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Technical Notes

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Thermodynamic Analysis of Equations of State for the Monopropellant Hydrazine

Martha C. Mitchell,[*] Robert W. Rakoff,[†] Timothy O. Jobe,[†]
and Danielle L. Sanchez[‡]
New Mexico State University, Las Cruces,
New Mexico 88003-8001
and
D. Bruce Wilson[§]
NASA White Sands Test Facility, Las Cruces, New Mexico
88012

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Nomenclature

f = fugacity, kPa
p = absolute pressure, kPa
R = gas constant, 8.131434 m^3 kPa/kmol K
T = absolute temperature, K
$\underline{V}$ = molar volume, m^3/kmol
Z = compressibility factor, $p\underline{V}/RT$
φ^j = fugacity coefficient in the j phase, $(f/p)^j$
ω = acentric factor

Subscripts

B = normal boiling point
c = critical
r = reduced

Superscripts

L = saturated liquid
V = saturated vapor

Introduction

ENGINEERING design and safety analysis of operating systems involving hydrazine require an appropriate mechanical equation of state (EOS). A review of the literature yielded three published EOS for hydrazine, namely Martin's equation of state [1], a modified Clausius equation of state [2], and the Peng–Robinson equation of state [3]. The cited works concluded that each equation of state was suitable for the authors' purposes; however, there has not been an evaluation of the three for the full range of engineering design and safety analysis problems that might be encountered in using hydrazine. This work is an evaluation of the applicability and thermodynamic consistency of these equations for hydrazine. We examined these equations when applied to the vapor–liquid phase transition using a thermodynamic consistency test comparing liquid and vapor fugacity coefficients and liquid volumes, as well as a test of mechanical stability. The three equations of state that were evaluated, all reparameterized for a consistent set of units, are shown in Table 1.

In all cases the following parameters for hydrazine were used: $T_c = 653$ K, $p_c = 14700$ kPa, MW $= 32.045$ kg/kmol.

Thermodynamic Consistency, Vapor Pressure Correlations

To validate an EOS for vapor–liquid equilibrium, vapor pressure data (or empirical correlations) are required. Each study of hydrazine previously published in the literature used a different vapor pressure correlation. Table 2 shows the two vapor pressure correlations used. The published vapor pressure function by Haws and Harden [1] contains errors and was not considered.

By creating a semilog plot of pressure versus inverse temperature the thermodynamic consistency of the vapor pressure correlations can be tested. Figure 1 shows the thermodynamic consistency of these two correlations over the temperature range 273 to 650 K (near the critical temperature). A further comparison in Table 3 compares calculated vapor pressures at the normal boiling temperature, 387.3 K and at the critical temperature, 653 K.

Figure 1 suggests both correlations are consistent, although Table 3 suggests the Barragan et al. [3] correlation gives a somewhat better fit at the two temperatures evaluated. Both are consistent within the error associated with the original experimental data.

Thermodynamic Consistency, Equality of Fugacity Coefficients

The thermodynamic definition of phase equilibrium requires equality of the liquid phase chemical potential and the vapor phase chemical potential for a given temperature and pressure. For a pure component, this is equivalent to the equality of the liquid fugacity coefficient φ^L and the vapor phase fugacity coefficient φ^V. Using a pressure-explicit EOS, Eq. (1) is the expression for the fugacity coefficient,

$$\ell\mathrm{n}\,\varphi^j = \frac{1}{RT}\int_0^{\underline{V}^j}\left[p - \frac{RT}{\underline{V}}\right]d\underline{V} + (Z^j - 1) - \ell\mathrm{n}\,Z^j \qquad (1)$$

where the superscript j refers to the phase and Z is the corresponding phase compressibility factor. Table 4 shows each EOS in terms of compressibility factors and the corresponding fugacity coefficients.

To calculate vapor–liquid coexistence, first a temperature in the two phase region was chosen. Then the corresponding vapor pressure was calculated. With this pressure and temperature combination, the EOS was solved for the specific volume of both the liquid and vapor, and compressibility factors for both phases was calculated.

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[*] Associate Professor, Department of Chemical Engineering, Jett Hall 259, MSC 3805.

