SAND2018-6390C

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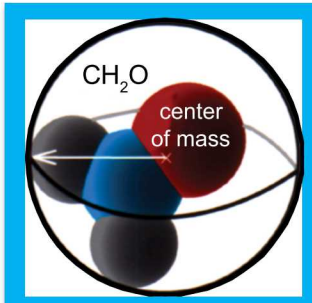
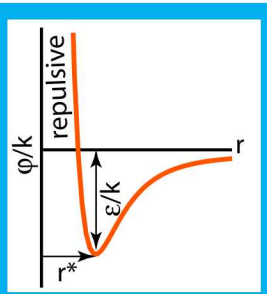
Code

CTH-TIGER

EOS



Covolume



Intermolecular Potential

Databases

BKWS
JCZ
JCZS
JCZS2
JCZS3
} covolume, r*, ε/k

EXP6L
EXP6S
r*, ε/k, α

JCZS3—An Improved Database for EOS Calculations

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Sandia National Laboratory, USA

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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Introduction—why a new JCZS database?

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- JCZS2 parameters (r* and ε/k) are the same as original JCZS parameters, which were obtained by
  - Hugoniot fits with C_p fits only good to 6,000 K
  - Simple corresponding states fits based on T_c and V_c
  - Correlations with BKW covolumes
  - Optimization with detonation velocities
  - Some species values were inaccurate (e.g. formic acid)
- Need **better predictions at high T and P** where dissociation and ionization are significant, for example, overdriven detonations, high temperature air shocks, etc.
- New r* and ε/k values for JCZS3 were determined with Hugoniots with heat capacity fits good to 20,000 K.
- Diffulty fitting Hugoniots with exp 6,13 potential with a constant stiffness

Differences between JCZS3 and Exp6 parameters

one-fluid mixture potential

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JCZS3

Lorentz-Berthelot

$$r_{ij} = \frac{r_{ii} + r_{jj}}{2} \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad \alpha_m = 13$$

vdW1f for r_m, simple rule* for ε_m, constant α

$$r_m^3 = \sum_{i,j} x_i x_j r_{ij}^3 \qquad \varepsilon_m = \sum_{i,j} x_i x_j \varepsilon_{ij} \qquad \alpha_m = 13$$

*W. Byers Brown and A. Amaee, "Review of EOS of Fluid Valid to High Densities, Health & Safety contract research report No. 39 (1992)." "…Jacobs EOS is a rather complicated semi-empirical equation, and its agreement with MC computer simulation results is poor…The same is true of the JCZ3 EOS for mixtures, which might be slightly improved by using the vdW1f mixing rule…Were it not for the fact that the mixture version …(JCZ3) has been incorporated into the well known TIGER ideal detonation code, the Jacobs EOS, …, would only be of historic interest."

Exp6

Lorentz-Berthelot

$$r_{ij} = \frac{r_{ii} + r_{jj}}{2} \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad \alpha_{ij} = \sqrt{\alpha_{ii}\alpha_{jj}}$$

Van der Waals, vdW1f**

$$r_m^3 = \sum_{i,j} x_i x_j r_{ij}^3 \qquad \varepsilon_m = \frac{\sum_{i,j} x_i x_j \varepsilon_{ij} r_{ij}^3}{r_m^3} \qquad \alpha_m = \frac{\sum_{i,j} x_i x_j \alpha_{ij} \varepsilon_{ij} r_{ij}^3}{\varepsilon_m r_m^3}$$

F.H. Ree, J. Chem. Phys., **78, 409 (1983). Ree provides a mixture model for the stiffness, α, and implies that variable stiffness is necessary for calculating detonation velocities of condensed explosives and predicting the interior compositions of Jupiter and Saturn where temperature may range from 5,000-10,000 K and pressures from 50-200 Gpa.

We contend that the JCZ3 EOS provides excellent agreement with MC simulations and that a constant α of 13 is adequate for detonation and Hugoniot calculations.

What makes a good= EOS? Sine qua none and acid test

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*W. Byers Brown, J. Chem. Phys., **87** (1), 566 (1987)

"Sine qua none" test (absolutely necessary to replicate MC data)

Monte Carlo calculations ($\alpha = 11.5$ ●, 13.5 ●, 15.5 ●)

Exp-6 integral theory ($\alpha = 11.5$ —, 13.5 —, 15.5 —)

Exp-6 variational perturbation theory ($\alpha = 11.5$ --, 13.5 --, 15.5 --)

JCZ3 ($\alpha = 11.5$ ▬, 13.5 ▬, 15.5 ▬)

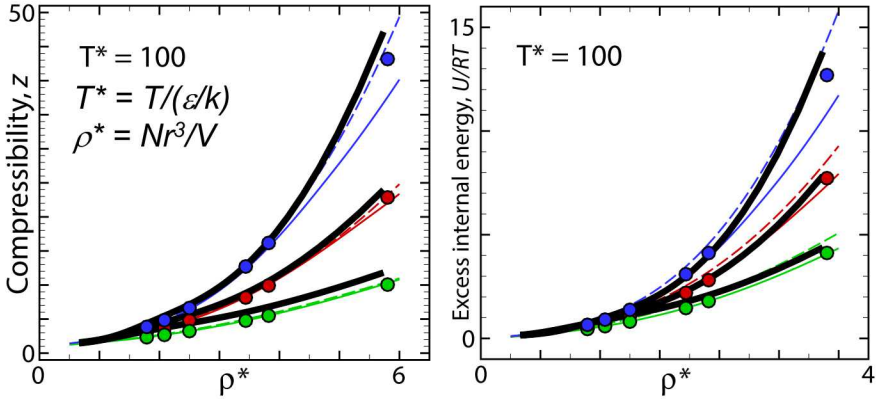
M. Ross and B. Adler, J. Chem. Phys., **46 (11) 4203 (1967)

