

# Work Principle For Predicting Explosive Toxic Fumes

Michael S. Wieland

## ABSTRACT

The work-principle method was developed for theoretically resolving toxic fumes from non-ideal charge formulations. The whole description of a wanted process refers to macroscopic changes resulting from removing and imposing constraints that work one at a time to chronologically render trajectory terminal (key) states. The trajectory resolution utilizes a thermodynamic quasi-potential or negative work function, and numeric results require some appropriate standard thermodynamic (equilibrium) reaction code TDRC. The underlying method is unable to restrict reactions, tailor the work output or resolve states within the trajectory transitions, so the trajectory terminology is used somewhat figuratively. The work-principle model has the working fluid (reaction material) interacting with a tremendous reservoir (chamber air and walls), while forecasting the work performed upon a mechanical agent.

Within the underground test chamber, the widening fume zone undergoes a decline in temperature, a reduction in reaction rates, resulting in out-of-equilibrium circumstances at the Q\*-point, representing the measurement state. Rather than coping with the hard issues of non-equilibrium, the toxic fumes are resolved numerically for the Z-point, rendered by a zero-net-interaction energy constraint. Though other techniques require complex equation-of-state EOS for the whole trajectory, the work-principle formulation eludes the issue, requiring an EOS that works just for the terminal-state. Under the circumstances, the Z-state is reconcilable with the ideal-gas domain, and relevant TDRC results yield the restricted state in a numerical way for different charge formulations. The work principle makes it hard to remedy or to tamper with the resulting Z-point fumes: non-macroscopic trajectory readjustment is forsaken, terminal states are results rather than stipulations, and resetting the EOS formula constants would be ineffectual. Though the non-equilibrium portion remains unresolved, it is noteworthy that the work principle rigidly fixes the Z-state, thereby reducing the uncertainty for rendering reaction-rate models characterizing the non-equilibrium Z-Q\* transition. Though more refinements are needed, some Z-point fume results are included to illustrate the threshold (minimum) resolving capacity of the work-principle formulation.

## INTRODUCTION

The NIOSH underground fumes facility for toxic fume measurements has a 274-m<sup>3</sup> chamber, representing a thermodynamic reservoir of walls and 324-kg air, and therefore quite massive compared to the 4.54 kg of mining explosives under test.<sup>1</sup> The coal-mine walls are a rather indefinite reservoir component, which poses no difficulty, and they confine the fumes and help regulate their temperature. The mining explosive is confined within a cylindrical steel pipe with a 10.2-cm diameter for proper detonation. Except for the rupture and fragmentation of the cylinder, the explosive works upon and transfers heat to the reservoir. The work-principle technique rendered within this report is tailored to

model the test circumstances, and not rock blasting. The reaction of mining explosives is quite non-ideal, and not reconcilable with the traditional requirements of the Zeldovich-von Neumann-Doering ZND theory of detonation.<sup>2,3</sup> For the traditional ZND theory, the reaction thermicity term in the referenced relation must vanish at the CJ condition. Non-ideal explosives undergo reaction through the CJ, so the zero-thermicity requirement is a recognized conflict. This is rendered moot by the introduction of some representative loss term in the theoretical formulation, so the relevant relationships remain numerically bounded.<sup>4</sup> The resolution raises questions about the proper choice of process description, and forms a little (philosophical) room for the unorthodox techniques undertaken with the work-principle.

For rock mining or fume testing, the restoring influences that try to maintain mechanical and thermal equilibrium rapidly widen the fume zone within the reservoir, via Le Châtelier's principle.<sup>5</sup> Under the transitory circumstances with declining fume zone temperatures, the restorative influences that try to maintain chemical equilibrium falter. For the post-detonation combustion process, total equilibrium remains plausible only while the fume zone stays hot, keeping chemical relaxation times small. With cooler temperatures, the relaxation times grow drastically, precipitating out-of-equilibrium circumstances within the working fluid. Wall or dust interactions and the residual non-equilibrium yield reactions that persist noticeably at the cooler temperatures within the underground chamber at the hour of measurement, ruin the presumption of non-reacting flow. TDRC yield results that require total equilibrium conditions for the working fluid and they would be quite inappropriate for resolving the non-equilibrium Q\*-point measurement state.

This raises the question of the former (not Q\*-point) thermodynamic state that was the last respectable remnant of total equilibrium, and therefore worthy of fume spectrum resolution with TDRC. Non-equilibrium conditions tend to remain rather intractable, so that non-work-principle techniques reckon reaction components as frozen for different temperatures on the late-stage (post CJ) trajectory. Numerical fume-spectrum results tracked downward from the high-density region could be wrong or unreliable, if the EOS formula constants are reckoned badly, which is undesirable for ranking fume toxicity. The work principle can not be tampered with or remedied in this fashion, which could be regarded as a disadvantage or a useful circumstance. Under the circumstances noted later the Z-points were thermally hot and rarefied and therefore the TDRC chosen for resolving the fumes was the NASA Lewis Complex Chemical Equilibrium Code.<sup>6</sup>

## THEORY UNDERLYING WORK PRINCIPLE

The work principle characterizes a thermodynamic system of three interacting components that otherwise remains isolated from the rest of the universe, and therefore is governed by the laws of thermodynamics for isolated systems. The technique utilizes constraints that chronologically work one at a time for representation of process, but they are not required until the work function or quasi-potential is resolved. The working fluid, the reservoir, and the mechanical agent constitute the interacting components, though the latter two are unable to interact directly. The reservoir must retain constant thermal-mechanical characteristics, and therefore have tremendous (mass) proportions compared to the other components. The working fluid may have a reactive composition, transfer heat and work upon the reservoir or work upon the mechanical agent in a reversible (non-expansion) way. None of the components interchange particles, so the working fluid mass remains constant.