[†] Undergraduate Student, Department of Chemical Engineering, Jett Hall 259, MSC 3805.

[‡] Graduate Student, Department of Chemical Engineering, Jett Hall 259, MSC 3805.

[§] Consultant.

Table 1 Published hydrazine equations of state

EOS	Functional form[a]	Coefficients	Ref.
Martin[b]	$p=\frac{RT}{\underline{V}-b}+\frac{A_2+B_2T+C_2e^{-xT/T_c}}{(\underline{V}-b)^2}+\frac{A_3+B_3T+C_3e^{-xT/T_c}}{(\underline{V}-b)^3}+\frac{A_4}{(\underline{V}-b)^4}+\frac{B_5T}{(\underline{V}-b)^5}$	$A_2=-889.02$, $B_2=0.14629$, $C_2=-32319$, $A_3=48.001$, $B_3=0.016731$, $C_3=2553.0$, $A_4=-2.2317$, $B_5=5.1295\times10^{-5}$, $x=8.0000$, $b=0.059905$	[1]
Modified Clausius	$p=\frac{RT}{\underline{V}-A}-\frac{C}{T^n(V+B)^2}$	$A=0.026556$, $B=0.019609$, $C=2.4660\times10^8$ $n=0.7$ Using $\hat{V}_c=3.710\times10^{-3}\ \frac{\mathrm{m}^3}{\mathrm{kg}}$	[2]
Peng–Robinson	$p=\frac{RT}{\underline{V}-b}-\frac{a(T)}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)}$	$\omega=0.316$ $b=\frac{0.07780RT_c}{p_c}$ $\kappa=0.3764+1.54226\omega-0.26992\omega^2$ $a(T)=\frac{0.45724R^2T_c^2}{P_c}\alpha(T)$ $\alpha(T)=[1+\kappa(1-\sqrt{\frac{T}{T_c}})]^2$	[3]

[a] All EOS have been reparameterized to be in the units chosen for this paper, that is, K, kPa, $\mathrm{m}^3/\mathrm{kmol}$.

[b] Das and Kuloor [4] used the Martin EOS with an additional term C_5e^{-xT/T_c} with $C_5=-0.088334\times10^{-3}$, $x=5.475$.

Table 2 Vapor pressure correlations

Source	Correlation (T in K)
Giordano [5]	$\ln p(\mathrm{atm})=58.7582-\frac{0.707\times10^4}{T}-7.088\ln T$ $+0.4757\times10^{-2}T$
Barragan et al. [3]	$\log_{10}p(\mathrm{kPa})=60.003-\frac{3880.3}{T}-20.575\log_{10}T$ $+1.5585\times10^{-2}T-5.0525\times10^{-6}T^2$

Equation (1) was then used to calculate the fugacity coefficient for each phase. Figures 2–4 show the results for the Peng–Robinson EOS fugacity coefficient calculations, the results from the Clausius EOS fugacity coefficient calculations, and the results from the Martin EOS fugacity coefficient calculations for the vapor–liquid equilibrium of hydrazine. A 45 deg line, marking where the fugacity coefficients would be equal, is drawn in each figure. Calculations were done using both vapor pressure correlations. Table 5 shows a comparison of selected compressibility factors for each EOS.

The results of the calculations show that the Peng–Robinson EOS predicts vapor–liquid coexistence values that are thermodynamically consistent. Neither the Martin nor the Clausius EOS produce liquid and vapor fugacities of near equivalence. This indicates some degree of thermodynamic inconsistency in these equations. Table 5 shows that the modified Clausius EOS and the Martin EOS give comparable

Table 3 Vapor pressures from correlations at T_B and T_c

	Published temperature	Published pressure, kPa	Giordano [5], calculated, kPa	Barragan et al. [3], calculated, kPa
Normal boiling point, K	387.3	101.3	104.89	103.1
Critical point, K	653	14700	14672	14694

Table 4 Compressibility factor and fugacity coefficient forms for equations of state