G. Zerah and J. Hansen, J. Chem. Phys., **84 (4) 2336 (1986)

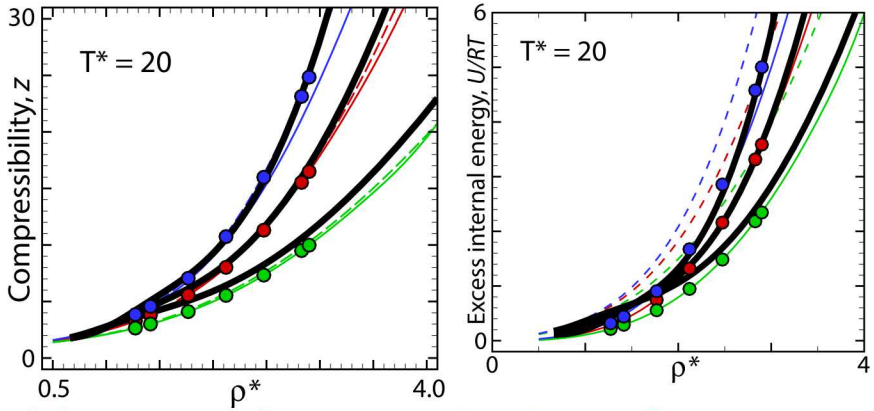
L. Fried and M. Howard, J. Chem. Phys., **109 (17) 7338 (1998)

$$\varphi(r) = \varepsilon\left[\left(\frac{6}{\alpha-6}\right)\exp\left[\alpha\left(1-\frac{r}{r^*}\right)\right]-\left(\frac{\alpha}{\alpha-6}\right)\left(\frac{r^*}{r}\right)^6\right]$$

T = 12,200 K, ρ = 0.7-6.7 g/cc



2,440 K , ρ = 0.7-6.7 g/cc



JCZ3 is as good as integral theory and better than variational perturbation theory in matching Monte Carlo results using Exp 6

Potential compensation

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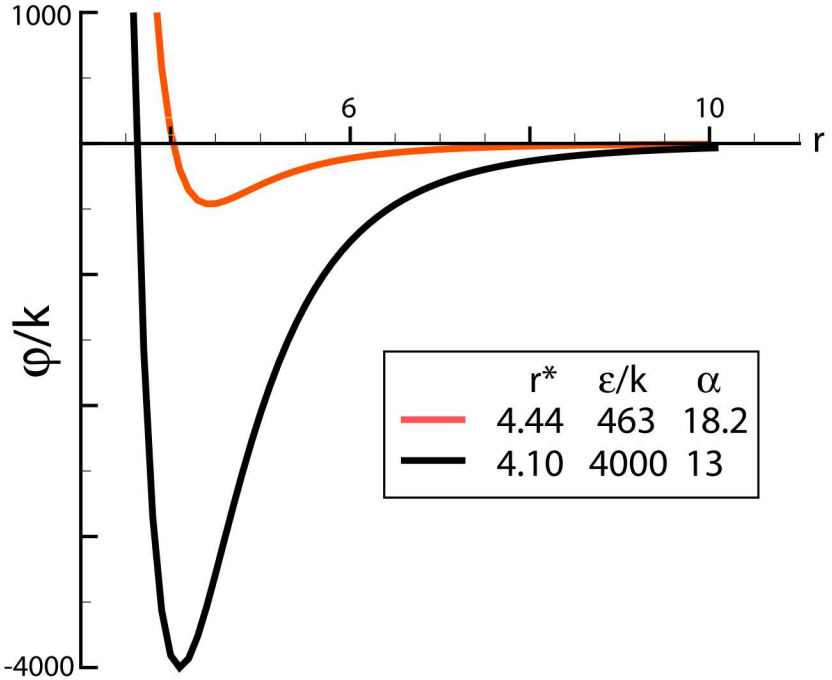
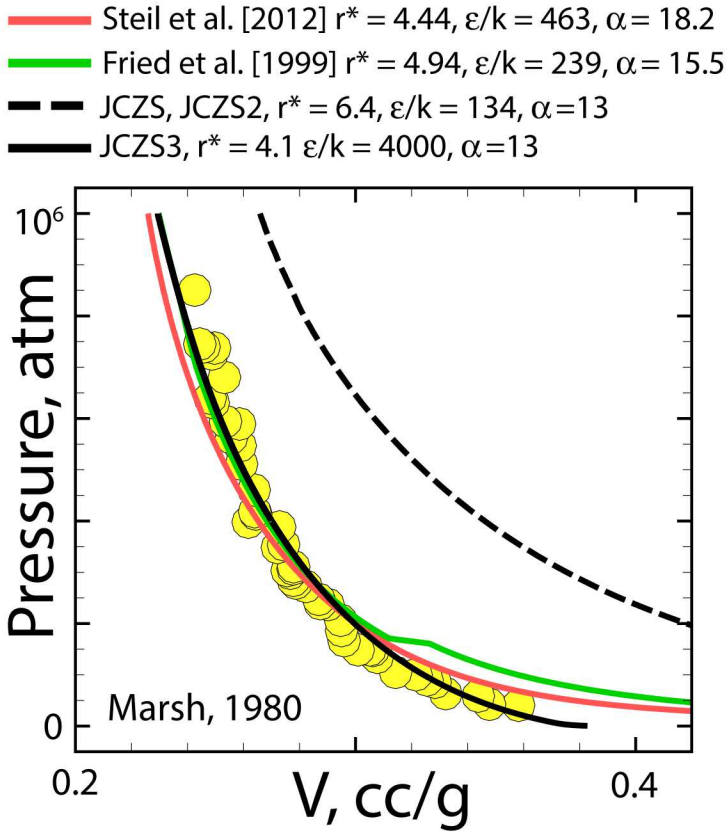
Justification of constant α model, even for stiff potential surfaces