The work-principle formulation is one of those ubiquitous inequality relationships of traditional thermodynamics that remains unchanged regardless of the process undertaken.<sup>7,8</sup> The work-principle

requirement utilizes a quasi-potential  $Y_Q$  or negative work function  $[-W_F]$ . The work-principle relation was written per unit working-fluid mass, since the TDRC render their numeric results that way. The work function  $W_F$  terminology tends to be redundant, though it has some relevance and is therefore retained. The defining relation for the work function  $W_F$  or the quasi-potential  $Y_Q$  is

$$-W_F \equiv Y_Q \equiv \left[ U - T_R \cdot S + \frac{P_R}{\rho} \right]$$

The quasi-potential  $Y_Q$  (or  $W_F$ ) depends upon the working fluid's energy per unit mass  $U$ , entropy per unit mass  $S$  and density  $\rho$  (or  $Rho$ ). Neither the quasi-potential nor the work function qualifies as a state function, because of the reservoir parameters, temperature  $T_R$  and pressure  $P_R$ , despite their constancy.<sup>9</sup> The resulting construction of the quasi-potential, represented as a superposition of working-fluid state functions with constant reservoir-multipliers, is trajectory pathway independent, regardless of the irreversibility, and therefore has formidable theoretical capacity. The work-principle inequality relation taken from the noted references<sup>7,8</sup> is then

$$\mathbf{Work} \leq \Delta W_F \equiv \Delta[-Y_Q]$$

The **Work** term represents the work done by the working fluid upon the mechanical agent, regardless of the type of process, and would change depending upon whether the process was reversible (the equality) or irreversible (the inequality). Reversible paths taken with infinitesimal quasi-static steps would take forever to render a finite thermodynamic transition. For a reversible path, the work done upon the mechanical agent would equal the work function rise  $\Delta W_F$  or  $\Delta[-Y_Q]$ . Restoration work refers to work rendered by (not upon) the mechanical agent when returning the working fluid to the original state along the reversible path in the opposite direction. The work function or quasi-potential register transitions like state functions, and taken over a closed cycle must return to their original numerical value. When closed-cycle integration is taken over the relationship, the  $W_F$  or  $Y_Q$  terms yield zero results. For the cyclic integration then, the resulting work done upon the mechanical agent would be zero or negative, **Work**  $\leq 0$ . Therefore, it is the mechanical agent that would have to render the restoration work. The restoration work reveals the system's propensity for chemical reaction work.<sup>10</sup>

It is worthwhile to invoke the terminology that natural processes refer to finite transitions with some irreversibility, however slight. Reversible infinitesimal transformations would have non-infinite response time and therefore are not excluded, though they could not wholly account for macroscopic transitions. For natural-process work, with fumes, the mechanical agent is not removed from the work-principle technique, though it is rendered inoperative or dysfunctional, so **Work** = 0. Since the mechanical agent is rendered moot, no device in the rampant reaction combustion process need be identified with it. With the dysfunction restriction, the work-principle relation reduces to

$$\Delta W_F \geq 0 \quad \text{or} \quad \Delta Y_Q \leq 0$$

Without the mechanical agent to render restoration work, returning to the starting state upon undergoing a natural process (inequality) is impossible. Restoration work remains an illusion that requires a reversible process taken in reverse time travel (or reverse chronology). With normal chronology, the reduction in the quasi-potential  $\Delta[-Y_Q]$  or the rise in the work function  $\Delta W_F$  registers the restoration work that would be needed to un-do the deterioration.

## WORKING FLUID STATE FUNCTION NOTATION

Just like the generalized coordinates of analytical mechanics ultimately prove their worth, the circumstances that logically render the model development of the work principle can benefit from some non-traditional and generalized notation. The logarithmic density  $y = \text{Ln}[\rho/\text{RHO}]$  is utilized in preference to the density  $\text{Rho}$  (or  $\rho$ ). The density and its reciprocal are required non-negative and non-zero for logical and theoretical reasons. The higher-order derivatives of the working fluid state functions with respect to  $y$  tend to remain constant over a wider thermodynamic range. The constant  $\text{RHO}$  is removable from any intermediate expressions and therefore is not stipulated. The reaction concentrations are not utilized for stipulating the thermal-mechanical type constraint-relations, so the working fluid has a differential form that can be rewritten in a useful way.

$$dU = T \cdot dS + \frac{P}{\rho} \cdot \frac{d\rho}{\rho} + \sum \mu_k \cdot dN_k$$

$$W \equiv P/\rho, \quad y \equiv \text{Ln}[\rho/\text{RHO}]$$

$$Q \equiv \frac{\sum \mu_k \cdot \nu_k}{M_w}, \quad d\tilde{r} \equiv \frac{dN_k}{N \cdot \nu_k}$$

$$dU = T \cdot dS + W \cdot dy + Q \cdot d\tilde{r}$$

The traditional first relation with terms per unit working-fluid mass was readjusted by expanding the reciprocal density term. The multiplier that works with the  $y$  differential,  $W$ , is referred to as the flow work per unit mass. The reaction terms in contracted form utilize the reaction coordinate  $\tilde{r}$  with  $Q$  as the multiplier. The reaction sum  $Q$  of stoichiometric coefficients  $\nu_k$ 's times their respective chemical potentials  $\mu_k$ 's is divided by the formula molecular weight  $M_w$  for the working fluid mixture.  $W$  and  $Q$  are recognized as working-fluid state functions,  $Q$  is not restricted in sign, and  $W$  and  $T$  remain positive for stable fluids.<sup>11</sup> There are no constancy requirements imposed on the working-fluid state functions for unresolved trajectory conditions.

The two choices for reaction conditions that are quite tractable for trajectory terminal points are those that would nullify the chemical-work: the requirement of  $\tilde{r}$  constant represents non-reactive or frozen flow and the requirement of zero  $Q$  represents chemical equilibrium. The latter would occur when the reverse reactions match their respective forward reactions, which is normally presumed for the TDRC. The requirement for zero  $Q$  arises strictly for the terminal state, not within the unresolved transitional trajectory, where the restorative influences for non-zero  $Q$  could readjust the reaction chemistry for the transitory conditions.

