

Theory of Liquids, Vapors, and Gases

by

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Abstract

This paper presents the derivation of the equations for the properties of liquids, vapors, and gases according to the Reciprocal System of physical theory developed by D. B. Larson. For each atom or molecule, the factors include the number of volumetric groups, the number of thermal groups, the number of internal groups, the number of initial groups, the number of temperature units and the temperature, the number of pressure units and the pressure, the gas constant, and atomic/molecular weight. Each Reciprocal System theoretical calculation is compared with the appropriate empirical regression equation from the scientific/engineering literature.

keywords: liquid state, vapor state, gas state, specific volume, density, specific heat, enthalpy, entropy, viscosity, surface tension, melting point, heat of fusion, heat of vaporization, critical temperature, orthobaric vapor volume, saturated vapor volume, vapor pressure, superheated vapor volume, real gas volume

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Introduction and Literature Survey

Dewey B. Larson was the developer of the Reciprocal System of theory; see Ref. [1]-[4] and [14]. The present author summarized the liquid state work in Ref. [5] and [6], and this paper is an update.

There is no practical liquid/vapor/gas theory in Quantum Mechanics. Engineers must resort to empirical methods to obtain practical values for matter properties. Ref. [7] and [8] are the two most useful works in this regard; the regression methods used in Ref. [8] will be utilized in this paper and in the Reciprocal System Database as a means of comparing the theoretical calculations with the observed values. Ref. [9], [10], and [11] contain tabulations of experimental data of liquids, vapors, and gases.

This paper is a runnable *Mathcad* program, so the equations are more detailed than they otherwise would be. Current screen shots of the Reciprocal System Database are displayed at <http://transpower.wordpress.com>.

Nomenclature

A, B, C, D, E, n = coefficients for Yaws' regression equations for calculation of liquid and vapor properties (some have subscripts)

$A_{RS}, B_{RS}, C_{RS}, D_{RS}$ = equivalent Reciprocal System coefficients for regression equation for calculation of liquid specific heats

A_v = Avogadro's number

B, B_0 = regression parameters for empirical vapor volume calculation

B_{mod} = bulk modulus of liquid, atm

$C_1 \dots C_{11}$ = Al-Hamid regression coefficients for empirical calculation of superheated vapor volume

$conv_{atm\ to\ dynes\ cm^2}$ = factor to convert atm to dynes/cm²

$conv_{cal\ to\ J}$ = factor to convert cal (calories) to J (joules)

$conv_{u\ to\ g}$ = factor to convert u (atomic or molecular mass) to g

c_p = Reciprocal System theoretical value of liquid specific heat at constant pressure, cal/mol K

$c_{p_avg_StrG}$ = *average* c_p per structural group, cal/mol K (note: this is an *overall* average for the different kinds of structural groups in the molecule)

$c_{p_conv_regr}$ = conventional empirical regression value of liquid specific heat at constant pressure, cal/mol K

$c_{p_conv_g_regr}$ = conventional empirical regression value of liquid specific heat at constant pressure, cal/g K

$c_{p_e_mean}$ = mean electron specific heat, eV/K per electron (or V/K)

c_{p_G} = specific heat of gas (from *both* internal and external motion), cal/mol K

c_{p_g} = Reciprocal System theoretical value of liquid specific heat at constant pressure, cal/g K

c_{p_m} = specific heat of liquid at melting point, cal/mol K

c_{p_Yaws} = Yaws' empirical regression value of liquid specific heat at constant pressure, J/mol K

c_{p_SI} = Reciprocal System theoretical value of liquid specific heat at constant pressure, J/mol K

c_{p_regr} = Reciprocal System equivalent of empirical regression equation for c_p , J/mol K

c_{p_u} = Reciprocal System natural unit of specific heat, stated in cal/mol K

$c_{p_u_SI}$ = Reciprocal System natural unit of specific heat, stated in J/mol K

$c_{p_V_H2O}$ = specific heat of water vapor, cal/mol K

$c_{p_V_H2O_Yaws}$ = Yaws regression value for specific heat of water vapor, converted to cal/mol K

d_{atom} = diameter of atom, fm

Dev_1 = first component of deviation of real gas from ideal gas volume, cm^3/mol

Dev_2 = second component of deviation of real gas from ideal gas volume, cm^3/mol

Dev_G , Dev_V , Dev_{LV} , Dev_L = deviations of real gas from ideal gas volume at P_G , P_V , P_{LV} , and P_L , cm^3/mol

Dev_{SH} = deviation in superheated vapor volume from normal gas volume at that temperature and pressure, cm^3/g

d_u = Reciprocal System natural unit for atomic diameter, stated in fm

f_L = liquid fluidity (inverse of viscosity), cp^{-1}

$f_{L_u_cgs}$ = Reciprocal System natural unit of fluidity, stated in cp^{-1}

frac_S = fraction of solid molecules in liquid aggregate

frac_VG = fraction of vapor and gas molecules in liquid aggregate

h_{fusion} = heat (or enthalpy) of fusion, cal/mol

$h_{\text{fusion_SI}}$ = heat (or enthalpy) of fusion, J/mol

h_G = enthalpy of gas, cal/mol

h_{L_0} = enthalpy of liquid at very beginning of transition to gas, cal/mol

h_{liq} = enthalpy of liquid, cal/mol

h_m = enthalpy of liquid at melting point, cal/mol

h_S = enthalpy of solid component (subscript m for melting point)

h_{V_H2O} = enthalpy of water vapor, cal/mol

h_{V_m} = enthalpy of vaporization at melting point, cal/mol

I = initial contribution to specific heat, cal/mol K

I_T = initial level in terms of natural temperature unit for 2D and 3D gas temperature (fraction)

I_R = inter-regional ratio (non-dimensional)

k = ratio of critical gas volume to critical liquid volume

k_{s1} = geometric factor for V_{01} , dimensionless

k_{s2} = geometric factor for V_{02} , dimensionless

k_{s3} = geometric factor for V_{03} , dimensionless (and always equals 1)

M_u = Reciprocal System natural unit of momentum, stated in g x cm/sec

m = slope of line for gas specific heat, (cal/mol K)/K

m_{u_g} = Reciprocal System natural unit of mass, stated in grams

n = number of elements in liquid compound (integer)

n_a = number of atoms per molecule (integer)

n_e = number of massless, chargeless electrons *harbored* by atom (normally = 1)

n_{GTG_0} = number of thermal groups in gas (integer or half integer) at 2D gas initial point

n_{GTG_1} = number of thermal groups in gas (integer or half-integer) just *before* going to zero at 3D gas initial point or beyond

$n_{initial}$ = number of initial units (extrapolated back to 0 K) for specific heat of liquid (integer)

n_{int} = number of structural groups having *internal motion* (solid-like vibration) per molecule (integer)

n_{LTG} = number of *liquid thermal groups* per molecule (integer or half-integer)

n_P = number of units (atoms or molecules) resisting external pressure (integer, possibly half-integer)

n_{s1} = number of *close-packed* groups per molecule in the solid state (as solution in liquid) (integer)

n_{s2} = number of *close-packed* groups per molecule in the liquid state (integer)

n_{StrG} = number of liquid structural groups per molecule (integer or half-integer)

n_T = number of liquid temperature units (integer or half-integer)

n_V = number of liquid volumetric units (integer or half-integer)

n_{vap} = fraction of vapor which has *not* recondensed at temperature T

P = *external* pressure on element or compound, atm (or if in bar, P_{bar}); subscript 1, 2, ..., for sample calculations

P_0 = *internal* pressure of element or compound in solid state, in same units as P (but usually atm)

P_{0_L} = *internal* pressure of element or compound in liquid state, in same units as P (but usually atm)

$P_{0_L_{cgs}}$ = internal pressure of element or compound in liquid state, dynes/cm²

P_c = critical vapor pressure, atm (subscript has compound name; obs = observed value)

P_L, P_{LV}, P_V, P_G = pressure on gas to obtain volume equal to that of *critical* liquid, liquid-vapor aggregate, vapor, or gas, atm

P_{L_u} = Reciprocal System natural unit of pressure for liquids, stated in atm

$P_{L_u_{cgs}}$ = Reciprocal System natural unit of pressure for liquids, stated in dynes/cm²

P_{u_atm} = Reciprocal System natural unit of pressure, stated in atm

P_{u_cgs} = Reciprocal System natural unit of pressure, stated in dynes/cm²

P_{Vap} = vapor pressure, atm

P_{Vap_Yaws} = vapor pressure calculated from Yaws regression equation, atm

R = gas constant, cal/mol K

R_{atm} = gas constant, atm x cm³ / mol K

s_G = entropy of gas, cal/mol K

s_L = entropy of liquid, cal/mol K

s_{L_0} = entropy of liquid at beginning of transition to gas, cal/mol K

s_V = entropy of vapor, cal/mol K

s_u = Reciprocal System natural unit of space, stated in cm

s_{t_u} = Reciprocal System natural unit of space in the time region (solid/liquid region), stated in cm

T = temperature of liquid or vapor, K ; subscript i = initial, subscript f = final ; subscript 1, 2, ..., for sample calculations

T_B = normal boiling temperature, K

T_{bc} = beginning temperature of electrical conduction, K (semiconductors)

T_c = theoretical critical temperature of liquid, K (subscript has element or compound symbol)

T_{c_obs} = observed critical temperature of liquid, K (subscript has element or compound symbol)

t_e = atomic electric displacement (integer, dimensionless)

t_{e_mod} = atomic electric displacement as modified by passage of current (integer or half integer, dimensionless)

T_{eff} = effective temperature of solid for electrical resistivity for purposes of thermal conductivity calculation, K

T_{eff_L} = effective temperature of liquid for purposes of liquid thermal conductivity calculation, K

$T_{G_3D_0}$ = temperature of 3D gas at initial point, K (when *internal motion* reaches the three-dimensional state)

$T_{G_2D_0}$ = temperature of 2D gas at initial point, K (when *internal motion* leaves the liquid state and assumes the status of a two-dimensional gas)

$T_{G_2.5D_0}$ = temperature intermediate between $T_{G_3D_0}$ and $T_{G_2D_0}$, K

T_L = liquid end-point temperature, K

T_{L_0} = temperature of liquid at very beginning of transition to gas, K

T_m = observed melting temperature of solid aggregate, K (subscript has element or compound name)

T_{m_P} = melting temperature when external pressure of P is applied, K

T_{m_RS} = theoretical aggregate melting temperature of solid, K

T_{offset} = temperature offset in effective liquid temperature to account for thermal conductivity at T_m or T_c , K

t_p = atomic primary magnetic rotational displacement of the element (integer, dimensionless)

T_S = solid end-point temperature, K (this is usually a few percent lower than the aggregate melting point)

t_s = atomic secondary magnetic rotational displacement of the element (integer, dimensionless)