Large well mimics a stiff potential



$$\varphi(r) = \varepsilon\left[\left(\frac{6}{\alpha-6}\right)\exp\left[\alpha\left(1-\frac{r}{r^*}\right)\right]-\left(\frac{\alpha}{\alpha-6}\right)\left(\frac{r^*}{r}\right)^6\right]$$

Teflon Hugoniot for CF_4



Stiff potential can be obtained with either a large α or a large ε/k

Major CHNO species parameters

determined from Hugoniots with 1 or 2 atoms

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Hugoniots of major CNHO species

Species	Description	ρ_o, g/cc	h_f, kJ/mol
CH_4	Methane (111.5 K)[a]	0.424	-14.6
CO	Carbon monoxide (77.4 K)[a]	0.808	-123.58
CO_2	Carbon dioxide (218 K)[b]	1.173	-417.1
C_6H_6	Benzene (298 K)[c]	0.875	48.95
H_2	Hydrogen (20 K)[c]	0.071	-8.8
H_2O	Water (298 K)[c]	1.000	-298.83
NH_3	Ammonia (203 K)[c]	0.726	-72.5
N_2	Nitrogen (75 K)[c]	0.820	-12.1
NO	Nitric Oxide (122 K)[d]	1.263	79.5
O_2	Oxygen (90 K)[c]	1.141	-13

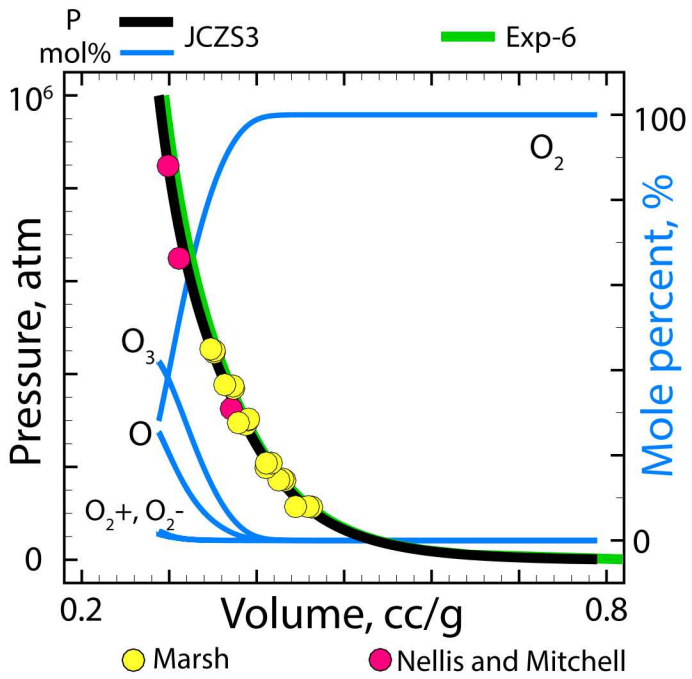
[a] W.J. Nellis, F.H. Ree, M. van Thiel, A.C. Mitchel, J. Chem. Phys, **75**, 3055 (1981).

[b] G.L Schott, High Pressure Research, **6**,187 (1991).

[c] S.P. Marsh, editor, LASL Shock Hugoniot Data, University of California Press, 1980.

[d] G. L. Schott, M.S. Shaw, J.D. Johnson, J. Chem. Phys., **82**, 4264 (1985).

Oxygen Hugoniot



1. P < 250000: o2
2. 250000 < P < 400000: o2, o3
3. 400000 < P < 500000: o2, o3, o
4. 500000 < P < 800000: o2, o3, o, o2-, o2+
5. 800000 < P : o2, o3, o, o2-, o2+, e-

After Hugoniot fits, we "acid" test the EOS with detonation velocities.

CH4, CO, CO2 Hugoniots

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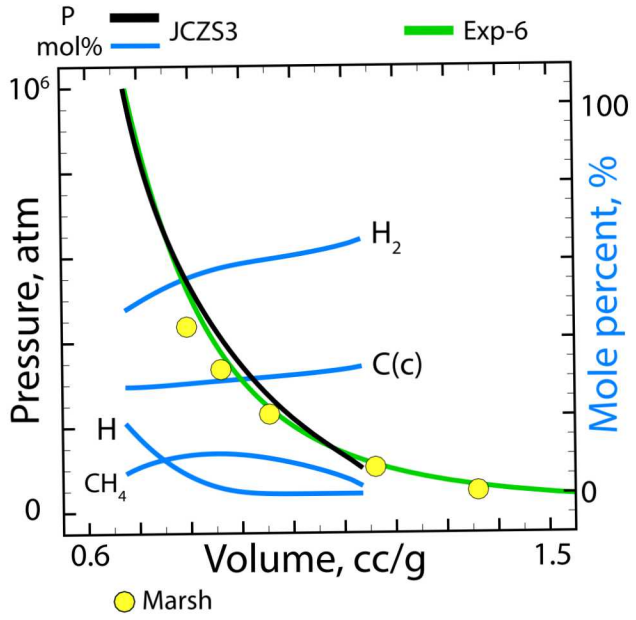
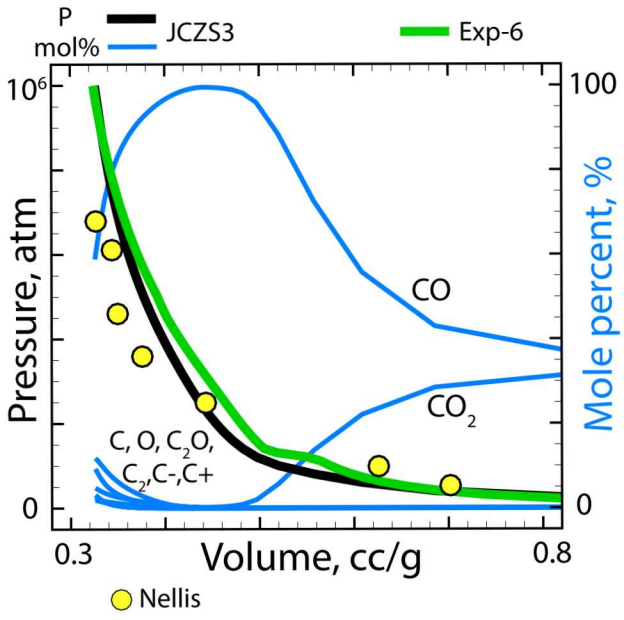
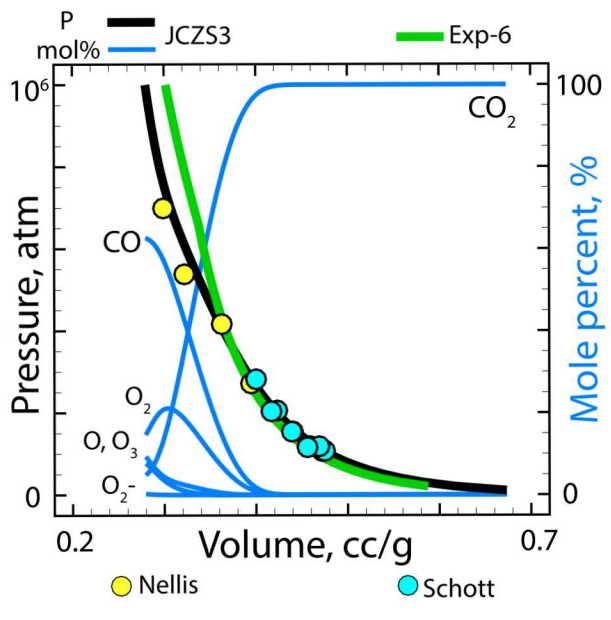
CH_4 (111.5 K)