## ROCK ON A HILL - THE QUASI-POTENTIAL

The reduction of the quasi-potential  $Y_Q$  or the rise in the working function  $W_F$  registers the restoration work necessary to undo the deterioration from the original thermodynamic state. The quasi-potential  $Y_Q$  is analogous to a rock that would roll downhill for irreversible processes, remain at rest for reversible processes, and would not roll uphill for forbidden processes. For natural processes with their recognizable finite irreversible transition(s), the rock's downhill motion would register notable

reduction in the quasi-potential. The restorative influences of non-equilibrium continually try to reduce the quasi-potential, so the rock travels downhill until no further  $Y_Q$  reduction can occur, stalling the trajectory motion, trapping the rock at rest, within reversible fluctuations and uncertainty tolerances. The unresolved trajectory route(s) and the un-relinquished constraint (curve) represent different notions, except when the rock is trapped. Without those constrained equilibrium circumstances there is no differential restriction on quasi-potential  $Y_Q$ , and therefore insufficient information for the work-principle technique to render the thermodynamic state of the working fluid. The restoration influences perform work to force the return of equilibrium even under imposed constraints, but when those restoration forces are not otherwise tracked, the related trajectory motion remains unresolved. For the work-principle formulation, the trajectory motion remains unresolved except for the trajectory terminal states, which is why it is referred to as an unresolved trajectory or non-trajectory algorithm.

TDRC fume results resolved for other thermodynamic states, which were not trajectory terminal (key) states, would probably not be relevant, and therefore rather worthless. Root-finding techniques are quite useful for determining the restriction on the thermodynamic state represented by the minimum trap and the imposed constraint, though that won't reveal the fume spectrum. Numerical results utilizing TDRC reveal the fume spectrum for the restricted key state, though they are not rigged internally for the requisite root finding. Therefore key-state results were reckoned by trial-and-error, taking tentative trial choices compatible with constraint, computing the working-fluid state functions with TDRC, hoping for further reductions in the quasi-potential and discarding the numerous wrong results on the way.

## REDUCTIONS FOR GIBBS AND HELMHOLTZ

Within this section, the quasi-potential  $Y_Q$  is restricted in form, so that the work principle can render the traditional inequality requirements for the Helmholtz energy  $F$  or  $G$  Gibbs energy.<sup>8,12</sup> The reservoir conditions must reflect the wanted working fluid conditions rather than the fume reservoir conditions. When the working fluid density is rigidly restrained (constant  $\rho$ ) and there is thermal equilibrium between the working fluid and the reservoir  $T = T_R$ , then  $Y_Q = U - T_R \cdot S + P_R/\rho = U - T \cdot S + \text{Constant} = F + \text{Constant}$ . Under transitional change the residual constant disappears and is therefore irrelevant. The requirement  $\Delta Y_Q \leq 0$  reduces to  $\Delta F \leq 0$ , where the reduction in  $F$  registers the restoration work. For the other requirement, take thermal equilibrium ( $T_R = T$ ) and mechanical equilibrium ( $P_R = P$ ) between the working fluid and the reservoir working fluid, then  $Y_Q = U - T_R \cdot S + P_R/\rho = U - T \cdot S + P/\rho = G$ . The requirement  $\Delta Y_Q \leq 0$  reduces to  $\Delta G \leq 0$ , where the reduction in  $G$  registers the restoration work. Under the two restricted transformations, the reservoir characteristics were replaced with working fluid characteristics, yielding two state functions  $F$  and  $G$  respectively. The restrictions illustrated underlying the minimization routines utilized within TDRC, depending on the circumstance wanted.<sup>13,14</sup>

## REPRESENTATION OF WANTED PROCESS

Reaction fume process(s) fluid are represented on a trajectory graph using two state functions for the working fluid, like the energy  $U$  and  $1/\rho$  (or  $1/\rho$ ) the reciprocal density. The representative thermodynamic diagram and the work-principle components are shown in Figure 1. For rigid confinement, the density would remain constant and the working fluid would transition from the reactant ingredient (initial) state or I-point to the J-point. For rock blasting, some notable reduction in  $U$  would occur in conjunction with the reduction in  $\rho$ , yielding the transition to the R-point. When the reduction in the resultant (or net) interaction energy is neglected, the work-principle technique yields

the Z-point, taken for predicting toxic fumes in underground chamber test. Future renditions could utilize a formulated constraint to replace the neglected interaction with the requisite energy reduction, yielding the trajectory motion to the N-point. Whether those refinements are warranted for fume spectrum results, or just for occasionally confirming the reliability of the Z-point results, remains unclear. The N-point would probably represent the last remnant of worthwhile equilibrium for the working fluid, which then drifts downward through the cooler out-of-equilibrium conditions ultimately reaching the reservoir conditions. The reservoir conditions are taken as the, Q\*-point, or the measurement state conditions, when they are readjusted to the reference standards [25 °C and 1 atmosphere].

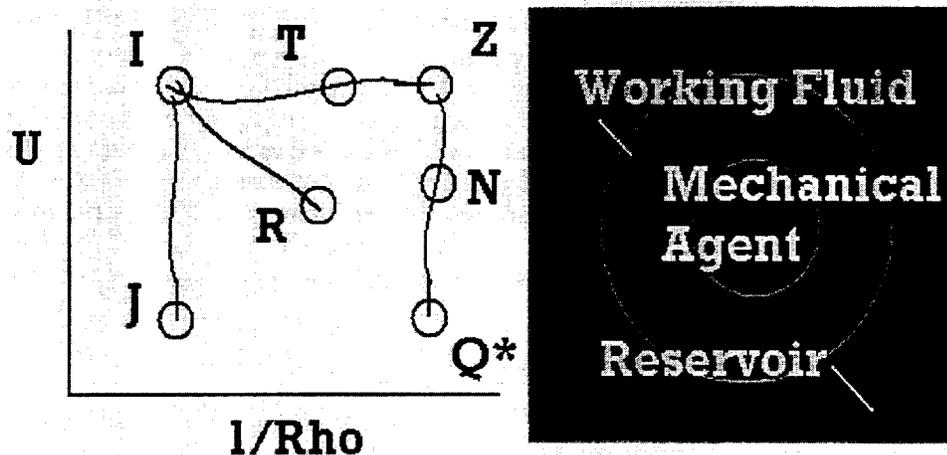


Figure 1. Work Principle Component Model, & Thermodynamic Diagram with Wanted Processes.

