B11[22], B22[22], B33[22], B44[22], B12[22], B13[22];
float B14[22], B23[22], B24[22], B34[22], Bmix[22], D3[22], D[22];
float C3[22], C[22], Cnew3[22], Cnew[22], M3[22], M[22], Bmix3[22];
float sum;
float CpM[22], CpE[22], CpP[22], CpN[22];
float A[22][22];
float Anew[22][22];

int i, j, k, P;

main()
{
char query;
printf("This is a directory program.\n");
printf("If you want to create a NEW data file enter --y--\n");

query=getche();

if ((query=='y')|(query=='Y'))
        take_raw();
else
        take_calculate();
}
```

```
take_raw()
{
store=fopen("mixgdata","w+");

for(i=0;i<21;++i)
        {
        printf ("\ninput #%d\n", i);

        scanf("%f %f %f %f %f %f %f %f %f %f %f\n",
                &B11[i],&B22[i],&B33[i],&B44[i],
                &B12[i],&B13[i],&B14[i],
                &B23[i],&B24[i],&B34[i],&T[i]);

        fprintf(store,"\t%14.6f%14.6f%14.6f%14.6f\n\t%14.6f%14.6f%14.6f\n",
                B11[i],B22[i],B33[i],B44[i],
                B12[i],B13[i],B14[i]);
        fprintf(store,"\t%14.6f%14.6f%14.6f%14f\n",
                B23[i],B24[i],B34[i],T[i]);
         }
}

take_calculate()
{
store=fopen("mixgdata","r");

output1=fopen("mix.B","w+");

i=0;
while(i<=20)
        {
        fscanf(store,"%f %f %f %f\n %f %f %f\n %f %f %f %f\n",
                        &B11[i],&B22[i],&B33[i],&B44[i],
                        &B12[i],&B13[i],&B14[i],
                        &B23[i],&B24[i],&B34[i],&T[i]);

        Bmix3[i]=Y11*B11[i]+Y22*B22[i]+Y3*B33[i]+
                        2*(X11*X22*B12[i]+X11*X3*B13[i]+X22*X3*B23[i]);

        Bmix[i]=Y1*B11[i]+Y2*B22[i]+Y3*B33[i]+Y4*B44[i]+

                        2*(X1*X2*B12[i]+X1*X3*B13[i]+X1*X4*B14[i]+
                                X2*X3*B23[i]+X2*X4*B24[i]+X3*X4*B34[i]);

        fprintf(output1,"\t%f     %f     %f\n",Bmix3[i],Bmix[i],T[i]);
        ++i;
        }

output=fopen("moutdata","w+");

printf("\nMIXTURE GASES B[i]/T[i]        T[i]\n");
fprintf(output,"\nMIXTURE GASES B3[i]/T[i]     B[i]/T[i]       T[i]\n");
```

```
for(i=0;i<21;++i)
        {
        D3[i]=Bmix3[i]/T[i];
        D[i]=Bmix[i]/T[i];

        printf("\t  %f      %f        %f\n",D3[i],D[i],T[i]);
        fprintf(output,"\t  %12.6f    %12.6f     %f\n",D3[i],D[i],T[i]);
        }

/* The following program use cubic spline method to calculate the slope
value Mj of curve (B/T) vs T at each temperature point.
   In cubic spline:  H[j]=T[j+1]-T[j]=5;
                     a[j]=H[j-1]/(H[j-1]+H[j])=1/2;
                     C[j]=3/10*(D[j+1]-D[j-1]), for j=1,19;
                     C[0]=3/5*(D[1]-D[0]);
                     C[20]=3/5*(D[20]-D[19]);
   The Mj value can be get by solving this tridiagonal matrix.      */