T_{SL_u} = Reciprocal System natural unit of temperature (condensed states of matter), K

T_{sc} = superconducting temperature, K (metallic elements)

V_{00} = base initial specific volume of liquid, cm^3/g

V_{01} = base initial specific volume of the solid component, cm^3/g

V_{02} = base initial specific volume of the liquid component, cm^3/g

V_{03} = base initial specific volume of the critical component, cm^3/g

V_1 = Reciprocal System theoretical specific volume increment at 0 K and that due to the solid molecules in solution of the liquid, cm^3/g

V_2 = Reciprocal System theoretical specific volume increment due to the liquid molecules of the substance, temperature above 0 K, cm^3/g

V_3 = Reciprocal System theoretical specific volume increment due to the critical (gaseous or vapor) molecules in solution of the liquid, cm^3/g

V_{c_G} = critical volume of gas, cm^3/g (subscript has compound or element symbol)

V_{c_L} = critical volume of liquid, cm^3/g (subscript has compound or element symbol)

$V_{c_L_mol}$ = critical volume of liquid, cm³/mol (subscript has compound or element symbol)

V_{c_LV} = critical volume of liquid-vapor aggregate, cm³/g (subscript has compound or element symbol)

$V_{c_LV_mol}$ = critical volume of liquid-vapor aggregate, cm³/mol (subscript has compound or element symbol)

V_{c_V} = critical volume of vapor, cm³/g (subscript has compound or element symbol)

V_G = ideal volume of gas at temperature T and pressure P, cm³/g

V_L = Reciprocal System theoretical specific volume of the liquid, cm³/g; with _P means at pressure P

V_{L_u} = Reciprocal System natural unit value of volume (not specific volume) in the time region, stated in cm³

V_{liq} = function using *Mathcad* internal programming to compute theoretical specific volume of liquid, cm³/g

V_{mol} = gram-molecular volume at standard condtions, cm³/mol

V_{mol_u} = gram-molecular volume at natural unit conditions, stated in cm³/mol

V_{molec} = volume of liquid compound or element, cm³

$V_{Peng_Robinson}$ = volume of gas calculated using Peng-Robinson regression equation, cm³/g

V_{RG} = real gas volume at temperature T and pressure P, cm³/g

$V_{V_crit_H2O}$ = specific volume of critical H2O molecules at temperature T, cm³/g

$V_{V_gas_H2O}$ = specific volume of gas water molecules at temperature T, cm³/g

V_{V_ortho} = specific single phase volume of vapor at pressure at temperature T and pressure P = 1 atm (usually), cm³/g

$V_{V_sat_H2O}$ = specific volume of saturated vapor volume (in a two-phase system), cm³/g

$V_{V_SH_H2O}$ = specific volume of superheated water vapor, cm³/g

$V_{V_SH_H2O_Al_Hamdi}$ = specific volume of superheated water vapor calculated from Al-Hamdi's regression equation, cm³/g

$V_{V_SH_sat_H2O}$ = specific vapor volume of superheated water at saturation, cm³/g

$V_{V_SH_aggr_P_0_H2O}$ = specific volume of superheated water *aggregate* at P = 0 atm, cm³/g

$V_{V_SH_aggr_P_H2O}$ = specific volume of superheated water *aggregate* at pressure P atm, cm³/g

$V_{V_simple_H2O}$ = specific volume of simple water vapor molecules (with 2-dimensions of movement), cm³/g

V_{uc} = volume of crystal unit cell, angstrom³ when s_{t_u} is expressed in angstrom³

w = atomic weight (average), subscript has element symbol or compound name

x = factor to determine heat of fusion of liquid molecules already present at melting point

x = factor used to determine fraction of vapor molecules which have *not* recondensed

x_L, x_{LV}, x_V, x_G = parameters to account for time-region attraction of 2-D gas molecules (integers or simple fractions)

y = factor to determine proportion of liquid molecules which end up contributing to vapor pressure

Z = number of atoms of element in liquid compound (integer, dimensionless)

Z = number of atoms in solid crystal unit cell (integer, dimensionless)

z_{c1} = first normal random variable used to determine proportion of critical liquid increment of liquid specific volume

z_{c2} = second normal random variable used to determine proportion of critical vapor/gas increment of liquid specific volume

z_{c3} = third normal random variable used to determine proportion of liquid molecules which end up contributing to vapor pressure

z_S = normal random variable used to determine solid increment of liquid specific volume

β = isobaric liquid volume expansivity, K^{-1}

γ_L = liquid surface tension, dynes/cm

$\gamma_{L_u_cgs}$ = Reciprocal System natural unit value of surface tension, stated in dynes/cm

η_L = liquid viscosity, cp

$\eta_{L_u_cgs}$ = Reciprocal System natural unit of liquid viscosity, stated in cp

Δh_{vap} = enthalpy of vaporization (Yaws subscript for regression equation), converted to cal/mol

Δs = specific volume increment due to solid molecules at any temperature of liquid, cm^3/g

ΔV = average specific volume difference between solid and liquid molecules, cm^3/g

κ = isothermal compressibility, atm^{-1}

κ_L = thermal conductivity of liquid, watt / cm K

κ_S = thermal conductivity of solid, watt / cm K

$\rho_{c_G_H2O}$ = density of water gas at critical point, g/cm³

ρ_L = density of liquid at temperature T, g/cm³

$\Phi_T(z_{c1})$ = normal probability distribution function of random variable z_{c1}

$\Phi_{3T}(z_{c2})$ = normal probability distribution function of random variable z_{c2}

$\Phi_m(z_s)$ = normal probability distribution function of random variable z_s ; sometimes the subscript may be omitted

$\Phi_u(z_{c3})$ = normal probability distribution function of random variable z_{c3}

Note: A black square in the upper right of an equation means that the equation is disabled from running in *Mathcad*. This is done because not all variables in the equation have, at that point in the program, been given numerical values. Because of the nature of this subject, it is necessary to use a mixture of cgs, SI, and natural units in the paper, but each individual equation utilizes just one set of units.

Reciprocal System Physical Constants (from Ref. [1]-[4] or derived therefrom)

$$l_R := 156.4444 \text{ (inter-regional ratio)} \quad s_u := 4.558816 \cdot 10^{-6} \text{ cm} \quad s_{t_u} := \frac{s_u}{l_R}$$

$$R := 1.9869 \text{ cal/mol K (gas constant)} \quad R_{\text{atm}} := 82.057 \text{ atm-cm}^3/(\text{g-K})$$

$$\text{conv}_{\text{caltoJ}} := 4.186 \quad c_{p_u} := \frac{3}{2} \cdot R \quad c_{p_u} = 2.98035 \text{ cal/mol K} \quad c_{p_u_SI} := c_{p_u} \cdot \text{conv}_{\text{caltoJ}}$$

$$\text{conv}_{\text{atmtodynescm2}} := 1.013 \cdot 10^6 \quad A_v := 6.02486 \cdot 10^{23} \quad \text{conv}_{\text{utog}} := \frac{1}{A_v} \quad \text{conv}_{\text{caltoev}} := 2.613 \cdot 10^{19}$$

$$m_{u_g} := 1.65979 \cdot 10^{-24} \text{ g} \quad T_{\text{SL}_u} := 510.8 \text{ K} \quad V_{L_u} := s_{t_u}^3 \text{ cm}^3$$

$$M_u := 4.97593 \cdot 10^{-14} \text{ g-cm/sec}$$

$$\rho_u := 25755070686.736 \text{ } \mu\text{-ohm-cm} \quad d_u := 3.359 \text{ fm} \quad T_u := 7.20423 \cdot 10^{12} \text{ K}$$

1. Liquid Specific Volume and Density

Reciprocal System

According to the Reciprocal System, each *individual* molecule of a liquid aggregate may be in the solid, liquid, or vapor/gaseous state, regardless of the state of the majority of the molecules. Furthermore, if a particular *molecule* is in the liquid state, the *individual* atoms of which it is comprised may be in the solid state *relative* to each other. The specific volume (volume/mass) of a liquid, V_L , is the sum of the contributions of the solid (V_1), liquid (V_2), and vapor/gaseous (V_3) components:

$$V_L := V_1 + V_2 + V_3 \quad \text{cm}^3/\text{g} \quad (1)$$

The *initial* values of these three components are designated V_{01} , V_{02} , V_{03} . These differ only by a geometric factor (k_{s1} , k_{s2} , k_{s3}) applied to a *base initial value*, V_{00} , determined as follows.

Just as the volume of a gas is determined by the *number of molecules*, so the volume of a liquid is determined by the *number of volumetric groups* which it contains. In an organic compound, for instance, each of the common interior groups, such as CH_2 , CH , or CO , constitutes one volumetric group. The CH_3 groups in the end positions of the aliphatic chains usually occupy two units each (although if the the H bonding to the CH_2 is very strong, it might be only one unit). So hexane, represented as $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, has 8 volumetric groups. Let n_V be the number of volumetric groups and recall that the factor .7071 expresses the geometric reduction obtained by the *close-packed* arrangement of the liquid groups because of their flexibility of movement. Then, in natural Reciprocal System units, the base initial volume is directly proportional to the number of volumetric groups, reduced by close-packing:

$$V_{00} := .7071 \cdot n_V \quad (\text{natural volume/mass units}) \quad (2)$$

In cgs units, this expression becomes

$$V_{00} := \frac{.7071 \cdot n_V \cdot V_{L_u}^{\frac{1}{3}}}{w \cdot m_{u_g}} \quad \text{cm}^3/\text{g} \quad (3a)$$

Simplifying, using functional representation and the *Mathcad* global equality operator:

$$V_{00}(n_V, w) \equiv \frac{10.54004 \cdot n_V}{w} \quad \text{cm}^3/\text{g} \quad (3b)$$

For hexane:

$$n_V := 8 \quad w_{\text{hexane}} := 86.175$$

$$V_{00_hexane} := V_{00}(n_V, w_{\text{hexane}}) \quad V_{00_hexane} = 0.97848 \quad \text{cm}^3/\text{g}$$

For the critical (vapor or gaseous) specific volume increment, the geometric factor k_{s3} is always 1.000. For the solid specific volume increment, the geometric factor k_{s1} is the cube root of .7071, .8909, where close-packing in the solid state can be achieved. Where such packing cannot be achieved the geometric factor k_{s1} is 1.000. The same applies to the geometric factor k_{s2} for the liquid specific volume increment. Note: in situations involving *hydrogen (or another lower group element) bonding*, the effective value for k_{s1} and k_{s2} may be *lower* than .8909, like .7795 for acetic acid and .8713 for water. The initial values of the three specific volume components may now be expressed as

$$V_{01}(n_V, w, n_{s1}) := V_{00}(n_V, w) \cdot k_{s1}(n_{s1}, n_V)^{\frac{1}{3}} \quad \text{cm}^3/\text{g} \quad (4)$$

$$V_{02}(n_V, w, n_{s2}) := V_{00}(n_V, w) \cdot k_{s2}(n_{s2}, n_V) \quad \text{cm}^3/\text{g} \quad (5)$$

$$V_{03}(n_V, w, k_{s3}) := V_{00}(n_V, w) \cdot k_{s3} \quad \text{cm}^3/\text{g} \quad (6)$$