The named points (except T) represent trajectory terminal (or key) states, and only the trajectory route through the Z-point displays the multiple segments needed for reaching the reservoir conditions. The TDRC with wanted reactant ingredients is resolved for some trial state, the T-point, with the constraint of zero-net interaction, which requires the retention or return of the working fluid energy  $U$  to the original  $U_I$  upon reaching the trajectory key state. The working-fluid state functions for the tentative T-point yields the corresponding  $Y_Q$  quasi-potential. The trial point T is readjusted as noted previously until there is no further reduction in the  $Y_Q$  quasi-potential. The tentative T-point results shown in Figure 2 show the downward trend(s) in the quasi-potential which was utilized to find the trapping minimum, Z-point, the only worthwhile point. The Z-point name is remindful of the zero-net-interaction energy, with zero tolerance for readjustment, and a logical zenith state since reduction of energy  $U$  would occur with non-zero-net interaction. Refinements in work-principle technique can only be rendered by readjustments in the constraints representing the wanted thermodynamic process, so while the work principle overcomes some hard issues, it has its own unique form of intractability.

## RENDERING OF IMPOSED CONSTRAINTS

The rendering of imposed constraints refers to the utilization of relative minimum trapping conditions to stall the trajectory motion. The imposed constraints are represented as  $Y_Q$  partial derivatives with respect to the unrestrained  $\chi$ , while holding  $\kappa$  constant. The variable functions  $\chi$  or  $\kappa$  are constructed

from the thermal-mechanical state functions like  $W$ ,  $y$ ,  $T$ ,  $S$ , (or  $U$ ), rather than from reaction variables like  $r$ -bar,  $Q$ , or the concentrations ( $N_j$ ). The unrestrained  $\chi$  taken while holding  $\kappa$  constant would remain otherwise unrestricted were it not for reductions in the quasi-potential. The change of the quasi-potential  $Y_Q$  or negative work function  $W_F$  is resolved according to a Taylor's expansion in unrestrained  $\chi$ , while  $\kappa$  remains constant. The capital-delta (small-case) notation represents finite (infinitesimal) differences, with normal (not-reverse) chronology understood.

$$\Delta[-W_F]_{\kappa} \equiv \Delta Y_Q|_{\kappa} \equiv \sum (\Delta\chi)^J \cdot \left. \frac{\partial^J Y_Q}{\partial \chi^J} \right|_{\kappa} \leq 0$$

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Technically the subscripts should include  $Q$  to bear witness to the restriction of chemical equilibrium. That requirement is universally implied for terminal state resolution, so the reduced notation just displaying  $\kappa$  thermal-mechanical constraint is tractable. For transformations that are infinitesimal, there is retention of only the lowest-order- $J$  non-zero terms. Recognition of the reduction in form is noted with the grave mark on the summation symbol, with later illustrations showing relevant results.

For resolving the minimum trapping state, the partial derivative  $\partial Y_Q / \partial \chi|_{\kappa}$  would reduce to zero for the terminal state, so the next non-trivial term determines the stable nature of the stationary condition. For the trajectory trapping minimum the second-order derivative  $\partial^2 Y_Q / \partial \chi^2|_{\kappa}$  is positive. The relational inequality suggests that unrestrained variation squared multiplying the second-order derivative would then have the wrong sign, for compliance. The only workable solution would require that the otherwise unrestrained  $\chi$  vanish, which represents stalled trajectory motion, which is the interpretation rendered for the rock rolling down the hill. The constraint curve obtained by graphing  $\Delta Y_Q$  with constant  $\kappa$  over a wider range with respect to unrestrained  $\chi$ , like in Figure 2, reveals the minimum trapping condition, with downward motion regardless of the pathway, since the route is unresolved.

Worthwhile conditions occur when the quasi-potential trapping minimum is reached, stalling trajectory motion (no choice - downward), until the constraint is replaced with a different restriction or left unrestrained. For the work-principle formulation, other types of stationary results are unregulated or worthless, since they refer to unstable or meta-stable conditions. The thermodynamic quasi-potential 'rock' rolls downhill, not uphill into a  $Y_Q$  maximum, unless something is ill resolved. For the non-traditional maximum starting condition, the trajectory is initially unregulated, with multiple branches downhill. Inflection point circumstances would be resolved in a similar fashion, using higher-order terms to understand the nature of the stability. Un-trapped trajectory motion would render the constraint worthless (one choice - downward) or unregulated (multiple choices - downward).

## NON TRAJECTORY AND THERMODYNAMIC UNCERTAINTY

Irreversible and reversible fluctuations render the chronological occurrences that force the reduction of the quasi-potential, though there is other rationale for the retention of pathway uncertainty. There is a quantum mechanics uncertainty principle and there is a thermodynamic uncertainty principle, though the latter is not as widely known.<sup>15</sup> Uncertainty principles tend to render strict trajectory notions obsolete and force worst-case minimum tolerances on canonically conjugate variables. When

multiplying the uncertainty tolerances for the canonical coordinates, the multiplication result in quantum mechanics has units of Heisenberg's constant (or action), while the multiplication result in thermodynamics has units of Boltzmann's constant (or entropy). While our restrained and unrestrained variable-functions do not necessarily form a canonically conjugate pair, there is still underlying uncertainty in the working fluid state functions from which they were formed. Resolution of trajectory motion remains the relevant issue, not the fact that the TRDC results are fraught with much greater numerical errors than the theoretical uncertainty. Although there are profound philosophical differences, it is worth noting that the work principle tends to work like the non-trajectory requirements of quantum mechanics, with terminal (key) states rendered as the only recognized or observable operations, and with intervening transitional states remaining unresolved or unobserved.