CO (77.4 K)



CO_2 (218 K)



After Hugoniot fits are as good as Exp-6, which has variable α

C_6H_6, H_2, H_2O Hugoniots

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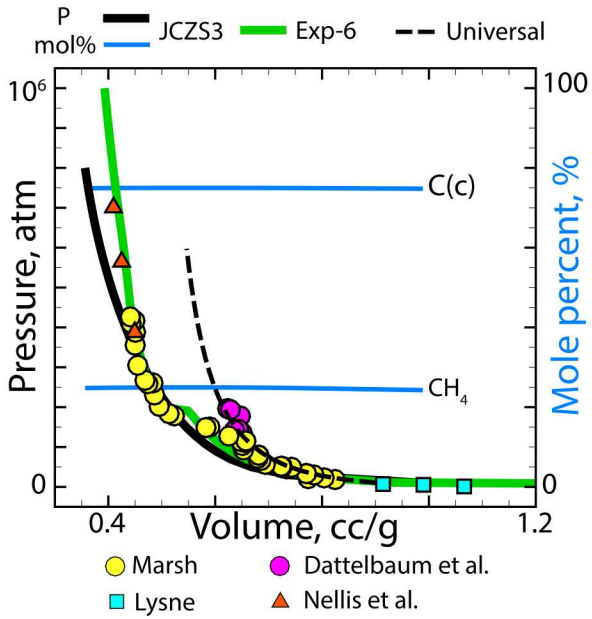
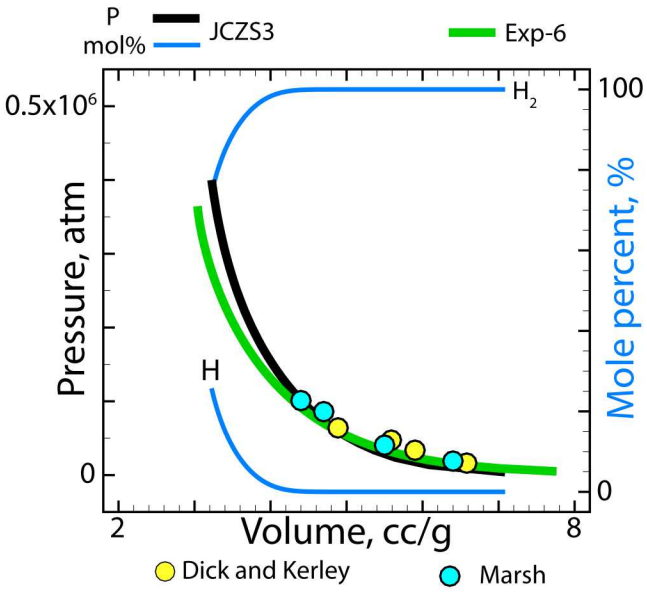
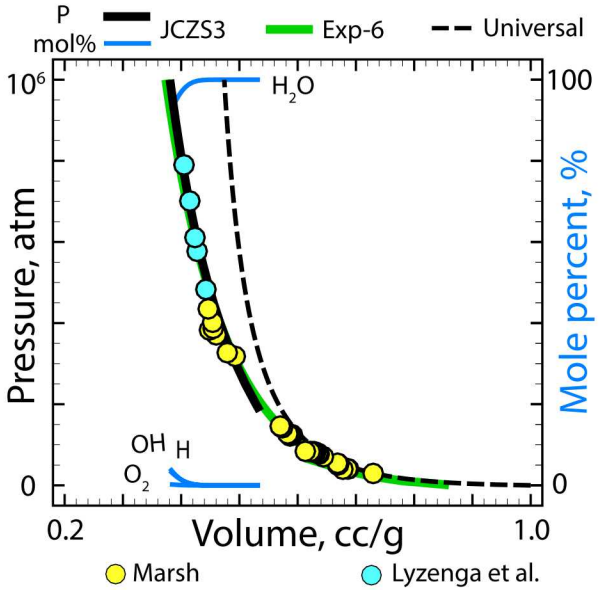
C_6H_6 (298 K)



H_2 (20 K)



H_2O (298 K)



Universal liquid Hugoniot implies low pressure C_6H_6 and H_2O are not in equilibrium.