EOS	Functions
Modified Clausius [2]	$Z^3+(2B'-A'-1)Z^2+(B'^2-2A'B'-2B'+C')Z+(-A'B'^2-B'^2-C'A')=0$ where $A'=Ap/RT$; $B'=Bp/RT$; $C'=Cp/R^2T^{2+n}$ $\ln\varphi^j=\ln(\frac{f}{p})^j=\ln(\frac{1}{Z^j-A'})-\frac{C'}{Z^j-B'}+(Z^j-1)$
Martin [1]	$d_5Z^5+d_4Z^4+d_3Z^3+d_2Z^2+d_1Z+d_0=0$ where $d_5=1.0$, $d_4=-(1+5B)$, $d_3=-[abc_2(\frac{p}{RT})^2-10B^2-4B]$ $d_2=-[10B^3+6B^2+abc_3(\frac{p}{RT})^3-3abc_2(\frac{p}{RT})^2]$ $d_1=-[-5B^4-4B^3-2abc_3B(\frac{p}{RT})^3+3abc_2B^2(\frac{p}{RT})^2+a_4(\frac{p}{RT})^4]$ $d_0=-[B^5+B^4-b_5(\frac{p}{RT})^5+abc_3B^2(\frac{p}{RT})^3+abc_2B^3(\frac{p}{RT})^2-a_4B(\frac{p}{RT})^4]$ $abc_2=(A_2+B_2T+C_2e^{-xT_r})/p$, with $abc_3=(A_3+B_3T+C_3e^{-xT_r})/p$ $a_4=A_4/p$; $b_5=B_5T/p$; $B=bp/RT$ $\ln\varphi^j=\ln(\frac{f}{p})^j=\ln(\frac{V^j}{\underline{V}^j-b})+\frac{abc_2(p/RT)}{\underline{V}^j-b}+\frac{abc_3(p/RT)}{[2(\underline{V}^j-b)]^2}+\frac{a_4(p/RT)}{[3(\underline{V}^j-b)]^3}+\frac{b_5(p/RT)}{[4(\underline{V}^j-b)]^4}+Z^j-1-\ln Z^j$
Peng–Robinson [3]	$Z^3+(B-1)Z^2+(A-3B^2-2B)Z+(B^3+B^2-BA)=0$ where $B=bp/RT$; $A=ap/(RT)^2$ $\ln\varphi^j=\ln(\frac{f}{p})^j=Z^j-1-\ln(Z^j-B)-\frac{A}{2\sqrt{2}B}\ln[\frac{Z^j+(1+\sqrt{2})B}{Z^j+(1-\sqrt{2})B}]$

Table 5 Comparison of compressibility factors for equations of state[a]

T, K	Peng–Robinson EOS		Clausius EOS		Martin EOS	
	Z^L	Z^V	Z^L	Z^V	Z^L	Z^V
300	2.71×10^{-5}	0.999	2.61×10^{-5}	0.999	9.50×10^{-5}	0.999
400	1.63×10^{-3}	0.983	1.62×10^{-3}	0.984	3.50×10^{-3}	0.988
500	0.0168	0.891	0.0175	0.901	0.0330	0.930
600	0.0878	0.643	0.0962	0.674	0.142	0.759
650	0.241	0.382	0.277[b]	0.413	0.281	0.497

[a] Based on Barragan et al. vapor pressures (Table 2). [b] Values are complex.

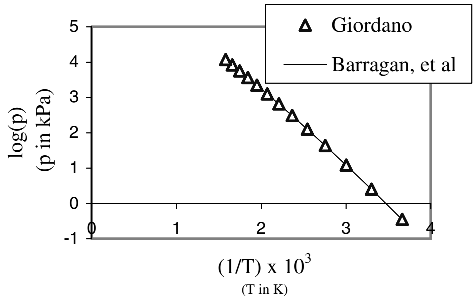

Fig. 1 Vapor pressure correlation comparison.

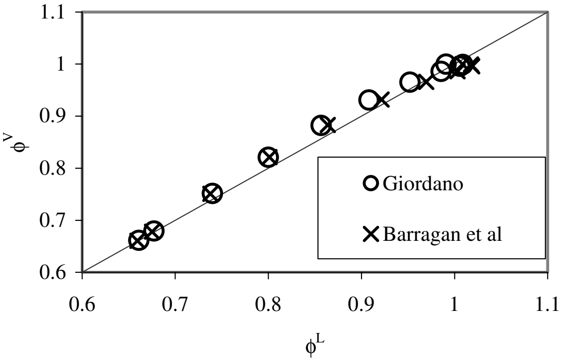

Fig. 2 Fugacity coefficients using Peng–Robinson EOS.