## ZERO-NET-INTERACTION ENERGY

For zero-net-interaction energy, the terminal trajectory state is resolved by requiring that the working fluid retain or recover the working fluid energy  $U_I$  of the I-point trajectory state. Non-trivial influence is possible, since the work-heat transfer with the reservoir is unrestricted except for registering the zero-net energy-change for the macroscopic process. There is no restriction on the working fluid's entropy change, thanks to the reservoir, though there must be a reduction in the quasi-potential. The restriction on the terminal trajectory is written  $U = \kappa$  for theoretical resolution, with  $\kappa = U_I$  for the numerical resolution using the relevant TDRC. Utilizing hindsight, the forthcoming results were reduced in form by defining the K-function,  $K \equiv P/R^*T$ , which remains useful regardless of the working fluid's EOS.  $R^*$  is the Universal Gas Constant. Upon reaching the reservoir state, the K-function would equal the constant  $K_R \equiv P_R/R^*T_R \equiv 40.874 \text{ } \mu\text{mol/cc}$  (or  $\text{mol/m}^3$ ). The reciprocal of  $K_R$  would equal  $24,470 \text{ cc/mole}$  for reservoir conditions taken at the reference standard. The unrestrained variation could be  $\chi = y$  or  $\chi = S$  yielding,

$$\delta[-W_F]_{|U} \equiv \delta Y_O|_{|U} = \delta y \cdot \left. \frac{\partial Y_O}{\partial y} \right|_U = W \cdot \delta y \cdot \left[ \frac{T_R}{T} - \frac{P_R}{P} \right] = \left( \frac{T_R W}{T} \right) \cdot \delta y \cdot \left[ 1 - \frac{K_R}{K} \right] \leq 0$$

$$\delta[-W_F]_{|U} \equiv \delta Y_O|_{|U} = \delta S \cdot \left. \frac{\partial Y_O}{\partial S} \right|_U = T \cdot \delta S \cdot \left[ \frac{P_R}{P} - \frac{T_R}{T} \right] = (-T_R) \cdot \delta S \cdot \left[ 1 - \frac{K_R}{K} \right] \leq 0$$

The working fluid ratio  $W/T$  remains positive for a thermal mechanical stable fluid. The reservoir-fluid state functions  $T_R$  and  $P_R$  are likewise restricted. Zero temperature is unattainable according to the third law of thermodynamics. The bracket term arises, regardless of the way  $\chi$  was chosen, provided that it was unrestrained for  $\kappa$  constant. When the Z-point K-function is larger (smaller) than the reservoir constant  $K_R$ , the brackets are positive (negative). Under those circumstances the entropy must rise (fall) and the density must fall (rise). The terms without parenthesis refer to the explosion-type processes, while the reverse cases refer to implosion-type processes. Transformations that obey the inequality occur, while reverse inequality conditions that violate the reduction of the quasi-potential  $Y_Q$  are forbidden.

*With the work principle, the theoretical restrictions or bracket terms, deduced from the quasi-potential minimum-trap requirement, hold for any working fluid regardless of its equation of state EOS. The tenability of the restrictions remains unaffected when studied numerically, though such results are worthwhile only if the TDRC and related EOS characterize the working fluid in the thermodynamic*

domain under investigation. When the zero-net interaction Z-point constraint is removed, non-equilibrium prevails with unresolved circumstances, though the restorative influences must ultimately recover the requisite  $K_R$  circumstances at the reservoir conditions or  $Q^*$ -point measurement state. The work principle renders a trapping minimum for the Z-point where  $K = K_R$  and forecasts that it would replicate  $K = K_R$  when the working fluid reaches the reservoir conditions. Real-gas formulations, like  $\Phi = W \cdot M_w / R \cdot T$ , evaluated at the K-function Z-point condition reduce to the ideal form ( $\Phi=1$ ), wholly compatible with the rarified-hot state resulting from no energy reduction and small-rho minimum. For such circumstances, the Z-point restriction  $K = K_R$  further requires that the Z-point molar density  $\rho/M_w = K_R = 40.874 \text{ mol/m}^3$ . Under the circumstances, the work principle renders the Z-point molar density of the reaction fumes, regardless of the charge formulation, and forecasts it would ultimately replicate that result for the reservoir conditions. The working fluid for the  $Q^*$ -point, taken at reservoir conditions, normally includes notable quantities of condensed phases, like water, which ruin the ideal-gas presumption for the reservoir conditions.

## ILLUSTRATION OF OTHER CONSTRAINTS

With the work principle, the only way to stipulate or refine the representation of some wanted natural process is to compose and readjust the constraints. Other renditions of trapping conditions, though rudimentary, are illustrated to represent the way model development transpires. With the work principle, the constraint must render the minimum trap for the downhill drift of the quasi-potential, represented theoretically by bracket terms that can reduce to zero. Though the bracket terms arise regardless of the choice of the unrestrained variable, the related multiplier could include zeros or poles that relate to the stability of the working fluid, which remains outside the scope of this report. For the results illustrated the unrestrained variable was chosen so that the multiplier would have a tractable form with obvious fixed sign. For isochoric process or constant density (or logarithm thereof) take  $y = \kappa$  and  $\chi = U$ , then compute  $\partial Y_Q / \partial U|_y$ . The subscript y is capitalized as are others for readability.

$$\delta[-W_F]_{|y} \equiv \delta Y_Q|_y = \delta U \cdot \left. \frac{\partial Y_Q}{\partial U} \right|_y = \delta U \cdot \left[ 1 - \frac{T_R}{T} \right] \leq 0$$

For natural processes this relationship dictates that the energy  $U$  of the working fluid would fall (rise) when it has a temperature  $T$  higher (lower) than  $T_R$  the reservoir temperature. Until this constraint is relinquished, there is no requirement that the working fluid pressure match that of the reservoir. For isentropic process take  $S = \kappa$  and  $\chi = U$ , then compute  $\partial Y_Q / \partial U|_s$ .

$$\delta[-W_F]_{|s} \equiv \delta Y_Q|_s = \delta U \cdot \left. \frac{\partial Y_Q}{\partial U} \right|_s = \delta U \cdot \left[ 1 - \frac{P_R}{P} \right] \leq 0$$

For natural processes this relationship dictates the energy  $U$  of the working fluid would fall (rise) when the working fluid has a pressure  $P$  higher (lower) than  $P_R$  the reservoir pressure. Until this constraint is relinquished there is no requirement that the working fluid temperature match that of the reservoir.