NH_3 N_2, and NO Hugoniot

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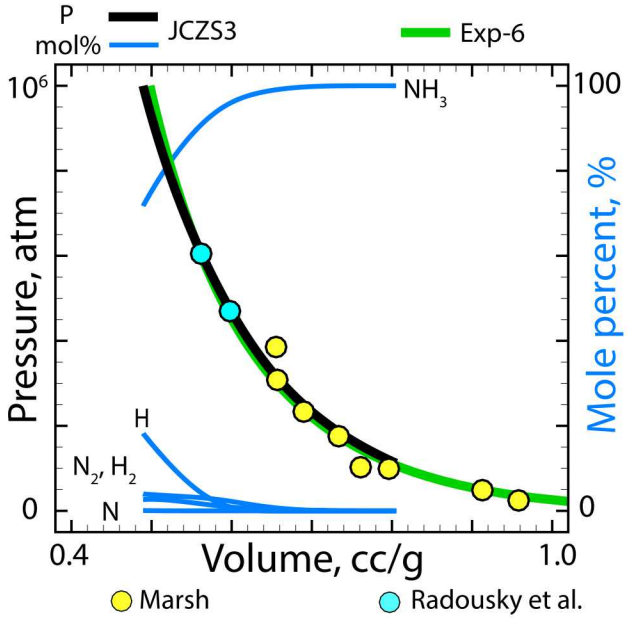
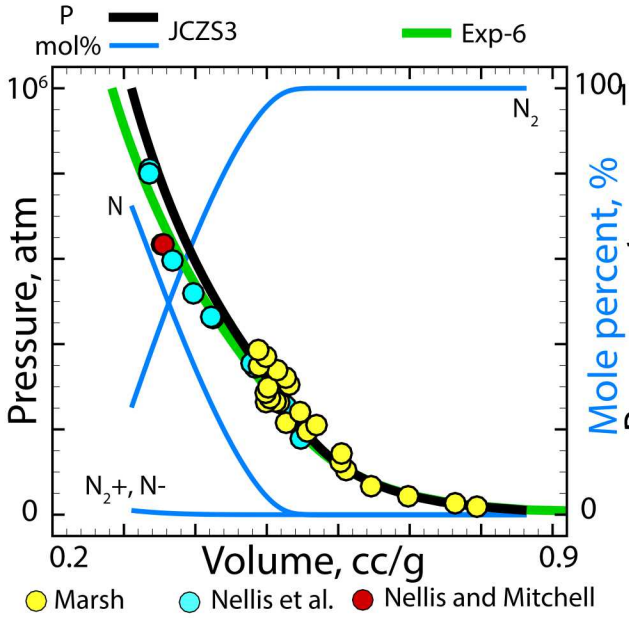
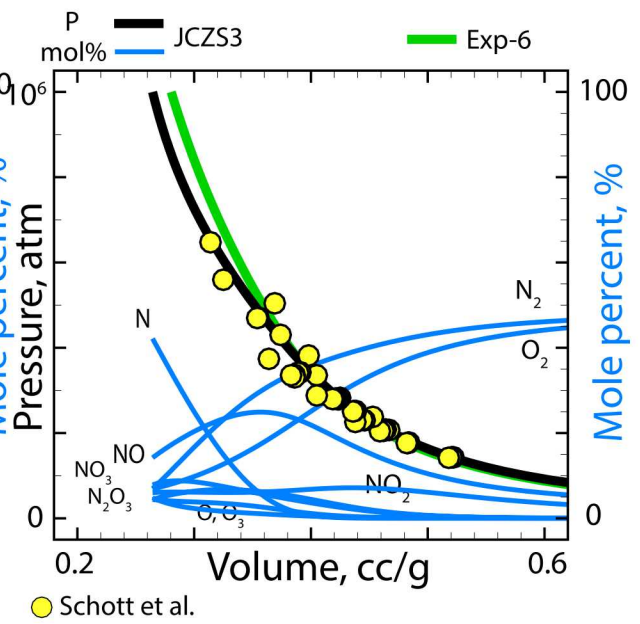
NH_3 (203 K)



N_2 (75 K)



NO (122 K)



The nitric oxide Hugoniot was used as a "acid" test, which is "agreement with data."* More validation to come.

*W. Byers Brown, J. Chem. Phys., **87** (1), 566 (1987).