In a *multi-group* molecule, the values of the geometric factors k_{s1} and k_{s2} represent *averages*, because some groups may be at .8909 while others are at 1.000. The Reciprocal System Database will allow the flexibility to designate the number of close-packed groups per molecule in the solid state, n_{s1} , and the number of close-packed groups per molecule in the liquid state, n_{s2} . Then

$$k_{s1}(n_{s1}, n_V) \equiv \left[\frac{n_{s1} \cdot .8909 + (n_V - n_{s1}) \cdot 1.000}{n_V} \right] \quad (7)$$

$$k_{s2}(n_{s2}, n_V) \equiv \left[\frac{n_{s2} \cdot .8909 + (n_V - n_{s2}) \cdot 1.000}{n_V} \right] \quad (8)$$

(Of course, if hydrogen (or another lower group element) bonding is involved, the coefficients could be lower.) For hexane, for instance, k_{s1} is .98636 (because 1 group is at .8909 and 7 groups are at 1.000) and k_{s2} is .97273 (because 2 groups are at .8909 and 6 groups are at 1.000). Therefore, for hexane, the initial values of the specific volume components are

$$n_{s1} := 1 \quad n_{s2} := 2$$

$$V_{01_hexane} := V_{00_hexane} \cdot .98636 \quad V_{01_hexane} = 0.96513 \quad \text{cm}^3/\text{g}$$

$$V_{02_hexane} := V_{00_hexane} \cdot .97273 \quad V_{02_hexane} = 0.95179 \quad \text{cm}^3/\text{g}$$

$$V_{03_hexane} := V_{00_hexane} \cdot 1.0000 \quad V_{03_hexane} = 0.97848 \quad \text{cm}^3/\text{g}$$

Now that we have the *initial* values as a function of *composition*, we can determine the values of the three components as a function of *temperature*. The solid specific volume increment not only includes the initial volume at 0 K but also a factor proportional to the number of *solid molecules* (and the difference in volume between solid and liquid) in the substance at any temperature, Δs , which can be determined by probability considerations.

$$V_{01}(n_V, w, n_{S1}) \equiv V_{00}(n_V, w) \cdot k_{S1}(n_{S1}, n_V)$$

$$V_1(n_V, w, n_{S1}, T, T_m, \Delta V) \equiv V_{01}(n_V, w, n_{S1}) + \Delta s(T, T_m, \Delta V) \quad \text{cm}^3/\text{g} \quad (9)$$

For the solid, liquid, and vapor states, the Reciprocal System uses the *normal probability distribution*; for the 3D gaseous state, the Reciprocal System, like conventional theory, uses the Maxwellian distribution.

To use the normal probability function or table we need to know the value of the applicable normal random variable, z_S . It should be proportional to the difference between the liquid temperature, T , and the melting point, T_m , both in degrees K, divided by the melting point. The coefficient and the intercept have--unfortunately--not yet been worked out theoretically, but are given empirically by Larson (Ref. [4]) as follows:

$$z_S(T, T_m) := \frac{4 \cdot (T - T_m)}{T_m} + .40 \quad (10)$$

We want the *right tail* of the normal probability distribution, so we subtract the value of the normal function, $\Phi_m(z_S)$, from 1 and then multiply by the average difference in specific volume between solid and liquid molecules, ΔV :

$$\Phi_m(T, T_m) := \text{cnorm}(z_S(T, T_m)) \quad (\text{Mathcad's cumulative normal probability function with mean} = 0 \text{ and variance} = 1) \quad (11a)$$

$$\Delta s(T, T_m, \Delta V) := (1 - \Phi_m(T, T_m)) \cdot \Delta V \quad \text{cm}^3/\text{g} \quad (11b)$$

Larson uses an average value of ΔV of .080 cm³/g for paraffin hydrocarbons (C₁₄ and below) and .084 cm³/g for paraffins above C₁₄ (rather than computing the individual values). A user of the Reciprocal System Database will be able to input the value as appropriate for each element or compound.

For hexane, let

$$T := 223.15 \quad \text{K}$$

$$T_{m_hexane} := 176.8 \quad \text{K} \quad (\text{observed value; see below for computation})$$

$$z_S(T, T_{m_hexane}) = 1.44864$$

$$\Phi_m(T, T_{m_hexane}) = 0.92628$$

$$1 - \Phi_m(T, T_{m_hexane}) = 0.07372$$

This means that 7.372 % of the molecules in the liquid hexane aggregate at 223.15 K (-50 deg. C) are actually in the solid state. Multiplying this figure by the approximate difference in specific volume between solid and liquid molecules, .080, we get

$$\Delta V := .080 \quad \text{cm}^3/\text{g}$$

$$\Delta s(T, T_{m_hexane}, \Delta V) = 0.0059 \quad \text{cm}^3/\text{g}$$

Therefore,

$$V_{1_hexane} := V_{01_hexane} + \Delta s(T, T_{m_hexane}, \Delta V) \quad V_{1_hexane} = 0.97103 \quad \text{cm}^3/\text{g}$$

And using our functional representation as a check:

$$V_1(n_V, w, n_{s1}, T, T_m, \Delta V) := V_{01}(n_V, w, n_{s1}) + \Delta s(T, T_m, \Delta V)$$

$$V_1(n_V, w_{hexane}, 1, T, T_{m_hexane}, \Delta V) = 0.97103 \quad \text{cm}^3/\text{g}$$

The thermal motion beyond the initial point of the liquid (extrapolating back to 0 K) is the *one-dimensional* equivalent of the thermal motion of a gas, and thus the volume generated is therefore *directly proportional to the temperature*, T. Let n_T be the number of *temperature units* or the temperature factor. Then

$$V_{02}(n_V, w, n_{s2}) := V_{00}(n_V, w) \cdot k_{s2}(n_{s2}, n_V)$$

$$V_2(n_V, w, n_{s2}, T, n_T) := \frac{T}{n_T \cdot T_{SL_u}} \cdot V_{02}(n_V, w, n_{s2}) \quad \blacksquare \quad (12)$$

For simple substances, $n_T = 1$. More complex or more electropositive substances have values of n_T of 2 up to 16. Hexane has a value of 1; water, 2; silver, 16. Compounds of electropositive and electronegative elements have intermediate values (some with half-integral values, which are averages), as would be expected.

For hexane: $n_T := 1$ $T = 223.15$ K (same as above)

$$V_{2_hexane} := \frac{T}{n_T \cdot T_{SL_u}} \cdot V_{02_hexane} \quad V_{2_hexane} = 0.4158 \quad \text{cm}^3/\text{g}$$

As a check: $V_2(n_V, w, n_{s2}, T, n_T) := \frac{T}{n_T \cdot T_{SL_u}} \cdot V_{02}(n_V, w, n_{s2})$

$$V_2(n_V, w_{hexane}, 2, T, n_T) = 0.4158$$

The gaseous or vapor increment of specific volume depends on the proportion of *critical molecules* existing in the aggregate at each temperature, which can be computed from probability considerations. Larson uses two random variables for this computation, both a function of the critical temperature, T_c .

$$z_{c1}(T_c, T) := \frac{9 \cdot (T_c - T)}{T_c + \frac{T_{SL_u}}{2}} \quad (13)$$

$$z_{c2}(T_c, T) := \frac{27 \cdot (T_c - T)}{T_c + \frac{T_{SL_u}}{2}} \quad (14)$$

These random variables appear to be empirical, not theoretical, but it seems evident that 9 and 27 are dimensional factors. The $9 = 3^2$ factor is for two dimensions, and $27 = 3^3$ factor is for three dimensions; therefore we may conclude that the first is for the vapor component, the second is for the gaseous component. Note: these components are still "trapped" in the liquid and do not have sufficient energy to escape into the space above the liquid; thus the normal probability distribution applies, rather than the Maxwellian.

The specific volume increment due to critical molecules in the substance is then

$$\Phi_T(T_C, T) := \text{cnorm}(z_{c1}(T_C, T)) \quad (15a)$$

$$\Phi_{3T}(T_C, T) := \text{cnorm}(z_{c2}(T_C, T)) \quad (15b)$$

$$V_3(n_V, w, T_C, T, k_{S3}) := [2 - (\Phi_T(T_C, T) + \Phi_{3T}(T_C, T))] \cdot V_{03}(n_V, w, k_{S3}) \quad (15c)$$

For hexane, at $T = 223.15$ K,

$$T_{c_hexane} := 507.43 \quad \text{K} \quad (\text{observed value; see below for computation})$$

$$\Phi_T(T_{c_hexane}, T) = 0.9996 \quad \Phi_{3T}(T_{c_hexane}, T) = 1$$

$$2 - \Phi_T(T_{c_hexane}, T) - \Phi_{3T}(T_{c_hexane}, T) = 0.0004$$

(only .04 % of the molecules are critical at $T = 223.15$ K)

$$V_{3_hexane} := [2 - (\Phi_T(T_{c_hexane}, T) + \Phi_{3T}(T_{c_hexane}, T))] \cdot V_{03_hexane} \quad \text{cm}^3/\text{g}$$

$$V_{3_hexane} = 0.00039$$

which is quite small, as would be expected at this temperature

Using our function form as a check:

$$V_3(n_V, w_{\text{hexane}}, T_{\text{c_hexane}}, T, 1) = 0.00039$$

Having calculated V_1 , V_2 , and V_3 , we now go back to Eq. (1) to get the total specific volume:

$$V_{\text{L_hexane}} := V_{1_hexane} + V_{2_hexane} + V_{3_hexane} \quad \text{cm}^3/\text{g}$$

$$V_{\text{L_hexane}} = 1.38722 \quad \text{cm}^3/\text{g}$$

Of course, the density is the inverse of the specific volume:

$$\rho_{\text{L}} := \frac{1}{V_{\text{L}}} \quad \text{g/cm}^3 \quad (16)$$

For hexane:

$$\rho_{\text{L_hexane}} := \frac{1}{V_{\text{L_hexane}}} \quad \rho_{\text{L_hexane}} = 0.72086 \quad \text{g/cm}^3$$

Yaws Regression

Yaws in Ref. [8] gives a modified form of the Rackett equation for the empirical calculation of *saturated liquid density* as a function of temperature:

$$\rho_{L_Yaws} := A \cdot B \left(1 - \frac{T}{T_c}\right)^n$$

For hexane, the table in Ref. [8] gives

$$A_{\text{hexane}} := .23242 \quad B_{\text{hexane}} := .26500 \quad n_{\text{hexane}} := .27810$$

$$\rho_{L_Yaws_hexane} := A_{\text{hexane}} \cdot B_{\text{hexane}} \left(1 - \frac{T}{T_{c_hexane}}\right)^{n_{\text{hexane}}} \quad \rho_{L_Yaws_hexane} = 0.71977 \text{ g/cm}^3$$

Let's graph the two curves for specific volume as a comparison.