For an isothermal process take  $T = \kappa$ , and  $\chi = y$ , then compute  $\partial Y_Q / \partial y|_T$ . Notice that for temperature conditions, some reductions in form could occur when the constraint constant  $\kappa$  refers to the  $T_R$  reservoir isotherm.

$$\delta[-W_F]_{\tau} \equiv \delta Y_Q|_{\tau} = \delta y \cdot \frac{\partial Y_Q}{\partial y}|_{\tau} = W \cdot \delta y \cdot \left[ \left\{ 1 - \frac{\Gamma_G}{\Gamma_J} \left( 1 - \frac{T_R}{T} \right) \right\} - \frac{P_R}{P} \right] \leq 0$$

The bracket terms were rewritten so the working fluid to reservoir pressure ratio  $P/P_R$  could be compared with the reciprocal of the brace term, including the constant  $T/T_R$  term. Recall that  $W$  was required positive, so if the brace term within the bracket term were negative or zero the density would rise. For the remaining conditions the brace term is regarded positive, and the reciprocal is taken. When the ratio  $P/P_R$  is higher (lower) than the reciprocal, the bracket term would be positive, so the working fluid density would fall (rise). The gamma factors represent dimensionless forms of higher-order thermodynamic derivatives, and therefore are not necessarily constant. The  $\Gamma_J \equiv W/C_V T$  remains positive, where  $1/C_V = \partial T/\partial U|_V = \partial \text{Ln}(T)/\partial S|_V$  is the reciprocal of the specific heat at constant density. The Gruneisen gamma is normally positive and has two useful representations  $\Gamma_G \equiv \partial W/\partial U|_V = \partial \text{Ln}(T)/\partial y|_S$ . For a working fluid on the reservoir isotherm, the bracket term reduces to  $[1 - P_R/P]$ , regardless of the state equation EOS. For thermodynamic domains where the working fluid reduces to the ideal-gas form,  $\Gamma_Q = \Gamma_G$ , the bracket term reduces to the bracket term resolved for the zero-net interaction. Whence the internal energy  $U$  reduces to just a function of the temperature  $T$ , and therefore it is logical that the work-principle yield identical indications.

## FUME RESULTS WITHOUT REACTANT AIR

Reaction fume results were computed for the Z-point to check the worthiness of the work-principle technique at this stage of model development. Three types of ANFO were resolved at the Z-point, depending on their hydrocarbon fuel, referred to as rocket-fuel kerosene RFK, jet-fuel kerosene JFK, and number-two heating fuel oil HFO. The representative formula for RFK or dodecane was  $C_{12}H_{26}$ , for JFK or Jet-A it was  $C_{12}H_{23}$ , and for HFO was  $C_{14}H_{24}$  (rather than  $C_7H_{12}$ ). The heat of formation for RFK was -350.9 kJ/mol as referenced and for HFO was -247 kJ/mol as estimated from the heavier hydrocarbon for that H/C ratio.<sup>16</sup> The heat of formation for JFK was -303.4 kJ/mol, from NASA chemical equilibrium reaction code utilized for rendering the TDRC results.<sup>6</sup>

The underground fumes chamber contains 274 m<sup>3</sup> or 324 kg of air, and the explosive mass is 4.54 kg or roughly 1.4% proportional weight. The toxic fumes molar concentration would normally be under 0.25%, when transformed to carbon monoxide CO equivalent toxicity.<sup>17</sup> The Z-point fume temperature, the CO and the nitrogen-oxides NOX results were graphed against the hydrocarbon fuel [%], shown in Figures 3, 4, and 5 respectively. The results were not sensitive to the choice of the hydrocarbon fuel, within the range of 1% to 10%. The CO rises monotonically under fuel rich conditions while the NOX tends to rise under opposite conditions with a maximum near 4%. Theoretical CJ-state fume-spectrum and temperature results for prill ANFO with different fuel [%] were reported.<sup>18</sup> Results were unit-transformed, the NOX=NO+NO<sub>2</sub> was computed, and the CJ-state results were plotted for comparison on our relevant Z-point graphs. The Z-point temperature is only ~20% smaller compared to the CJ-state, which is over thousand times denser. The two CO trends were comparable throughout, and the two NOX trends were comparable at very rich and stoichiometric conditions. Otherwise there are noteworthy differences, which might be understood with further theoretical refinements.

Toxic fumes concentrations [cc/g] taken during underground hard-rock metal mine operations, yield results somewhat different than typical gallery cannon fixtures. Their range of tabulated mean concentration results for six different explosives including two semi-gel dynamites, three slurry explosives, and mostly ANFO (\*some dynamite) were transformed to metric units and displayed in the

next table,[added NOX=NO+NO<sub>2</sub>].<sup>19</sup> The hard rock mine shots and closed-gallery results correspond to Q\*-point results rather than Z-point results. The Z-Q\* numerical difference for some fume species is rather minor, suggesting that further model refinements would be worthwhile.

Toxic Fumes Concentrations [cc/g] Underground Hard-Rock Mine						
Range	CO <sub>2</sub>	CO	SO <sub>2</sub>	NO	NO <sub>2</sub>	NOX
Overall	47-106	3.9-18.5	0.1-2.9	0.6-2.1	0.2-1.2	0.8-3.3
~ANFO	58	4.6	0.1	0.7-1.1	0.8-1.0	1.6-2.1

One major theoretical discrepancy that was noted (not graphed) was that the Z-point NO<sub>2</sub>/NOX ratio is negligible, though it is a noticeable fraction for most Q\*-point observations. Resolving the transformation of NOX components requires non-equilibrium reaction code models formulated to yield the cool temperature results that occur within the hour of measurement. The work principle rigidly requires that K is numerically fixed (=K<sub>R</sub>) at the Z-point regardless of the working fluid's EOS or the charge formulation, which ought to facilitate the formulation of the non-equilibrium reaction-rate kinetic model for rendering Q\*-point results from Z-point results.

### FUME RESULTS WITH REACTANT AIR

The work principle can incorporate reactant-air as a working fluid ingredient, while retaining the rest as non-reactive reservoir material. The ratios of reactant-air mass to explosive mass RAX were taken as 0%, 25%, 50%, 75%, and 100%. For the highest RAX of 100%, the total working-fluid mass doubles to roughly 9 kg, while the original 324-kg of chamber air drops to 320 kg non-reactant-air mass, hardly readjusting the tremendous reservoir (walls and air) required for the work-principle model. For the jet-fuel kerosene with 4%, 5%, 6%, and 7% fuel, the trend parameters were resolved with respect to RAX [%]. The Z-point graphs of temperature, density, CO and NOX are shown in Figures 6, 7, 8, and 9 respectively. The temperature which were roughly 2500 °K for the 4% to 7% fuel range, for zero RAX, diminishes rapidly with respect to rising RAX [%]. The NOX roughly doubled and the CO rapidly disappeared with rising RAX [%], so fume sensitivity with respect to RAX is rather high. Normally when resolving toxic fumes with some TDRC, reactant-air is neglected, so RAX = 0% represents traditional results. The trends from the work-principle warn of difficulty with the traditional presumption, if the Q\*-point measurement results were noticeably influenced by reactions with the surrounding air.