Overdriven shock Hugoniot of explosives

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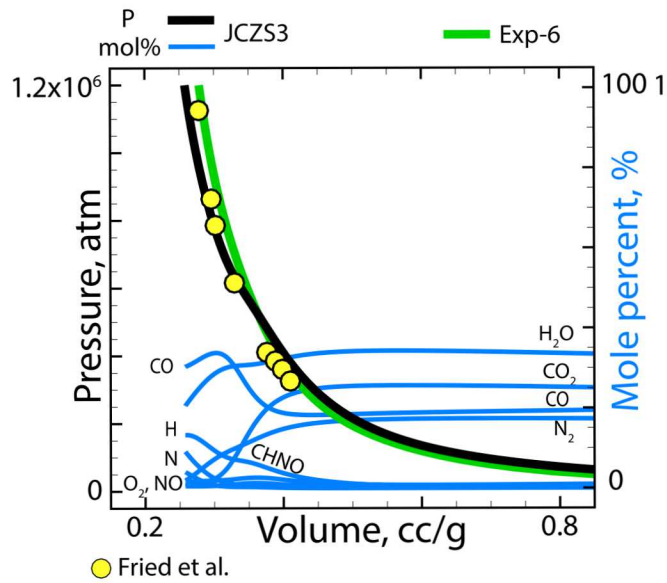
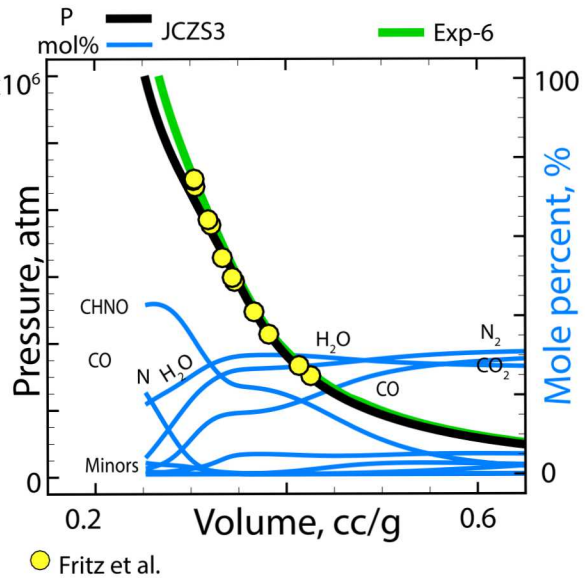
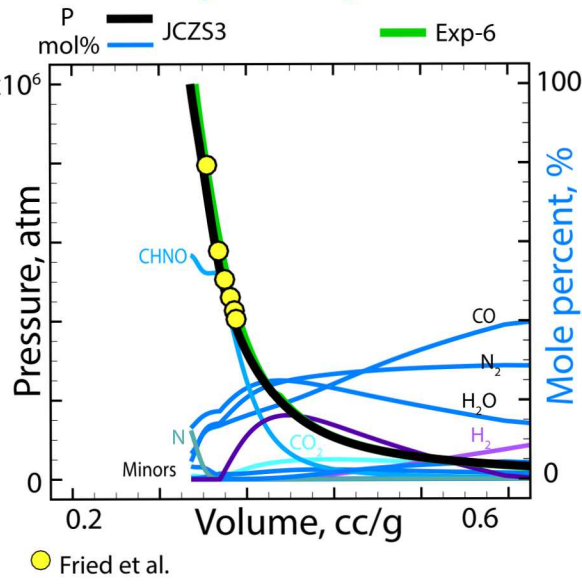
PETN



PBX 9501



HMX, TATB, Estane 49%, 47%, 4%

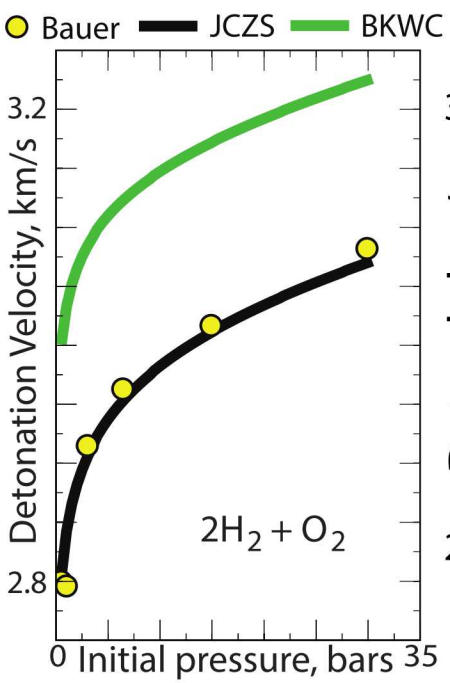


The inability of the older JCZS databases to match these Hugoniots was due to inaccurate parameterization of the radicals H and N. The JCZS3 parameters were determined with the H_2 and N_2 Hugoniots shown previously.

Gas detonation at elevated initial pressures

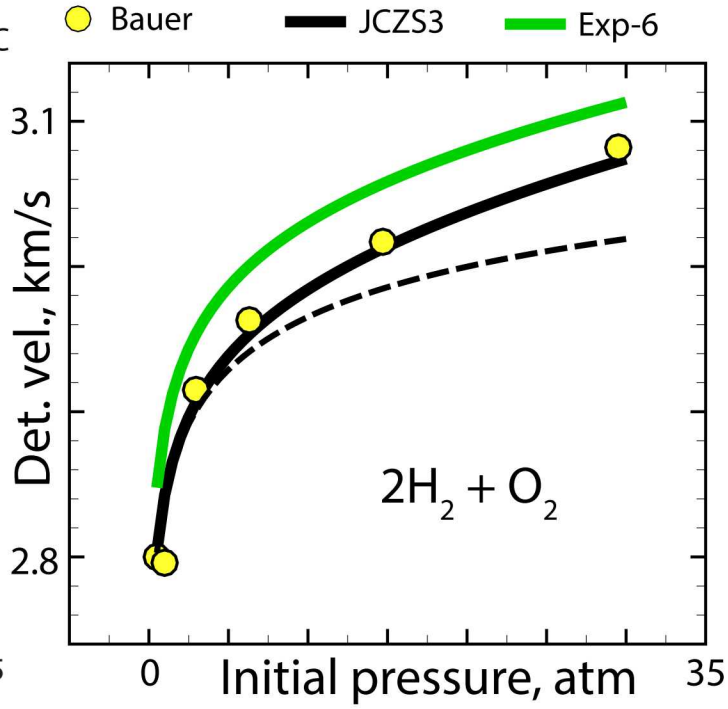
A blast from the past!