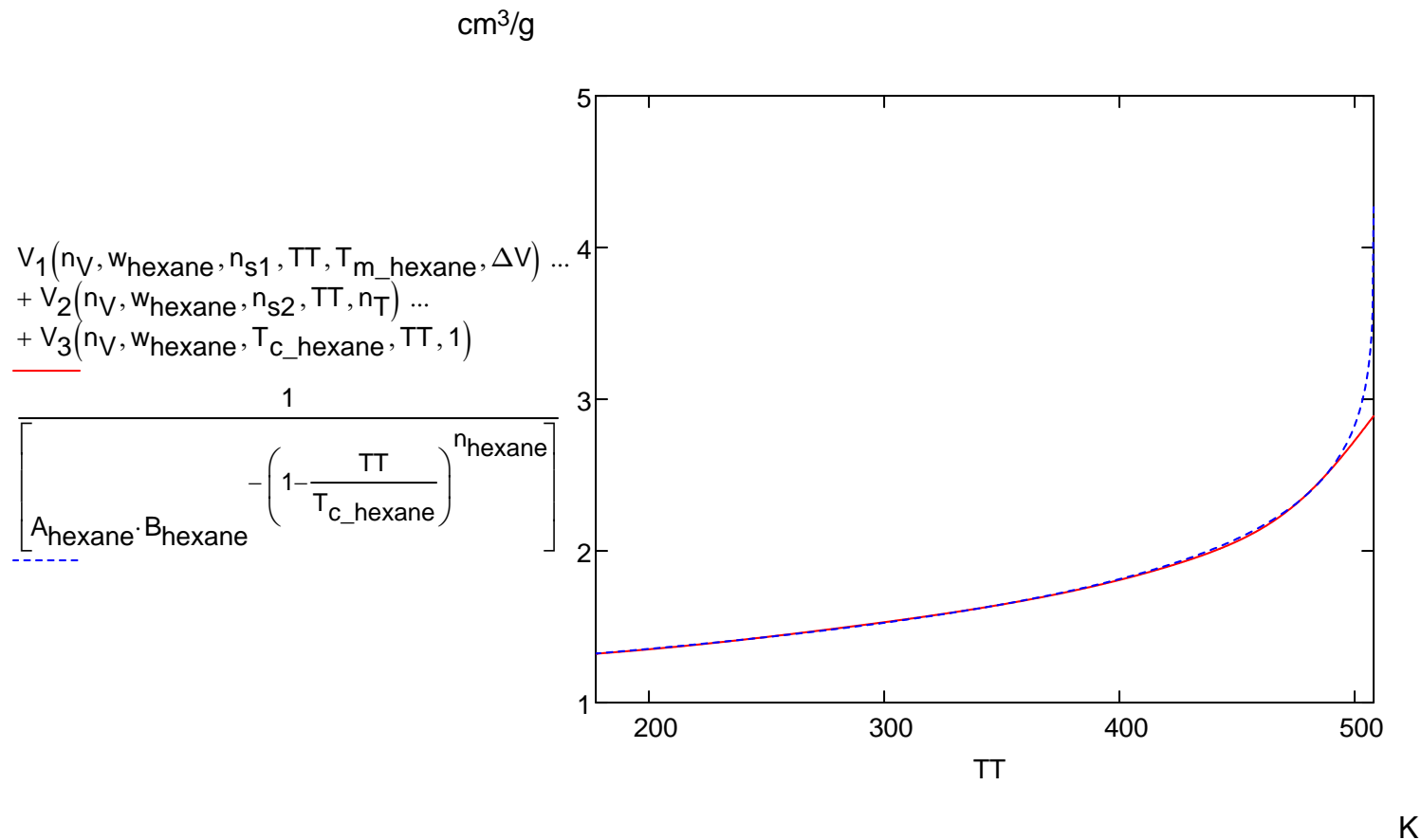


Figure 1a. Specific Volume of Liquid Hexane

There is very close agreement.

There is only approx. .1 % difference between the Reciprocal System computation and the empirically-based computation. But: the Reciprocal System provides us with a clear *theoretical* explanation, whereas the empirical expression does not. The Reciprocal System Database will make it very easy to determine the specific volume and density of any liquid at any temperature. The user will be able to enter the Yaws regression coefficients so that comparisons between the theory and the empirical data may be made.

As another example, let's consider the specific volume and density of liquid water.

Reciprocal System

$$T_{m_H2O} := 273.15 \text{ K} \quad T_{c_H2O} := 647.13 \text{ K} \quad w_{H2O} := 18.015 \quad \Delta V := 0 \quad (\text{negligible})$$

$$n_V := 1.5 \quad n_T := 2 \quad n_{s1} := 1.77 \quad n_{s2} := 1.77 \quad k_{s1}(n_{s1}, n_V) = 0.87126 \quad k_{s2}(n_{s2}, n_V) = 0.87126$$

$$k_{s3} := 1.000 \quad (\text{as usual}) \quad \text{Note: the H-bonding is the cause for non-integer values of } n_{s1} \text{ and } n_{s2}.$$

Yaws Regression

$$A_{H2O} := .34710 \quad B_{H2O} := .27400 \quad n_{H2O} := .28571$$

And here's the graph comparing the results

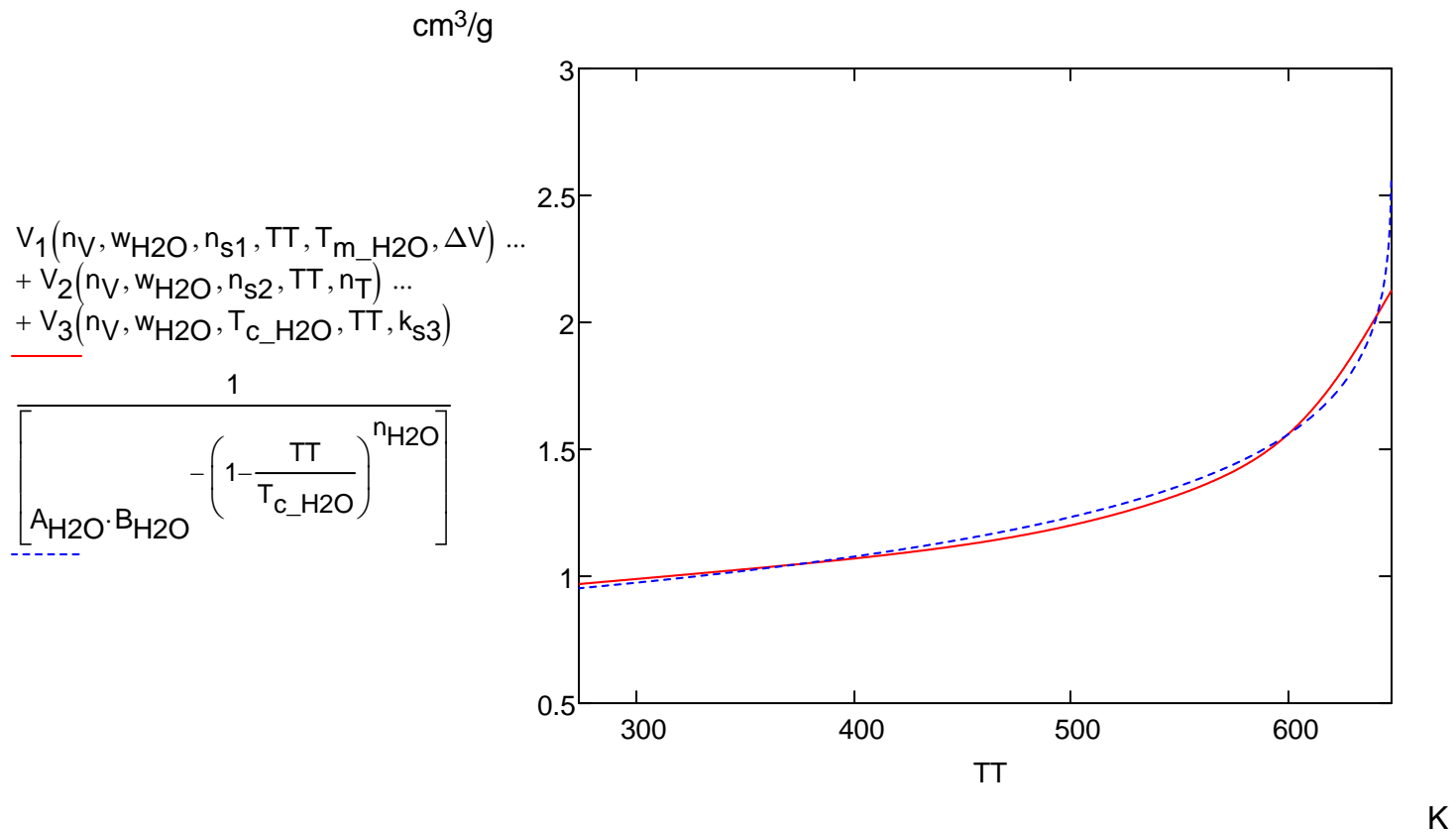


Figure 1b. Specific Volume of Liquid Water

Again, there is close agreement

Liquid Specific Volume Modified by Pressure

Reciprocal System

Liquid specific volume and density are not only a function of temperature but also of pressure. Whereas solid bonding is *three-dimensional*, liquid bonding is *two-dimensional*. For a solid under pressure (see Chapter 4 of Ref. [1]), the volume is multiplied by

$$\sqrt{\frac{P_0}{P + P_0}} \quad (\text{pressure factor for solids})$$

whereas for liquids, the volume is multiplied by the *square* of the above factor:

$$\frac{P_{0_L}}{P + P_{0_L}} \quad (\text{pressure factor for liquids})$$

where P_0 = the *internal* pressure due to *solid* chemical bonding and P_{0_L} is the *internal* pressure due to *liquid* chemical bonding. Of course, P and P_0 must be in the same units, such as atm or bars or pascals. This factor multiplies just the liquid volume component of the liquid, not the solid component and not the vapor/gaseous component. Therefore:

$$V_{L_P} := V_1 + V_2 \cdot \frac{P_{0_L}}{P + P_{0_L}} + V_3 \quad \text{cm}^3/\text{g} \quad (17)$$

The natural unit of pressure, stated in atm, in the the Reciprocal System is

$$P_{u_atm} := 15538642 \quad \text{atm}$$

To calculate the internal pressure of a solid we divide this number by the inter-regional ratio, I_R . For a liquid, we divide by the *square* of the inter-regional ratio. Because liquid cohesion is two-dimensional rather than three-dimensional we must multiply the expression by 2/3. Therefore,

$$P_{L_u} := \frac{2}{3} \cdot \frac{15538642}{I_R^2} \quad P_{L_u} = 423.25467 \quad \text{atm} \quad (18)$$

The liquid internal pressure is then P_{L_u} multiplied by the effective number of atoms or molecular groups of the molecule acting against the pressure, n_P , and divided by the ratio of the base volume to 1, raised to the 2/3 power.

$$P_{0_L} := \frac{P_{L_u} \cdot n_P}{\left(\frac{V_{00}}{1}\right)^{\frac{2}{3}}} \quad \text{atm} \quad (19)$$

(Of course, other pressure units could be used, and the Reciprocal System Database offers many choices.)