### COMPARISON TO THEORETICAL & RELIABILITY

For wide variations in trial density the trapping profile of the quasi-potential Y<sub>Q</sub> were obvious, but near the terminal state it was harder to resolve because of slight irregularities in the working fluid's state functions that were transmitted into the quasi-potential. Trials were normally run until the Z-point until deviations were under 5% and often under 2%. The restriction on K resolved theoretically for the zero-net-interaction energy constraint could not be utilized directly, since the K and U would not yield a workable pair of input conditions for the TDRC. Utilizing the graphic and tabular minimization of the quasi-potential Y<sub>Q</sub>, the working fluid state functions were obtained for Z-point. The theoretical restriction K = K<sub>R</sub> was checked for different charge formulation including those with inert additives. The K reciprocal for the Z-point fumes was compared with the theoretical K<sub>R</sub> reciprocal or R\*T<sub>R</sub>/P<sub>R</sub> = 24,470 cc/mol. This comparison was confirmed numerically, with the worst-error under 5%. This was

regarded as rather remarkable, since the TDRC was not tuned for the trapping minimization technique that is utilized in conjunction with the work principle.

With such rarefied Z-point indications, it is worthwhile working with a TDRC developed specifically for the ideal gas form.<sup>6</sup> Though it removes the nuisance of readjustable constants and the complex formula with worthless terms, it raises the likelihood of reliable results. The related reference material and tables can range over more types of molecular species, which noticeably raises the types of reactions considered in TDRC. The more unrestricted the reaction possibilities, the more likely the work-principle results reflect reality, and for toxic fumes this reliability is wanted.

## CONCLUSIONS AND RECOMMENDATIONS

Whether or not the work-principle with zero-net-interaction energy technique is used to render toxic fumes or recognition of more refined interaction is required remains unclear. The zero-net interaction constraint was noted to resemble test conditions for the underground fumes chamber rather than those for rock blasting. Foremost this restriction renders fume spectrum resolution without readjustable constants, optional choices, or selection of EOS constants, when the reservoir and original charge state are taken at reference standard conditions, [25 °C and 1 atmosphere]. The remarkable characteristics of the zero-net interaction Z-point are noteworthy and were rendered in theoretical form for the working fluid of any charge formulation, regardless of its equation of state EOS. The K function at the Z-point reduces to the K-function result for a reservoir  $K_R \equiv P_R/R^*T_R \equiv 40.874 \mu\text{mol/cc}$  or the reciprocal of 24,470 cc/mol. It was recognized that the K-function, though unresolved in trajectory transition, would ultimately replicate the result  $K_R$  for the cool temperature Q\*-point reservoir or measurement state. It was forecast that this result would occur regardless of the EOS taken for the working fluid, or the cool temperature.

For the working fluid at the Z-point, the temperature is over two thousand degrees, the trial density is roughly 1 mg/cc, and the fraction of condensed phase material is rather small or negligible. The reciprocal of K or  $R^*T/P = 24,470 \text{ cc/mol}$  at the Z-point represents a thermodynamic regime where the real-gas EOS forms reduce to the ideal-gas form. Reckoned as an ideal gas, the working fluid for the reaction products would have a molar density of 40.874  $\mu\text{mol/cc}$  at the Z-point, regardless of the charge formulation. Furthermore, the working fluid molar density would return to that numeric value upon ultimately reaching the reservoir conditions, were the ideal form retained. Unlike the former forecast, the latter one would falter, since the working fluid is not a simple fluid that can always be reckoned as an ideal gas. The working fluid representing the fumes has a rather complex nature, and a noticeable number of the mixture components would transform into condensed products on the way to the reservoir conditions, characterizing the Q\*-state.

For mining explosives, which have non-ideal performance characteristics, there remain notable uncertainty in the rationale and the underlying presumptions regarding their detonation reaction or related fume results. The work principle requires different suppositions, and thereby overcomes some of the hard issues, though it has its own unique intractability and philosophical difficulty. It remains unclear what discrepancies will remain when the work principle is refined with non-zero interaction terms and out-of-equilibrium reaction models are utilized to render cool-temperature fume results, for it is an unfinished work in progress.

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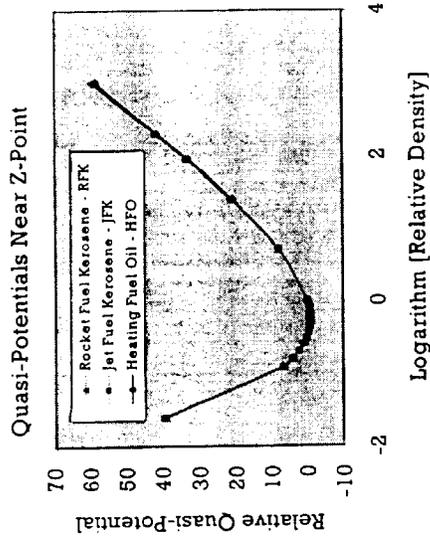


Fig 2. Quasi-Potentials for Choices of Trial Density Near the Z-point.

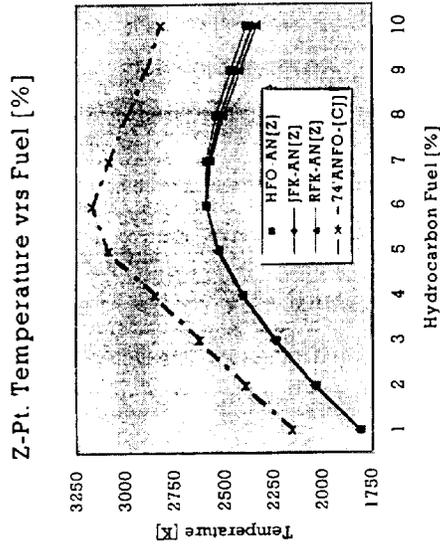


Fig 3. Z-point Temperatures with respect to Hydrocarbon Fuel [%].