        C[0]=0.6*(D[1]-D[0]);
        C3[0]=0.6*(D3[1]-D3[0]);
        C[20]=0.6*(D[20]-D[19]);
        C3[20]=0.6*(D3[20]-D3[19]);

j=0;
for(j=j+1;j<20;++j)
        {
        C3[j]=0.3*(D3[j+1]-D3[j-1]);
        C[j]=0.3*(D[j+1]-D[j-1]);
        }

printf("This is C data\n");
fprintf(output, "\t C3[i]       C[i]\n");
printf("        C3[j]          C[j]\n");

for(j=0;j<21;++j)
        {
        printf("\t %f     %f\n", C3[j],C[j]);
        fprintf(output,"\t %f     %f\n", C3[j],C[j]);
        }

/* The following data are matrix A.                       */
```

```
for(i=0;i<21;++i)
        for(j=0;j<21;++j)
                {
                if(j==i)
                        {
                        A[i][j]=2.0;
                        }
                else
                        if(j==(i-1)||j==(i+1))
                                {
                                if(i!=0||i!=20)
                                        A[i][j]=0.5;
                                else
                                        A[i][j]=1.0;
                                }
                else
                        A[i][j]=0.0;
                }

printf("output the matrix A data\n");

for(i=0;i<21;++i)
        {
        for(j=0;j<21;++j)
                {
                printf("%2.1f ", A[i][j]);
                }
        printf("\n");
        }

for(j=0;j<21;++j)
        {
        i=j+1;
        Cnew3[i]=C3[i]-A[i][j]*C3[j]/A[j][j];
        C3[i]=Cnew3[i];

        Cnew[i]=C[i]-A[i][j]*C[j]/A[j][j];
        C[i]=Cnew[i];

        for(k=j;k<21;++k)
                {
                Anew[i][k]=A[i][k]-A[i][j]*A[j][k]/A[j][j];
                }

        for(k=j;k<21;++k)
                {
                A[i][k]=Anew[i][k];
                }
        }
```

```
printf("Following data is NEW matrix\n");

for(i=0;i<21;++i)
        {
        for(j=0;j<21;++j)
                {
                printf("%2.1f ", A[i][j]);
                }
        printf("\t%f   %f\n", C3[i], C[i]);
        }

M3[20]=C3[20]/A[20][20];
M[20]=C[20]/A[20][20];

for(i=19;i>=0;--i)
        {
        sum=0.0;
        for(j=20;j>=(i+1);--j)
                {
                sum=sum+A[i][j]*M3[j];
                }
                M3[j]=(C3[j]-sum)/A[i][i];
        }

for(i=19;i>=0;--i)
        {
        sum=0.0;
        for(j=20;j>=(i+1);--j)
                {
                sum=sum+A[i][j]*M[j];
                }
                M[j]=(C[j]-sum)/A[i][i];
        }

printf("This is slope value M[j] data.\n");

output2=fopen("slope.B","w+");

for(i=0;i<21;++i)
        {
        printf("\t%f     %f\n", M3[i], M[i]);
        fprintf(output2,"\t%f    %f    %f\n",M3[i],M[i],T[i]);
        }

fcloseall();
}
```

PROGRAM TO CALCULATE THE HEAT CAPACITY OF MIXTURE GAS SYSTEMS

```
#include <stdio.h>
#include <io.h>
#include <math.h>
#include <conio.h>

#define R   0.08206

FILE *store;
FILE *store1;
FILE *store2;
FILE *store3;
FILE *store4;
FILE *store5;
FILE *store6;
FILE *half1;

float B11[22], B22[22], B33[22], B44[22];
float VM[22], VM1[22], VE[22], VE1[22], VP[22], VP1[22], VN[22], VN1[22];
float T[22], CpM[22], CpE[22], CpP[22], CpN[22], CpNN[22], CpC[22];
float CpM1[22], CpE1[22], CpP1[22], CpN1[22], CpNN1[22], CpC1[22];
float CpMIX4[22], CpMIX3[22];

int P, i;

main()
{
char query;
printf("this is a test program.\n");
printf("If you want to create a NEW data file please type --y--\n");

query=getche();

if((query=='y')¦(query=='Y'))
        take_raw();
else
        take_calculate();
}

take_raw()
{
store=fopen("coef.B","w+");
store2=fopen("IUPNM.Cp","w+");

for(i=0;i<21;++i)
        {
        printf("\n input #%d\n",i);
        scanf("%f %f %f %f %f\n",&B11[i],&B22[i],&B33[i],&B44[i],&T[i]);
        fprintf(store,"\t %f  %f  %f  %f  %f\n",
                                B11[i], B22[i], B33[i], B44[i], T[i]);
```