For hexane, n_P appears to have the same value as n_V (which is often the case for organic compounds), so

$$n_P := 8$$

$$P_{0_L_hexane} := \frac{P_{L_u} \cdot n_P}{\left(\frac{V_{00_hexane}}{1}\right)^{\frac{2}{3}}} \quad P_{0_L_hexane} = 3435.50915 \quad \text{atm}$$

Continuing with the above calculation for the liquid specific volume for hexane at 223.15 K and assuming an external pressure of 100 atm, we have

$$P := 100 \quad \text{atm}$$

$$V_{L_P_hexane} := V_{1_hexane} + V_{2_hexane} \cdot \frac{P_{0_L_hexane}}{P + P_{0_L_hexane}} + V_{3_hexane}$$

$$V_{L_P_hexane} = 1.37546 \text{ cm}^3/\text{g}$$

$$\rho_{L_P_hexane} := \frac{1}{V_{L_P_hexane}} \text{ g/cm}^3 \quad \rho_{L_P_hexane} = 0.72703 \quad \frac{.72703}{0.72086} = 1.00856$$

or .856 % more dense due to the external pressure of 100 atm.

Also, please note that determining the proper values of n_V , n_T , and n_P can take some practice.

In acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, the CH_3 group contributes 3 units to n_P , whereas the CO_2H group contributes 4, for a total of 7, which is considerably more than $n_V (= 4)$ here. In ethyl acetate, $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$, each volumetric group contributes a unit; $n_V = 6$ and $n_P = 6$. In water, H_2O , there are 3 molecules of 3 atoms each acting against the external pressure, for a total of $n_P = 9$, which is considerably more than $n_V (= 1.5)$ here. The Reciprocal System is a quantized theory, so only integral or half-integral values (which are averages of adjacent integers) are allowed for n_V , n_T , and n_P .

Now we can give the complete functional form for liquid volume in the Reciprocal System:

$$V_{\text{liq}}(n_V, w, n_{S1}, T, T_m, \Delta V, n_{S2}, n_T, n_P, P, T_c) := V_1(n_V, w, n_{S1}, T, T_m, \Delta V) + V_2(n_V, w, n_{S2}, T, n_T) \cdot \frac{\frac{P_{L_u} \cdot n_P}{\left(\frac{V_{00}(n_V, w)}{1}\right)^{\frac{2}{3}}}}{P + \frac{P_{L_u} \cdot n_P}{\left(\frac{V_{00}(n_V, w)}{1}\right)^{\frac{2}{3}}}} +$$

And for future use, we'll define a function to compute the fraction of critical vapor and gas molecules in the liquid at any temperature T:

$$\text{frac_VG}(T_c, T) := \begin{cases} z_1 \leftarrow \frac{9 \cdot (T_c - T)}{T_c + \frac{T_{SL_u}}{2}} \\ z_2 \leftarrow \frac{27 \cdot (T_c - T)}{T_c + \frac{T_{SL_u}}{2}} \\ \Phi_1 \leftarrow \text{cnorm}(z_1) \\ \Phi_2 \leftarrow \text{cnorm}(z_2) \\ 2 - \Phi_1 - \Phi_2 \end{cases}$$

Tait Plus Yaws Regression

Ref. [7]-[12] provide some experimental data for liquid density as a function of pressure. However, none of them provide a simple regression expression. The well-known Tait equation can, however, be used for comparison. With B_{mod} as bulk modulus and C an adjustable constant, the Tait equation can be expressed as

$$V_{\text{Tait}} := V_L \cdot \left(1 - C \cdot \log \left(\frac{B_{\text{mod}} + P}{B_{\text{mod}} + 1} \right) \right)^{\blacksquare}$$

Computation of B_{mod} is given later for hexane; the result is

$$B_{\text{mod_hexane}} := 11467.42 \quad \text{atm} \quad (\text{assumed approximately constant})$$

Now we can plot the two expressions as a function of pressure (after iterating on C).

For hexane: $n_V := 8$ $n_{S1} := 1$ $n_{S2} := 2$ $n_P := 8$ $\Delta V := .08$ $n_T := 1$ $T = 223.15$ K (same as before)

$$T_{m_hexane} = 176.8 \text{ K} \quad T_{c_hexane} = 507.43 \text{ K} \quad C := 3.2 \text{ (iterated)}$$

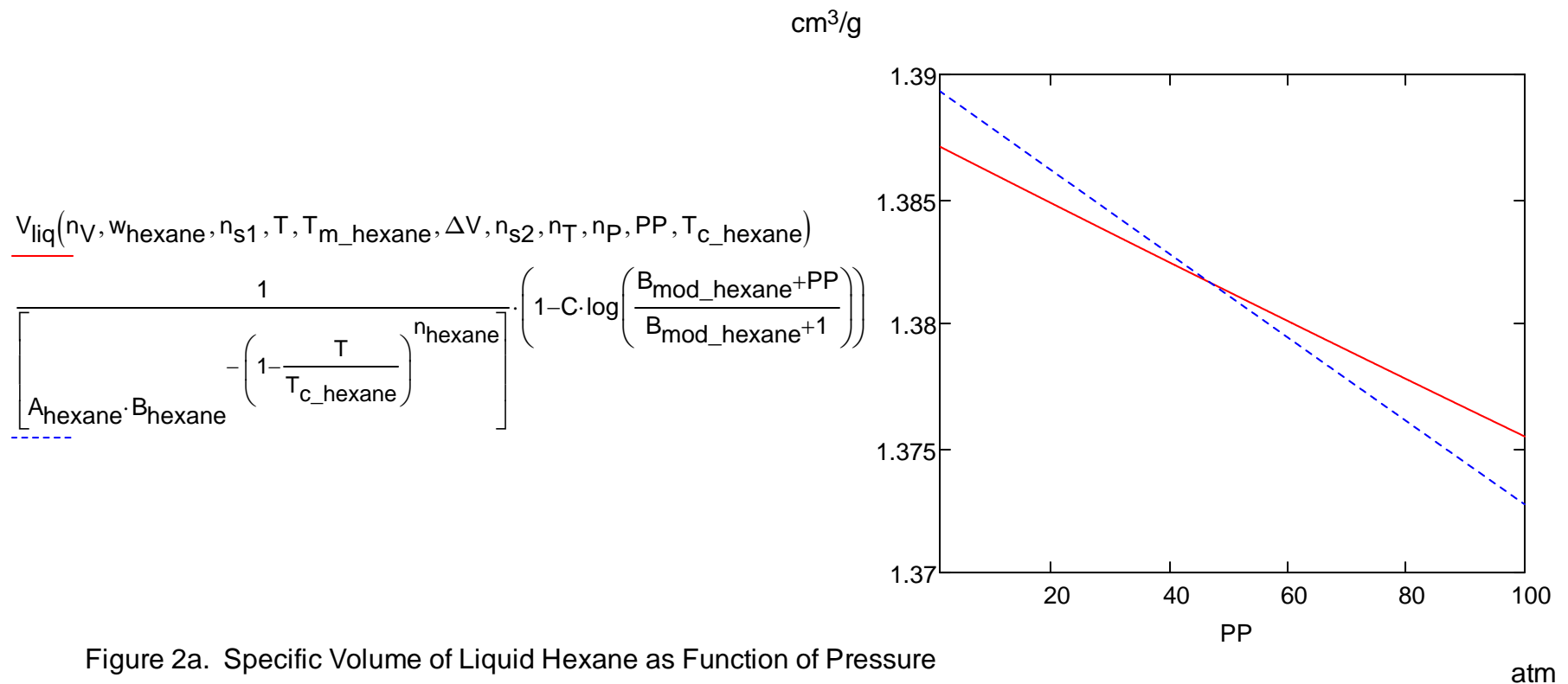


Figure 2a. Specific Volume of Liquid Hexane as Function of Pressure

Assuming that the value of C is accurate, the two curves are in close agreement.

For water: $n_V := 1.5$ $n_{S1} := 1.77$ $n_{S2} := 1.77$ $n_P := 9$ $\Delta V := 0$ $n_T := 2$ $T := 293.15$ K

$T_{m_H2O} = 273.15$ K $T_{c_H2O} = 647.13$

$B_{mod_H2O} := 19697.992$ atm (from Reciprocal System Data Base) $C := 3.2$ (Iterated)