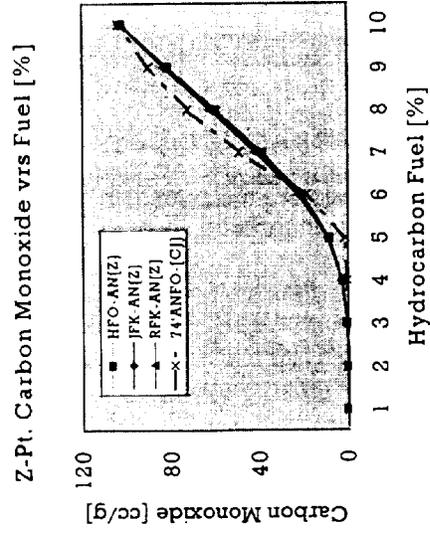


Fig 4. Z-point Carbon Monoxide with respect to Hydrocarbon Fuel [%].

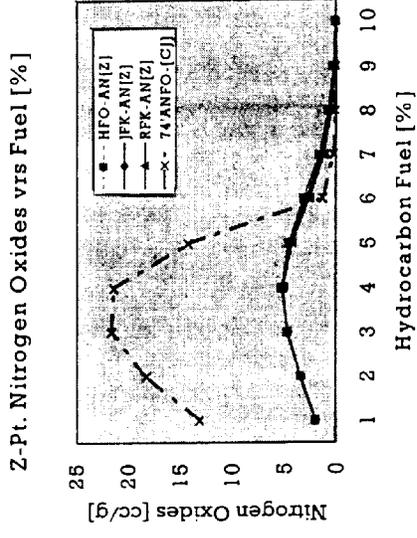


Fig 5. Z-point Nitrogen Oxides NOX with respect to Hydrocarbon Fuel [%].

Z-Pt. Temperature vrs RAX [%]

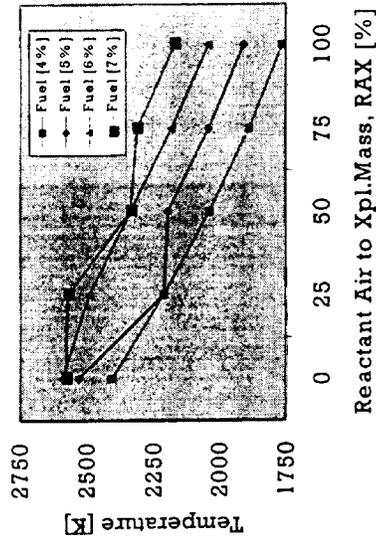


Fig 6. Z-point Temperature with respect to Reactant Air Included, RAX [%].

Z-Pt. Fume Density vrs RAX [%]

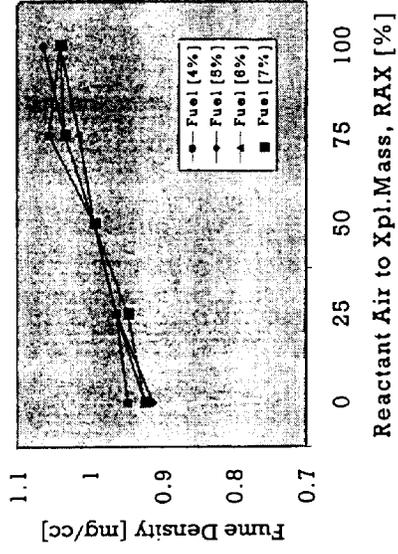


Fig 7. Z-point Density with respect to Reactant Air Included, RAX [%].

Z-Pt. Carbon Monoxide vrs RAX [%]

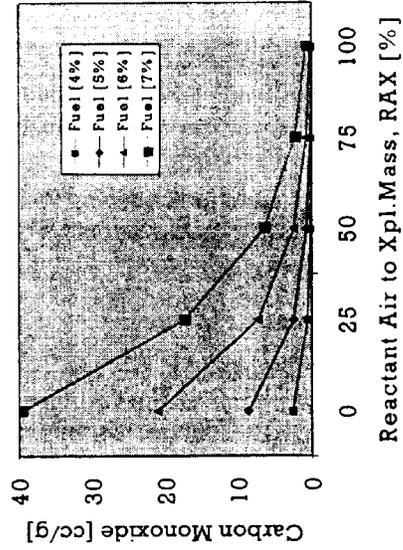


Fig 8. Z-point Carbon Monoxide with respect to Reactant Air Included, RAX [%].

Z-Pt. Nitrogen Oxides vrs RAX [%]

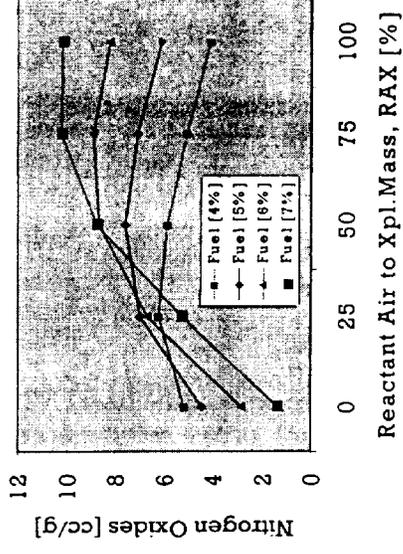


Fig 9. Z-point Nitrogen Oxides NOX with respect to Reactant Air Included, RAX [%].

# Work Principle For Predicting Explosive Toxic Fumes

## -- Erratum

Michael S. Wieland

Two relationships that represent Taylor expansions were written incorrectly, in the report. The terms within the summations are missing J-factorials [J!] in the denominator. The relationships should be replaced by the following two formulas, respectively:

$$\Delta[-W_F]_{|_k} \equiv \Delta Y_O|_k = \sum \frac{(\Delta\chi)^J}{J!} \cdot \frac{\partial^J Y_O}{\partial \chi^J} \Big|_k \leq 0$$

$$\delta[-W_F]_{|_k} \equiv \delta Y_O|_k = \sum \frac{(\delta\chi)^J}{J!} \cdot \frac{\partial^J Y_O}{\partial \chi^J} \Big|_k \leq 0$$

The J-factorial errors were not propagated, and therefore modifications to the other relationships are not required.