```
        scanf("%f  %f\n", &CpNN[i],&CpC[i]);
        fprintf(store2,"\t %f    %f\n", CpNN[i], CpC[i]);
        }

store3=fopen("IUPNM1.Cp","w+");

for(P=5;P<=20;P+=5)
    for(i=0;i<21;++i)
        {
        scanf("%f    %f\n",&CpNN1[i],&CpC1[i]);
        fprintf(store3,"\t%f    %f\n",CpNN1[i],CpC1[i]);
        }
}

take_calculate()
{
store=fopen("coef.B","r");

for(i=0; i<21; ++i)
        {
        fscanf(store,"\t%f   %f   %f   %f   %f\n",
                        &B11[i], &B22[i], &B33[i], &B44[i], &T[i]);
        printf("%f   %f   %f  %f  %f\n",B11[i],B22[i],B33[i],B44[i],T[i]);
        }

/* calculate each component heat capacity value a P=1 atm. */

store1=fopen("dat1.Cp","w+");

fprintf(store1,"\tCpM[i]      CpE[i]      CpP[i]     CpN[i]     T[i]\n");

for(i=0;i<21;++i)
        {
        CpM[i]=4.184*(3.381+0.01804*T[i]-0.0000043*T[i]*T[i]);
        CpE[i]=4.184*(2.247+0.0382*T[i]-0.00001105*T[i]*T[i]);
        CpP[i]=4.184*(2.410+0.0572*T[i]-0.00001753*T[i]*T[i]);
        CpN[i]=4.184*(6.83+0.0009*T[i]-12000/(T[i]*T[i]));

        printf("\t%f  %f  %f  %f %f\n",CpM[i],CpE[i],CpP[i],CpN[i],T[i]);
        fprintf(store1,"\t%f   %f   %f   %f   %f\n",
                                CpM[i],CpE[i],CpP[i],CpN[i],T[i]);
        }

/* calculate each component volume value at P=1 atm. */

half1=fopen("volx.dat","w+");

fprintf(half1,"\t     VN[i]     VM[i]     VE[i]     VP[i]     T[i]\n");

P=1;
```

```
for(i=0;i<21;++i)
        {
        VN[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B11[i]*R*T[i]))/(2*P);
        VM[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B22[i]*R*T[i]))/(2*P);
        VE[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B33[i]*R*T[i]))/(2*P);
        VP[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B44[i]*R*T[i]))/(2*P);

        printf("\tP=1  %f  %f  %f  %f  %f\n",VN[i],VM[i],VE[i],VP[i],T[i]);
        fprintf(half1,"\tP=1   %f   %f   %f   %f   %f\n",
                                VN[i], VM[i], VE[i], VP[i], T[i]);
        }

/* calculate heat capacity value at different pressure.*/

fprintf(half1,"This is table for volume and Cp at different P\n");
printf("this is volume data for different P\n");

store5=fopen("Ethane.Cp","w+");

for(P=5;P<=20; P+=5)
     for(i=0;i<21;++i)
        {
        VN1[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B11[i]*R*T[i]))/(2*P);
        VM1[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B22[i]*R*T[i]))/(2*P);
        VE1[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B33[i]*R*T[i]))/(2*P);
        CpN1[i]=CpN[i]+2*R*(VN1[i]+B11[i])*
            (VN[i]-VN1[i])/(VN1[i]*VN1[i]+2*VN1[i]*(B11[i]+1)+2*B11[i]);
        CpM1[i]=CpM[i]+2*R*(VM1[i]+B22[i])*
            (VM[i]-VM1[i])/(VM1[i]*VM1[i]+2*VM1[i]*(B22[i]+1)+2*B22[i]);
        CpE1[i]=CpE[i]+2*R*(VE1[i]+B33[i])*
            (VE[i]-VE1[i])/(VE1[i]*VE1[i]+2*VE1[i]*(B33[i]+1)+2*B33[i]);