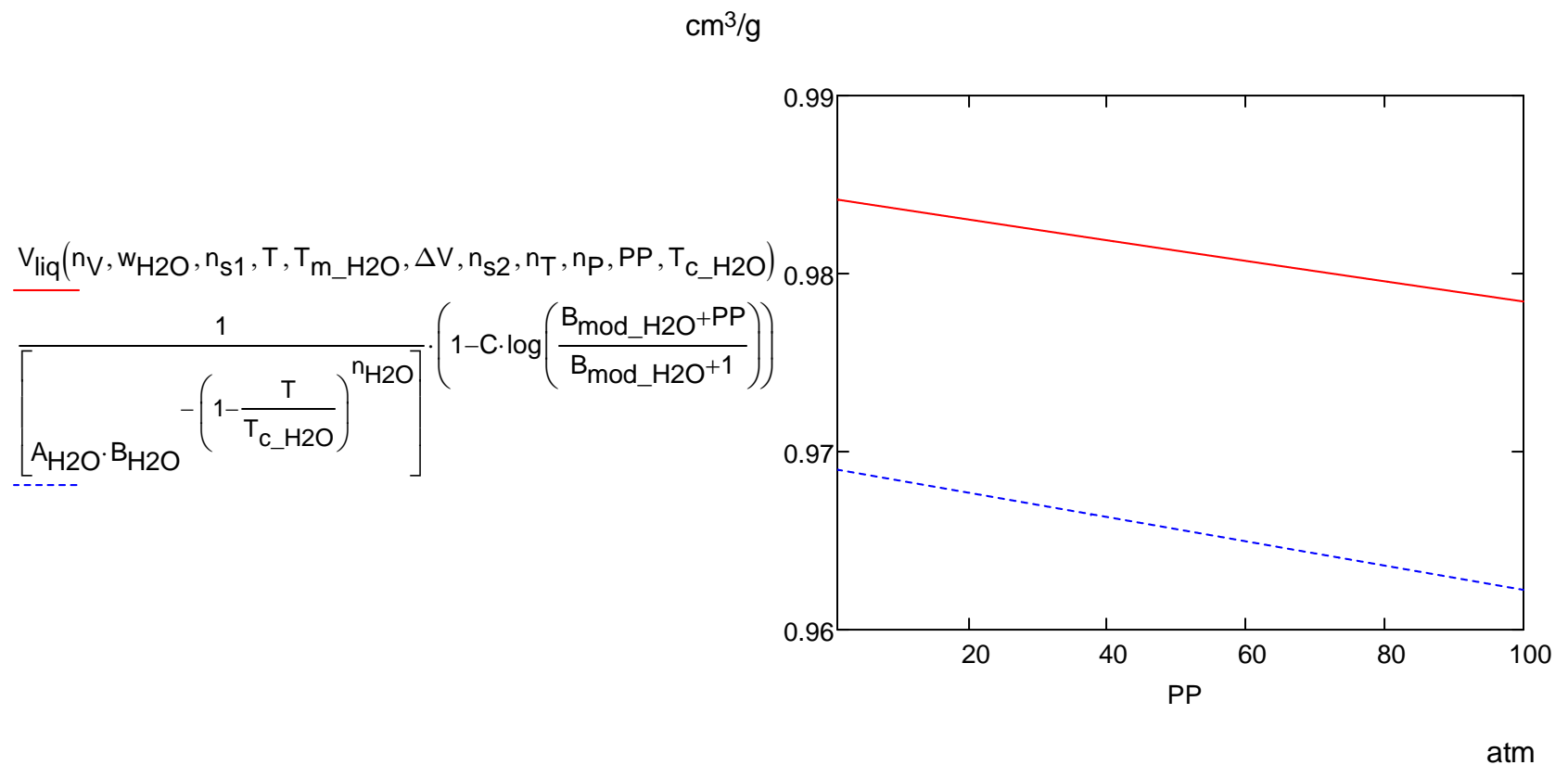


Figure 2b. Specific Volume of Liquid Water as Function of Pressure

The slopes are the same, but the regression expression starts off considerably too low--and is therefore not very accurate.

Thermodynamic Equation of State for Pure Substance

Now that we have expressions for the variation of specific volume with respect to temperature and pressure, we can make use of the standard thermodynamic equation of state for a pure substance (Ref. [12], p. 105):

$$\frac{dV}{V} := \beta \cdot dT - \kappa \cdot dP \quad (20)$$

where β is the isobaric volume expansivity and κ is the isothermal compressibility. By definition:

$$\beta := \frac{1}{V} \cdot \left(\frac{\partial}{\partial T} V \right) \quad (\text{at constant pressure}) \quad K^{-1}$$

$$\kappa := \frac{-1}{V} \cdot \left(\frac{\partial}{\partial P} V \right) \quad (\text{at constant temperature}) \quad \text{atm}^{-1}$$

Of course, the bulk modulus, B_{mod} , is the inverse of κ :

$$B_{\text{mod}} := \frac{1}{\kappa} \quad \text{atm}$$

For simplicity, we can replace the partial derivatives with a small finite difference in volumes at $T + \Delta T$ and $T - \Delta T$ K and $P + \Delta P$ and $P - \Delta P$ atm:

$$\beta := \frac{1}{V} \left(\frac{V(T + \Delta T) - V(T - \Delta T)}{2 \cdot \Delta T} \right) \quad K^{-1}$$

$$\kappa := \frac{-1}{V} \cdot \frac{(V(P + \Delta P) - V(P - \Delta P))}{2 \cdot \Delta P} \quad \text{atm}^{-1}$$

For hexane, with $\Delta T = 1$ K and $\Delta P = .1$ atm: $T := 223.15$ $P := 1$

$$T_i := T - 1 \quad T_f := T + 1 \quad P_i := P - .1 \quad P_f := P + .1 \quad (\text{but using } P = 1 \text{ for } \beta \text{ calculation})$$

$$n_V := 8 \quad n_{s1} := 1 \quad n_{s2} := 2 \quad n_p := 8 \quad \Delta V := .08 \quad n_T := 1$$

$$V_{L_hexane_i} := V_{liq}(n_V, w_{hexane}, n_{s1}, T_i, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_hexane})$$

$$V_{L_hexane_i} = 1.38548 \quad \text{cm}^3/\text{g}$$

$$V_{L_hexane_f} := V_{liq}(n_V, w_{hexane}, n_{s1}, T_f, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_hexane})$$

$$V_{L_hexane_f} = 1.38873 \quad \text{cm}^3/\text{g}$$

Therefore:

$$\beta := \frac{1}{V} \left(\frac{V(T + \Delta T) - V(T - \Delta T)}{2 \cdot \Delta T} \right)$$

$$\beta := \frac{1}{V_{L_hexane}} \cdot \frac{(V_{L_hexane_f} - V_{L_hexane_i})}{2 \cdot 1}$$

$$\beta = 0.00117 \quad \text{K}^{-1}$$

Now moving on to the calculation for κ :

$$V_{L_P_hexane_i} := V_{liq}(n_V, w_{hexane}, n_{s1}, T, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P_i, T_{c_hexane})$$

$$V_{L_P_hexane_i} = 1.38711 \quad \text{cm}^3/\text{g}$$

$$V_{L_P_hexane_f} := V_{liq}(n_V, w_{hexane}, n_{s1}, T, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P_f, T_{c_hexane})$$

$$V_{L_P_hexane_f} = 1.38709 \quad \text{cm}^3/\text{g}$$

$$\kappa := \frac{-1}{V} \cdot \frac{(V(P + \Delta P) - V(P - \Delta P))}{2 \cdot \Delta P} \quad V := \frac{V_{L_P_hexane_i} + V_{L_P_hexane_f}}{2} \quad V = 1.3871 \quad \text{cm}^3/\text{g}$$

(must use average here)

$$\kappa := \frac{-1}{V} \cdot \frac{(V_{L_P_hexane_f} - V_{L_P_hexane_i})}{2 \cdot 1}$$

$$\kappa = 0.00009 \quad \text{atm}^{-1} \quad B := \frac{1}{\kappa} \quad B = 11467.41136 \quad \text{atm}$$

Another approximate equation for β is

$$\beta := \frac{\ln\left(\frac{V_f}{V_i}\right)}{T_f - T_i} \quad \text{K}^{-1}$$

$$\beta := \frac{\ln\left(\frac{V_{L_hexane_f}}{V_{L_hexane_i}}\right)}{T_f - T_i} \quad \beta = 0.00117 \quad \text{K}^{-1} \quad (\text{same as above})$$

The Reciprocal System Database will calculate these parameters automatically.

Before moving on to the next liquid state property, specific heat, let's see if we can calculate the melting temperature and critical temperature by means of the Reciprocal System.

2. Melting Temperature and Critical Temperature

When $T = T_S$ (the solid end-point temperature), approx. 40% of the molecules of an *aggregate* are in the solid state. Therefore

$$1 - \Phi_m(z_S) := .40 \quad \Phi_m(z_S) = .60 \quad z_S := .2534$$

But:

$$z_S := \frac{4 \cdot (T_S - T_{m_RS})}{T_{m_RS}} + .4 \quad .2534 = \frac{4 \cdot (T_S - T_{m_RS})}{T_{m_RS}} + .4$$

$$T_{m_RS} := 1.038 \cdot T_S \quad (\text{but see note below--the coefficient is not always the same}) \quad (21)$$

For hexane,

$$T_{S_hexane} := 169.72 \quad \text{K} \quad (\text{from Reciprocal System Database, revised from p. 92 of Ref. [1]})$$

$$T_{m_hexane} := 1.038 \cdot T_{S_hexane} \quad T_{m_hexane} = 176.16936 \quad \text{K}$$

which is close to the measured value, 176.80 K. This shows that, for hexane, the aggregate melting point is 3.8% higher than the molecular solid end-point temperature. Also note that right at the melting point, $z_S = .4$,

$$\Phi_m(T_{m_hexane}, T_{m_hexane}) = 0.65542 \quad (1 - \Phi_m(T_{m_hexane}, T_{m_hexane})) = 0.34458$$

which means that 34.458% of the liquid aggregate is comprised of solid molecules, rather than 50%, as one might expect, at the melting point. By inspection, one can also see that the actual temperature at which 50% of the molecules are in the solid state is $.9 \times T_m$.

In order to obtain the change in melting temperature with external pressure, we simply invert the *solid state pressure factor* and use that to multiply the regular melting temperature:

$$T_{m_P} := \sqrt{\frac{P + P_0}{P_0}} \cdot T_{m_RS} \quad \text{K} \quad (22)$$

For hexane at 100 atm:

$$P := 100$$

$$P_{0_hexane} := 14000 \quad \text{atm} \quad (\text{from Reciprocal System Database for } \textit{solid} \text{ hexane})$$

$$T_{m_P_hexane} := \sqrt{\frac{P + P_{0_hexane}}{P_{0_hexane}}} \cdot T_{m_hexane}$$

$$T_{m_P_hexane} = 176.79742 \quad \text{K} \quad (\text{slightly higher than regular } T_{m_hexane})$$

For water:

$$T_{S_H2O} := 251.08 \quad \text{K} \quad (\text{from Reciprocal System Database})$$

$$T_{m_H2O} := 1.0879 \cdot T_{S_H2O} \quad T_{m_H2O} = 273.14993 \quad \text{K}$$

which is close to the measured value, 273.15 K. This shows that, for water, the aggregate melting point is 8.79% higher than the molecular solid end-point temperature. Clearly, the coefficient in Eq. (21) is *not the same for all substances*.

$$T_{m_P} := \sqrt{\frac{P + P_0}{P_0}} \cdot T_{m_RS} \quad \text{K}$$

For water at 100 atm:

$$P_{0_H2O} := 1283000 \quad \text{atm} \quad (\text{ice, not liquid water})$$

$$T_{m_P_H2O} := \sqrt{\frac{P + P_{0_H2O}}{P_{0_H2O}}} \cdot T_{m_H2O}$$

$$T_{m_P_H2O} = 273.16058 \quad \text{K} \quad (\text{just very slightly higher})$$