1998 calculation*



*Hobbs et al., 11th Det. Symp (1998)
also in Prop. Exp. Pyro, **24**, 269 (1999)

2018 calculation



Species in databases

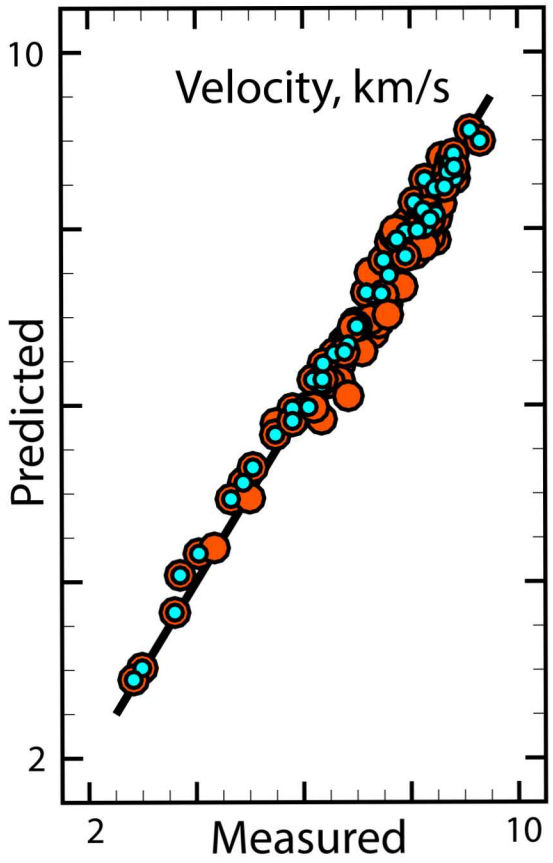
	BKWC	JCZS	Exp-6	JCZS3
Major	h2o	h2o	h2o	h2o
	h2	h2	h2	h2
		oh		oh
		h	h	h
	o2	o2	o2	o2
		o	o	o
Minor		o3	o3	o3
		h2o(l)		h2o(l)
		h2o2		h2o2
		ho2		ho2
				h2-
				h2+
				h2o+
				ho2-
				e-
				o-
				o+
				h-
				o2-
				o2+
				h+
				oh-
				oh+

Composition (Po = 30 atm)

JCZS3	Exp-6
62.7%	68.8%
13.7%	14.7%
13.3%	missing
4.5%	5.7%
3.5%	6.7%
2.2%	4.1%
99.9%	100.0%

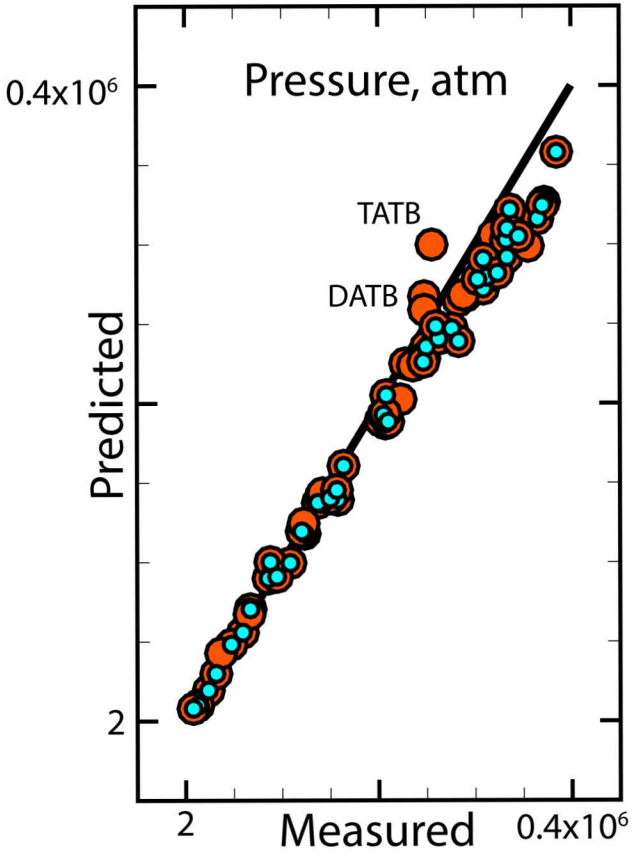
The problem with BKWC and Exp-6 is not the EOS, it's the databases, which did not include major species for this calculation. H, O, and OH were missing for BKWC; OH was missing for Exp-6.

JCZS3 Detonation predictions



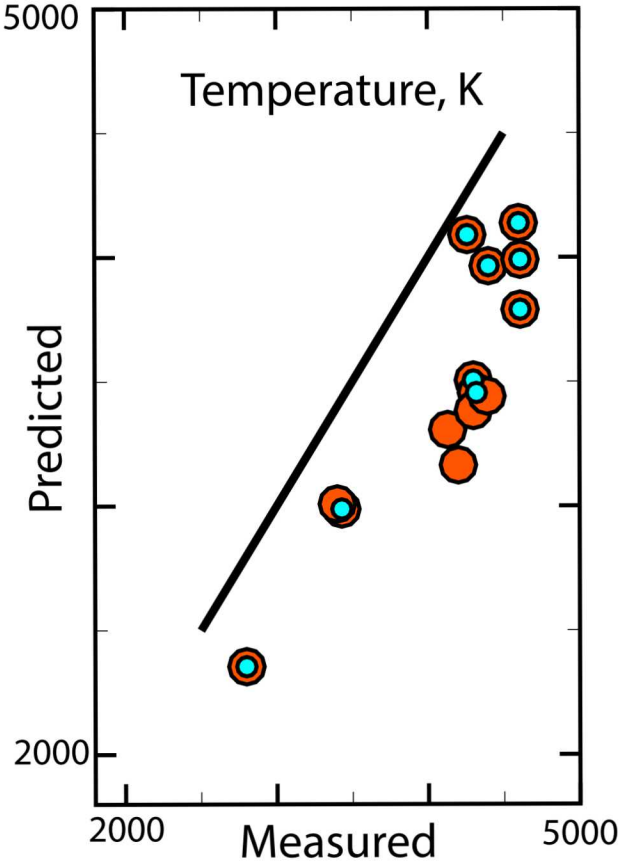
108 det. vel. (Hobbs et al., 2014)

50 of the 108 det. velocities that do not form carbon in the C-J plane.