        printf("P=%3d  %f  %f  %f  %f  %f  %f  %f\n",
                     P,VN1[i],VM1[i],VE1[i],CpN1[i],CpM1[i],CpE1[i],T[i]);

        fprintf(half1,"P=%3d  %f  %f  %f  %f  %f  %f  %f\n",
                     P,VN1[i],VM1[i],VE1[i],CpN1[i],CpM1[i],CpE1[i],T[i]);

        fprintf(store5,"\t%f\n",CpE1[i]);
        }

store6=fopen("Prop.Cp","w+");

for(P=5;P<=10;P+=5)
     for(i=0;i<21;++i)
        {
        VP1[i]=(R*T[i]+sqrt(R*R*T[i]*T[i]+4*P*B44[i]*R*T[i]))/(2*P);
        CpP1[i]=CpP[i]+2*R*(VP1[i]+B44[i])*
            (VP[i]-VP1[i])/(VP1[i]*VP1[i]+2*VP1[i]*(B44[i]+1)+2*B44[i]);
```

```
        fprintf(half1,"\tP=%3d   %f   %f   %f\n",P,VP1[i],CpP1[i],T[i]);
        fprintf(store6,"\t%f\n",CpP1[i]);
        printf("\tP=%3d    %f    %f    %f\n",P,VP1[i],CpP1[i],T[i]);
        }

store2=fopen("IUPNM.Cp","r");

for(i=0;i<21;++i)
        {
        fscanf(store2,"\t%f    %f\n",&CpNN[i], &CpC[i]);
        printf("\t%f    %f\n",CpNN[i], CpC[i]);
        }

/*The following program is to calculate mixture gas Cp. */

store4=fopen("MIX.Cp","w+");

printf("the following data is mixture gases heat capacity at P=1\n");

for(i=0;i<21;++i)
        {
        CpMIX4[i]=0.30*CpNN[i]+0.30*CpC[i]+0.20*CpE[i]+0.20*CpP[i];
        CpMIX3[i]=0.4*CpNN[i]+0.40*CpC[i]+0.20*CpE[i];

        printf("\tP=1   %f   %f    %f\n",CpMIX3[i],CpMIX4[i],T[i]);
        fprintf(store4,"\t%f    %f    %f\n",CpMIX3[i],CpMIX4[i],T[i]);
        }

fcloseall();
}
```

PROGRAM TO CALCULATE μ_{JT} DATA OF MIXTURE GAS SYSTEMS

```
#include <stdio.h>
#include <io.h>
#include <math.h>
#include <conio.h>

FILE *output1;
FILE *output2;
FILE *store2;
FILE *store3;
FILE *store4;
FILE *store5;
FILE *store6;
FILE *store7;
FILE *store8;
FILE *store9;
FILE *store10;
FILE *store11;

#define R    0.08206

float T[22], M3[22], M[22], Bmix3[22], Bmix[22];
float CpC[22], CpC1[22],  CpMIX3[22], CpMIX4[22], CpNN[22], CpNN1[22];
float CpE1[22], CpP1[22], CpMIX33[22],CpMIX44[22];
float UJT3[22], UJT4[22], UJT33[22], UJT44[22];

int i, P;

main()
{
output1=fopen("mix.B","r");
printf("\tBmix3[i]       Bmix[i]       T[i]\n");

for(i=0;i<21;++i)
        {
        fscanf(output1,"\t%f    %f    %f\n",&Bmix3[i],&Bmix[i],&T[i]);
        printf("\t%f    %f    %f\n",Bmix3[i],Bmix[i],T[i]);
        }

output2=fopen("slope.B","r");
printf("\tM3[i]          M[i]          T[i]\n");

for(i=0;i<21;++i)
        {
        fscanf(output2,"\t%f    %f    %f\n",&M3[i],&M[i],&T[i]);
        printf("\t%f    %f    %f\n",M3[i],M[i],T[i]);
        }