Larson provides a derivation of the equation for critical temperature (at which the liquid and vapor of a substance cannot be distinguished) in Ref. [3]. Generalizing his results:

$$T_{SL_u} := 510.8 \quad \text{K} \quad (\text{natural unit of temperature for solids and liquids})$$

$$T_{c_RS} := \frac{T_{SL_u} \cdot n_T}{2} \cdot \left[\left(\frac{w}{1} \right)^{\frac{1}{4}} - 1 \right] + 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w}{1}} \quad \text{K} \quad (23a)$$

(calculated critical temperature--the second component can be *plus* or *minus*--it is the *initial* contribution)

or

$$T_{c_RS} := \frac{T_{SL_u} \cdot n_T}{2} \cdot \left[\left(\frac{w}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w}{1}} \quad \text{K} \quad (23b)$$

or

$$T_{c_RS} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w}{1} \right)^{\frac{1}{4}} - 1 \right] + 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w}{1}} \quad (\text{without } n_T \text{ in first term}) \quad (23c)$$

or

$$T_{c_RS} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w}{1}} \quad (\text{without } n_T \text{ in first term}) \quad (23d)$$

For hexane, using Eq. (23b):

$$n_T = 1 \quad (\text{note: this parameter must be same as that used in Eq. (12)})$$

$$T_{c_RS_hexane} := \frac{T_{SL_u} \cdot n_T}{2} \cdot \left[\left(\frac{w_{hexane}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{hexane}}{1}} \quad T_{c_RS_hexane} = 510.90024 \quad K$$

vs. 507.43 K observed

For water, using Eq. (23a):

$$n_T := 2 \quad (\text{must be same as that used in Eq. (12)})$$

$$T_{c_RS_H2O} := \frac{T_{SL_u} \cdot n_T}{2} \cdot \left[\left(\frac{w_{H2O}}{1} \right)^{\frac{1}{4}} - 1 \right] + 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{H2O}}{1}} \quad T_{c_RS_H2O} = 654.96478 \quad K$$

vs. 647.13 K observed

The temperature factor, n_T , is zero for most of the the lower members of the various organic groups, but increases with more branching. Octane, like hexane, has a value of n_T of 1. 2-methyl heptane has a a value of 2, as does 2,2-dimethyl hexane; 2,4-dimethyl hexane has a value of 3. Both 2,2,3-tri-methyl pentane and 2,2,3,3-tetramethyl butane have values of 4. Larson, Ref. [3], p. 16.2, says "The initial levels of the benzenes are higher, ranging from 5 to 9 in the lower members of the series, and the cycloparaffins have values intermediate between those of the aromatic and aliphatic hydrocarbons. In the substituted compounds we likewise find that each family follows a definite pattern. Thus the esters, chlorides, and ethers have low initial levels, whereas the acids, alcohols and nitriles have initial levels in the same range as the benzenes. Others take the intermediate values." The Reciprocal System Database will enable entry of the observed critical temperature so as to allow comparison with that calculated from Eq. (23a) or Eq. (23b) or Eq. (23c) or Eq. (23d). For most of the following, for the purpose of comparisons, we will use the empirical values in both the Reciprocal System and the empirical regression equations.

The normal boiling point (at least for inorganic compounds) can be computed from the critical temperature, as follows (Ref. [13], p.1.233):

$$T_B := \frac{T_C}{1.64}$$

3. Liquid Specific Heat, Enthalpy, and Entropy

Specific Heat

Reciprocal System

Most liquids show a gentle rise in specific heat with temperature. In the Reciprocal System, the specific heat of each *thermal group* of the liquid molecules of the liquid aggregate is $3R + I$, where I is the initial component. This expression is *independent of temperature*. But the *internal* bonds between the atoms of a liquid molecule are like *solid* state bonds, and so these contribute a *linear temperature dependent term*. Putting all this into a functional representation, we have:

$$c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, T) := 3 \cdot R \cdot n_{\text{LTG}} + c_{p_avg_StrG} \cdot n_{\text{StrG}} \dots \\ + (3 \cdot R \cdot n_{\text{int}} + c_{p_avg_StrG} \cdot n_{\text{initial}}) \cdot \frac{T}{T_{\text{SL_u}}} \quad \text{cal/mol K} \quad (24) \\ T \leq T_c$$

Let's again work with hexane to see how this function works.

hexane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ $T = 223.15$ K

$n_{\text{LTG}} := 3$ (number of *liquid thermal groups*; the two end CH_3 groups plus the internal group of CH_2 's)

$n_{\text{StrG}} := 6$ (total number of *structural groups*, by inspection)

$c_{p_avg_StrG} := \frac{2}{3} \cdot R$ (a suitable *average* over all 6 groups)

$n_{\text{int}} := 6$ (number of *internal units*, here equal to number of structural groups)

$n_{\text{initial}} := 1$ (number of *initial units*, just 1 here)

$$c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, T) = 42.03245 \quad \text{cal/mol K}$$

$$T_{m_hexane} = 176.16936 \quad \text{K}$$

$$c_{p_m_hexane} := c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, T_{m_hexane}) \quad c_{p_m_hexane} = 38.62122 \quad \text{cal/mol K}$$

(at melting point)

Yaws Regression

Ref. [8] gives an empirical regression equation for the calculation of liquid specific heats:

$$c_{p_Yaws} := \frac{A + B \cdot T + C \cdot T^2 + D \cdot T^3}{\text{conv}_{\text{caltoJ}}} \quad \text{cal/mol K}$$

For hexane, Yaws provides these regression coefficients:

$$A_{\text{hexane}} := 78.848 \quad B_{\text{hexane}} := 8.8729 \cdot 10^{-1} \quad C_{\text{hexane}} := -2.9482 \cdot 10^{-3} \quad D_{\text{hexane}} := 4.1999 \cdot 10^{-6}$$

$$T := T_{m_hexane}$$

$$c_{p_Yaws} := \frac{A_{\text{hexane}} + B_{\text{hexane}} \cdot T + C_{\text{hexane}} \cdot T^2 + D_{\text{hexane}} \cdot T^3}{\text{conv}_{\text{caltoJ}}} \quad \text{cal/mol K}$$

$$c_{p_Yaws} = 39.80533 \quad \text{cal/mol K} \quad \text{which is close to the Reciprocal System calculation}$$

We can transform Yaws' equation into a semi-theoretical expression by utilizing the Reciprocal System natural unit values of specific heat and temperature.

$$\begin{aligned}
 A_{RS} &:= \frac{A}{c_{p_u_SI}} & B_{RS} &:= \frac{B \cdot T_{SL_u}}{c_{p_u_SI}} & C_{RS} &:= \frac{C}{c_{p_u_SI}} \cdot T_{SL_u}^2 & D_{RS} &:= \frac{D}{c_{p_u_SI}} \cdot T_{SL_u}^3 \\
 c_{p_coef}(A, B, C, D) &:= \begin{pmatrix} \frac{A}{c_{p_u_SI}} \\ \frac{B \cdot T_{SL_u}}{c_{p_u_SI}} \\ \frac{C}{c_{p_u_SI}} \cdot T_{SL_u}^2 \\ \frac{D}{c_{p_u_SI}} \cdot T_{SL_u}^3 \end{pmatrix} & & & & & & & (25)
 \end{aligned}$$

$$c_{p_coef}(A_{hexane}, B_{hexane}, C_{hexane}, D_{hexane}) = \begin{pmatrix} 6.3201 \\ 36.32871 \\ -61.6584 \\ 44.8668 \end{pmatrix}$$

$$c_{p_regr} := \frac{c_{p_u_SI}}{\text{conv}_{\text{caltoJ}}} \left[A_{RS} + B_{RS} \cdot \frac{T}{T_{SL_u}} + C_{RS} \cdot \left(\frac{T}{T_{SL_u}} \right)^2 + D_{RS} \cdot \left(\frac{T}{T_{SL_u}} \right)^3 \right] \quad (26)$$

For hexane:

$$c_{p_regr_hexane} := \frac{c_{p_u_SI}}{\text{conv}_{\text{caltoJ}}} \left[6.3201 + 36.32871 \cdot \frac{T}{T_{SL_u}} - 61.6584 \cdot \left(\frac{T}{T_{SL_u}} \right)^2 + 44.8668 \cdot \left(\frac{T}{T_{SL_u}} \right)^3 \right]$$

$$c_{p_regr_hexane} = 39.80532 \quad \text{cal/mol K} \quad \text{(same as before, as would be expected, but at least the equation is dimensionally consistent now)}$$

Note that one interpretation of the regression equation would be that the term linear in T is for the solid component of the liquid; the term with the squared value of T is for the liquid component; and the third term with the cubed value of T is for the vapor/gas component. But there is actually no *physical* support for this interpretation. So although Eq. (26) can be used in practice, Eq. (24) is the correct theoretical representation of the facts.

It seems apparent from specific heat data that $c_{p_avg_StrG}$ varies in increments of 1/6

R:

$$c_{p_avg_StrG} := \{1/6 R, 1/3 R, 1/2 R, 2/3 R, 5/6 R, R, 7/6 R, 4/3 R, 1 \ 1/2 R, 1 \ 2/3 R, 1 \ 5/6 R, 2 R, 2 \ 1/6 R, 2 \ 1/3 R, 2 \ 1/2 R\} \\ \text{cal/mol K} \quad (27)$$

The overall average of c_p per structural group should therefore be one of these values. Ref. [7], pp. 137-140, discusses the group contribution method of Missenard; but in that method the group contributions to c_p vary with temperature, whereas they do not here. The Reciprocal System Database will enable a user to enter in Yaws' regression coefficients so that the empirical value of specific heat can be calculated and compared with that calculated from the Reciprocal System. The empirical values and Missenard's values may, of course, be used to assist in determining the value of the parameters of Eq. (24)--but these parameters still must make perfect *physical* sense to be *physically* correct.