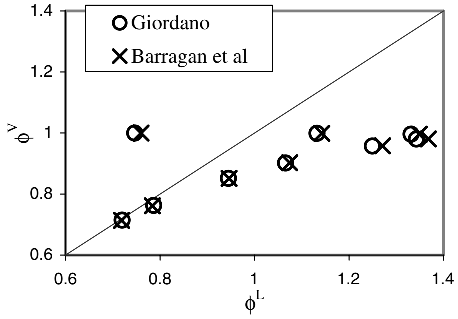

Fig. 3 Fugacity coefficients using Clausius EOS.

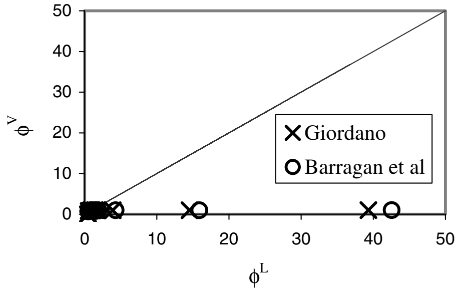

Fig. 4 Fugacity coefficients using the Martin EOS.

vapor phase compressibility factors to the Peng–Robinson EOS over this temperature and pressure range, indicating that all of these equations adequately model the vapor phase of hydrazine.

Vapor Pressure Adjustment Using the Peng–Robinson EOS

The liquid-vapor fugacity coefficient comparison outlined above indicates that the Peng–Robinson EOS is the most appropriate for calculating liquid and vapor phase fugacity coefficients for hydrazine. It is important also to note that, while it appears to be most appropriate, it is not without shortcomings. The fugacity coefficients follow the 45 deg line for only a short segment before deviating. To improve subsequent calculations, adjustment of the vapor pressures to produce fugacity coefficients that more closely follow the 45 deg line was required. To accomplish this, the predictive power of the Peng–Robinson EOS was used. Using the vapor pressure predicted by the Barragan et al. [3] vapor pressure correlation as a starting point and then iterating on the vapor pressure until the liquid and vapor phase fugacities were equivalent, a thermodynamically consistent value of the low temperature vapor pressures was obtained. Despite the fact that a few of these temperatures are below the applicability of the vapor pressure correlation (according to Barragan et al. [3], this vapor pressure correlation is accurate from 288 to 653 K), using the adjustment procedure described, thermodynamically consistent vapor pressure values were extracted. None of the vapor pressures required more than a 5% adjustment, indicating consistency of the vapor pressure data. Table 6 shows selected adjusted vapor pressures.

Thermodynamic Consistency, Mechanical Stability

Another measure of the suitability of the three equations of state for modeling both liquid and vapor phase hydrazine is to evaluate whether they predict stable phases under appropriate temperature and pressure conditions. An appropriate temperature and pressure condition is one corresponding to vapor–liquid equilibrium, where both phases must be thermodynamically stable [6]. Mechanical stability requires that

$$-\left(\frac{\partial p}{\partial \underline{V}}\right)_T > 0 \tag{2}$$

Table 7 shows $(\partial p/\partial \underline{V})_T$ for the three equations of state.

Table 8 shows computed values for the mechanical stability criterion for each EOS at saturated liquid and vapor conditions. These calculations show that at 650 K the Clausius EOS predicts only one phase present, that is, one real root and two complex roots. Note that for the Martin EOS there were five roots from which to choose. The results shown in Table 8 use only the real roots that most closely match the results from the Clausius and the Peng–Robinson EOS.