63 det. pressures (Hobbs et al., 2014)

42 of the 63 det. pressures that do not form carbon in the C-J plane.



14 det. temperatures (Hobbs et al., 2014)

9 of the 14 det. temperatures that do not form carbon in the C-J plane.

Detonation predictions are similar to other Exp-6 EOS models

HMX, RDX, PETN, and TNT

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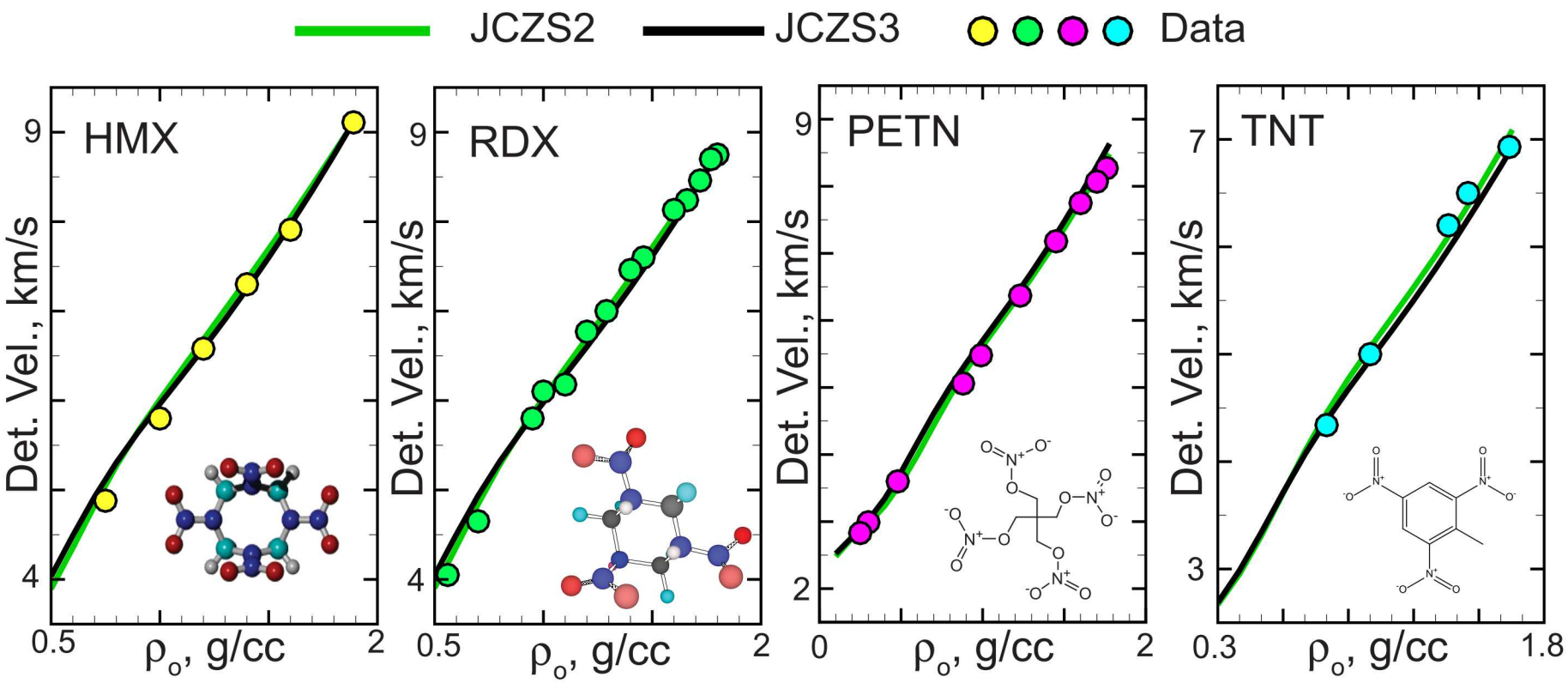
Detonation Velocities



Detonation predictions JCZS3 is almost as good as JCZS2, which used detonation velocities for some parameter estimation.

Danger of using detonation velocity to Fit potential parameters

Simple system: 90.5 wt.% H_2O_2 + 9.5 wt.% H_2O

Same EOS with identical composition in CJ plane, why is the predicted velocities so different?

	D,* km/s	Species
JCZS2	5.54	70.6% H_2O, 29.4% O_2
JCZS3	6.11	70.6% H_2O, 29.4% O_2

*Measured D = 6.14 km/s

	JCZS2		JCZS3	
	r*	ε/k	r*	ε/k
H_2O	3.06	356	3.85	50
O_2	3.86	125	3.83	130

JCZS2 Hugoniot fit for H2O were good, but the JCZS3 fit was better. If individual species fit Hugoniots well, detonation predictions will be good for ideal explosives.

Summary and Conclusions

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- Criticisms of the JCZ3 EOS has been address. Specifically Brown and Amaee's comments regarding poor agreement with Monte Carlo data (Sin Que Non test) and various "acid" tests showing agreement with data.
  - MC predictions are good as other Exp-6 based EOS model's based on integral theory and variational perturbation theory.
  - Excellent matches with liquid Hugoniot data made possible with specific heat fits to 20,000 K (CH_4, CO, CO_2, C_6H_6, H_2, H_2O, NH_3, N_2, NO, O_2)
  - Overdriven Hugoniots for PETN, PBX 9501, HMX/TATB mixtures.
  - Detonation predictions are as good or better than other Exp-6 databases.
- EOS calculations that are valid over a wide range of conditions should consider a large number of species, radicals, and ions. These individual species should be fit using Hugoniot data where that species dominates.
- Finally, don't forget OH, when calculating $H2/O_2$ gas detonation!