store3=fopen("IUPNM1.Cp","r");
store5=fopen("Ethane.Cp","r");
```

```
store7=fopen("MIX1.Cp","w+");
store9=fopen("MIX1.UJT","w+");

printf("P   CpNN1[i]   CpC1[i]     CpE1[i]     CpMIX33[i]   UJT33[i]\n");

for(P=5;P<=20;P+=5)
        for(i=0;i<21;++i)
                {
                fscanf(store3,"\t%f    %f\n",&CpNN1[i],&CpC1[i]);
                fscanf(store5,"\t%f\n",&CpE1[i]);
                CpMIX33[i]=0.4*CpNN1[i]+0.4*CpC1[i]+0.2*CpE1[i];

UJT33[i]=T[i]*T[i]*M3[i]/(CpMIX33[i]*sqrt(1+4*P*0.001*Bmix3[i]/(R*T[i])));

printf("%3d   %f   %f   %f   %f    %f\n",
                P,CpNN1[i],CpC1[i],CpE1[i],CpMIX33[i],UJT33[i]);
fprintf(store7,"\tP=%3d    %f     %f\n",P,CpMIX33[i],T[i]);
fprintf(store9,"\tP=%3d    %f     %f\n",P,UJT33[i],T[i]);
                }

store3=fopen("IUPNM1.Cp","r");
store5=fopen("Ethane.Cp","r");
store6=fopen("Prop.Cp","r");
store8=fopen("MIX2.Cp","w+");
store10=fopen("MIX2.UJT","w+");

printf("P   CpP1[i]     CpE1[i]     CpNN1[i]     CpMIX44[i]   UJT44[i]\n");

for(P=5;P<=10;P+=5)
        for(i=0;i<21;++i)
                {
                fscanf(store3,"\t%f    %f\n",&CpNN1[i],&CpC1[i]);
                fscanf(store5,"\t%f\n",&CpE1[i]);
                fscanf(store6,"\t%f\n",&CpP1[i]);
        CpMIX44[i]=0.3*CpNN1[i]+0.3*CpC1[i]+0.2*CpE1[i]+0.2*CpP1[i];

UJT44[i]=T[i]*T[i]*M[i]/(CpMIX44[i]*sqrt(1+4*P*0.001*Bmix[i]/(R*T[i])));

printf("%3d   %f   %f   %f   %f   %f\n",
               P,CpP1[i],CpE1[i],CpNN1[i],CpMIX44[i],UJT44[i]);
fprintf(store8,"\tP=%3d     %f      %f\n",P,CpMIX44[i],T[i]);
fprintf(store10,"\tP=%d     %f      %f\n",P,UJT44[i],T[i]);
                }

/* The final step is to calculate UJT of 3-component and 4-component.*/

printf("\nThis is UJT of 3-component and 4-component at P=1.\n");

store4=fopen("MIX.Cp","r");
store11=fopen("MIX.UJT","w+");
```

```
P=1;
for(i=0;i<21;++i)
        {
        fscanf(store4,"\t%f    %f    %f\n",&CpMIX3[i],&CpMIX4[i],&T[i]);
UJT3[i]=T[i]*T[i]*M3[i]/(CpMIX3[i]*sqrt(1+4*P*0.001*Bmix3[i]/(R*T[i])));
UJT4[i]=T[i]*T[i]*M[i]/(CpMIX4[i]*sqrt(1+4*P*0.001*Bmix[i]/(R*T[i])));

printf("\t%f  %f  %f  %f  %f\n",CpMIX3[i],CpMIX4[i],UJT3[i],UJT4[i],T[i]);
fprintf(store11,"\t%f    %f      %f\n",UJT3[i],UJT4[i],T[i]);
        }

fcloseall();
}
```

VITA

Yali Xie

Candidate for the Degree of

Master of Science

Thesis: A CALCULATION OF THE REFRIGERATION EFFICIENCY OF A CH_4, C_2H_6, C_3H_8 AND N_2 MIXTURE OVER THE TEMPERATURE RANGE 270-330K USING THE SECOND VIRIAL COEFFICIENT

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