Conclusions

Three different equations of state have been published in the literature to predict the behavior of hydrazine. In this work we have

Table 6 Predicted and adjusted (thermodynamically consistent) vapor pressure values for hydrazine

Temperature, K	Predicted vapor pressure, MPa	Adjusted vapor pressure, MPa	% difference
273	0.0003494	0.00034944	0.0114
280	0.0005781	0.000578127	2.67×10^{-5}
290	0.0011308	0.001144697	1.22
530	2.9534942	2.8659	3.06
540	3.4727922	3.364	3.23
550	4.0564456	3.9249	3.35
630	11.492242	11.340000	1.34
640	12.811631	12.711631	0.79
650	14.223756	14.223756	3.42×10^{-6}

Table 7 Mechanical stability expressions for equations of state

EOS	Function
Peng–Robinson	$-(\frac{\partial p}{\partial \underline{V}})_T = \frac{RT}{(\underline{V}-b)^2} - \frac{2a(T)(\underline{V}+b)}{[\underline{V}(\underline{V}+b)+b(\underline{V}-b)]^2}$
Clausius	$-(\frac{\partial p}{\partial \underline{V}})_T = \frac{RT}{(\underline{V}-A)^2} - \frac{2C}{T^n(\underline{V}+B)^3}$
Martin	$-(\frac{\partial p}{\partial \underline{V}})_T = \frac{RT}{(\underline{V}-b)^2} + \frac{2abc_2p}{(\underline{V}-b)^3} + \frac{3abc_3p}{(\underline{V}-b)^4} + \frac{4a_4p}{(\underline{V}-b)^5} + \frac{5b_5p}{(\underline{V}-b)^6}$

Table 8 Computed values of pressure derivatives

T, K	EOS		
	Peng–Robinson	Mod. Clausius	Martin
		Saturated liquid	
273	-2.15×10^8	-1.49×10^8	-6.06×10^6
350	-9.77×10^7	-6.08×10^7	-3.33×10^8
430	-4.01×10^7	-2.36×10^7	-7.08×10^8
510	-1.33×10^7	-7.63×10^6	-2.39×10^8
550	-6.39×10^6	-3.66×10^6	-1.05×10^8
580	-3.14×10^6	-1.79×10^6	-4.77×10^7
600	-1.69×10^6	-9.51×10^5	-2.43×10^7
620	-7.24×10^5	-3.90×10^5	-9.77×10^6
640	-1.61×10^5	-6.96×10^4	-2.02×10^6
650	-2.18×10^4	$1.38 \times 10^3 + 5.71 \times 10^3i$	-2.46×10^5
		Saturated vapor	
273	-5.38×10^{-5}	-5.38×10^{-5}	-5.38×10^{-5}
350	-0.235	-0.235	-0.235
430	-37.6	-37.6	-37.6
510	-966	-968	-970
550	-3.23×10^3	-3.25×10^3	-3.27×10^3
580	-6.90×10^3	-6.99×10^3	-7.08×10^3
600	-1.06×10^4	-1.08×10^4	-1.10×10^4
620	-1.45×10^4	-1.52×10^4	-1.56×10^4
640	-1.48×10^4	-1.65×10^4	-1.69×10^4
650	-6.98×10^3	-9.39×10^3	-8.25×10^3

used two criteria for thermodyanamic consistency: equality of vapor and liquid fugacity coefficients at equilibrium, as well as mechanical stability, to evaluate the applicability of the three equations of state in safety and design calculations for hydrazine. We have demonstrated that the published Clausius equation of state for hydrazine is limited in its applicability, based on the inequality of liquid and vapor fugacity coefficients, to vapor phase calculations well below critical conditions. Furthermore, the transition to positive imaginary values in the Clausius pressure derivatives suggests some degree mechanical instability in the Clausius model. The Peng–Robinson equation of state and the Martin equation of state perform equally well with respect to mechanical stability and compressibility factors. The key difference between these two equations of state is in their ability to predict thermodynamically consistent vapor–liquid equilibrium by predicting equal vapor and liquid fugacity coefficients. While neither of these EOS predicts equal liquid and vapor phase fugacity coefficients for the entire temperature range evaluated, the Peng–Robinson equation of state followed the 45 deg line more closely than the Martin equation of state. From this analysis, the Peng–Robinson equation of state appears to be a superior model for predicting a wide range of thermodynamic properties for hydrazine. Future work will be aimed at evaluating modifications to the Peng–Robinson equation of state to further refine its applicability for hydrazine and related aerospace fuels.

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