Here's the comparison graph:

$$c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, TT)$$

$$\frac{c_{p_u_SI}}{\text{conv}_{\text{caltoJ}}} \left[6.3201 + 36.32871 \cdot \frac{TT}{T_{\text{SL_u}}} - 61.6584 \left(\frac{TT}{T_{\text{SL_u}}} \right)^2 + 44.8668 \cdot \left(\frac{TT}{T_{\text{SL_u}}} \right)^3 \right]$$

cal/mol K

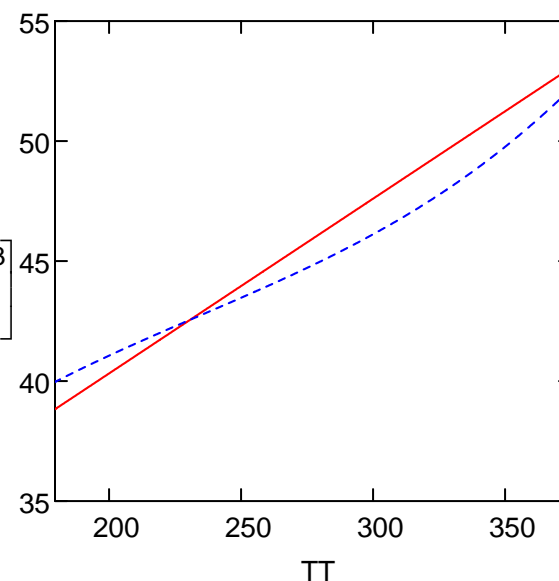


Figure 3a. Hexane Liquid Specific Heat

K

The elements are simpler than the compounds, of course. Here, if we ignore the remaining solid molecules in the liquid aggregate, the liquid specific heat is independent of temperature and is expressed as

$$c_p := 3 \cdot R + I \quad \text{cal/mol K} \quad (28)$$

where I = the initial level and may be one of these values:

$$I = \{ 0, 1/3 R, 2/3 R, R, 4/3 R, 7/3 R \} \quad (29)$$

For H, $I = 0$. For simple liquids and many of the metallic elements, $I = 4/3 R$. For the noble elements, $I = 7/3 R$. For the electronegative elements, $I = R$ or $2/3 R$ or $1/3 R$.

Where there is a non-negligible number of solid molecules in the liquid aggregate, one would have to compute an average of the solid state specific heat and the liquid state specific heat, appropriately apportioned. The Reciprocal System Database will handle this calculation automatically.

Let's repeat the above calculation for the specific heat for water.

Reciprocal System

$$T_{m_H2O} := 273.15 \quad T_{c_H2O} := 647.13 \quad n_{int} := 0 \quad n_{LTG} := 1.5 \quad c_{p_avg_StrG} := 3 \cdot R \quad n_{initial} := 0 \quad n_{StrG} := 1.5$$

$$(same\ as\ n_v) \quad c_{p_avg_StrG} = 5.9607 \quad (3R)$$

$$c_{p_m_H2O} := 3 \cdot R \cdot n_{LTG} + c_{p_avg_StrG} \cdot n_{StrG} \dots \quad c_{p_m_H2O} = 17.8821 \quad cal/mol\ K$$

$$+ (3 \cdot R \cdot n_{int} + c_{p_avg_StrG} \cdot n_{initial}) \cdot \frac{T_{m_H2O}}{T_{SL_u}}$$

$$c_{p_c_H2O} := 3 \cdot R \cdot n_{LTG} + c_{p_avg_StrG} \cdot n_{StrG} \dots \quad c_{p_c_H2O} = 17.8821 \quad cal/mol\ K$$

$$+ (3 \cdot R \cdot n_{int} + c_{p_avg_StrG} \cdot n_{initial}) \cdot \frac{T_{c_H2O}}{T_{SL_u}}$$

The same! The specific heat of liquid water is constant.

Yaws Regression

$$A_L := 92.053 \quad B_L := -3.9953 \cdot 10^{-2} \quad C_L := -2.1103 \cdot 10^{-4} \quad D_L := 5.3469 \cdot 10^{-7}$$

$$c_{p_Yaws_H2O} := \frac{A_L + (B_L) \cdot (T) + (C_L) \cdot (T)^2 + D_L \cdot (T)^3}{conv_{caltoJ}}$$

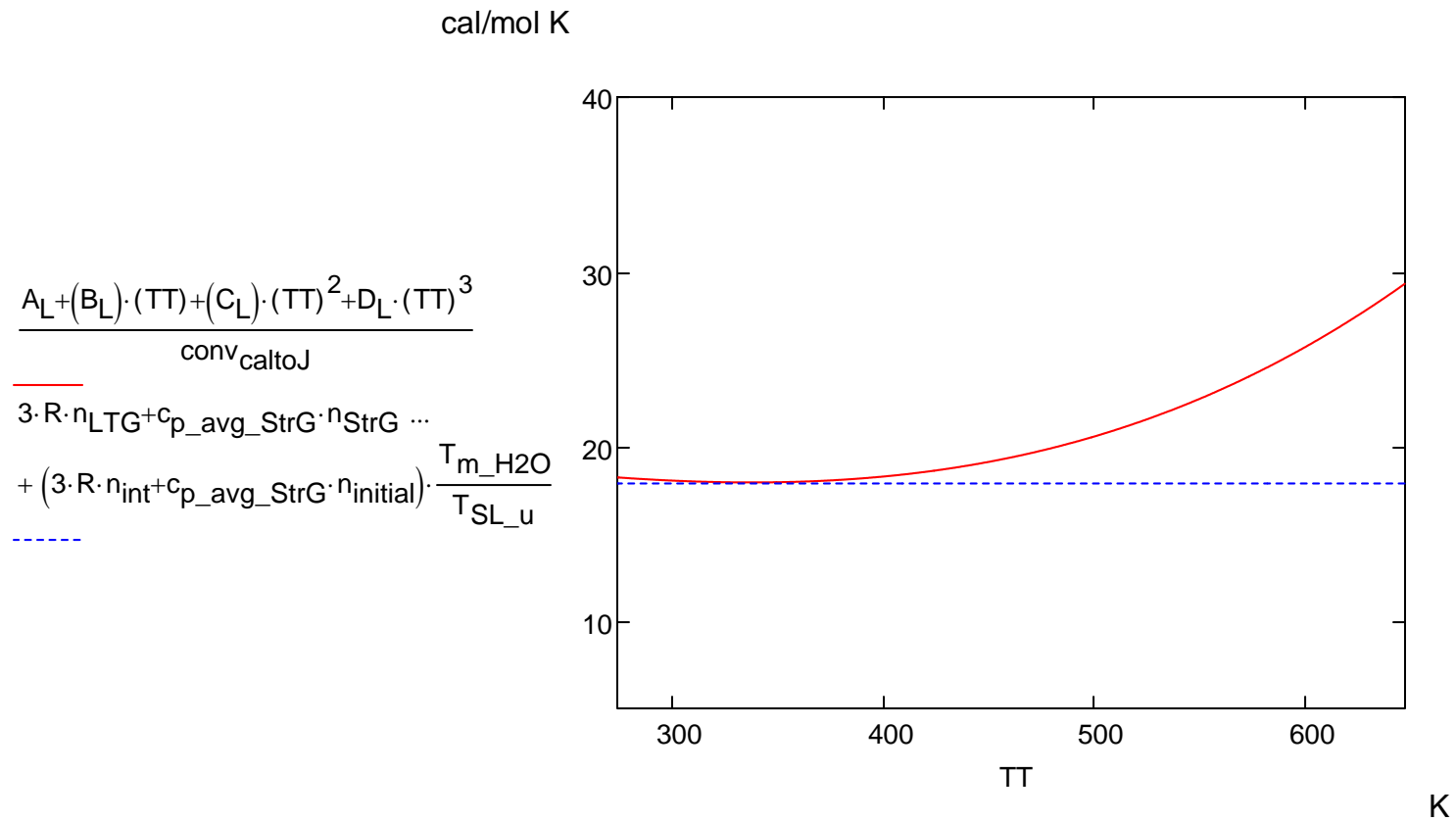


Figure 3b. Water Liquid Specific Heat

Obviously the regression expression was designed to match enthalpy, to which we turn now.

Enthalpy--General Equation

Reciprocal System

Enthalpy is defined as the integral with respect to temperature of the specific heat. Therefore, for liquids, with c_{p_m} as the specific heat of the liquid at the melting point, we have

$$h_{liq} := c_{p_m} \cdot T_m + \int_{T_m}^{T_f} \left(3 \cdot R \cdot n_{LTG} + c_{p_avg_StrG} \cdot n_{StrG} + \left(3 \cdot R \cdot n_{int} + c_{p_avg_StrG} \cdot n_{initial} \right) \cdot \frac{T}{T_{SL_u}} \right) dT \quad \text{cal/mol} \quad (30a)$$

$T_f > T_m \quad T \leq T_{SL_u}$

Carrying out the integration and converting to functional form:

$$h_{liq}(c_{p_m}, T_m, T, n_{int}, n_{LTG}, c_{p_avg_StrG}, n_{initial}, n_{StrG}) := c_{p_m} \cdot T_m + \frac{(T - T_m) \cdot \left(3 \cdot R \cdot T \cdot n_{int} + 3 \cdot R \cdot T_m \cdot n_{int} + 6 \cdot R \cdot T_{SL_u} \cdot n_{LTG} + T_m \cdot c_{p_avg_StrG} \cdot n_{initial} + 2 \cdot T_{SL_u} \cdot c_{p_avg_StrG} \cdot n_{StrG} \right)}{2 \cdot T_{SL_u}} \quad \text{cal/mol} \quad (30b)$$

Enthalpy of Fusion

If h_{S_m} is the solid state enthalpy at the melting temperature, then it's easy to see that the *true* heat (or enthalpy) of fusion is given by

$$h_{\text{fusion}} := c_{p_m} \cdot T_m - h_{S_m} \quad \text{cal/mol} \quad (31)$$

For hexane:

$$n_{\text{LTG}} := 3 \quad n_{\text{StrG}} := 6 \quad c_{p_{\text{avg_StrG}}} := \frac{2}{3} \cdot R \quad n_{\text{int}} := 6 \quad n_{\text{initial}} := 1$$

$$T_{m_{\text{hexane}}} = 176.16936 \quad \text{K} \quad (\text{calculated above})$$

$$c_{p_m_{\text{hexane}}} = 38.62122 \quad \text{cal/mol K} \quad c_{p_m_{\text{hexane}}} \cdot T_{m_{\text{hexane}}} = 6803.87621 \quad \text{cal/mol}$$

From the Reciprocal System Database:

$$h_{S_m} := 3008.724 \quad \text{cal/mol} \quad (\text{molecular, not aggregate since we want the value precisely at } T_m)$$

Then:

$$h_{\text{fusion_hexane}} := c_{p_m_{\text{hexane}}} \cdot T_{m_{\text{hexane}}} - h_{S_m}$$

$$h_{\text{fusion_hexane}} = 3795.15221 \quad \text{cal/mol} \quad (\text{true heat of fusion}) \quad h_{\text{fusion_hexane}} \cdot \text{conv}_{\text{caltoJ}} = 15886.50716$$

But the *measured* heat of fusion depends on the *proportion* of solid and liquid molecules present at the melting temperature. At the melting point, for many substances, only 34.458% of the molecules are in the *solid* state, 65.542% are *already* in the liquid state (as calculated previously for hexane). Therefore, the *actual* enthalpy of the *aggregate* at T_m is the proportional sum:

$$h_{\text{liq}_m} := .65542 \cdot c_{p_m} \cdot T_m + .34458 \cdot h_{S_m} \quad \text{cal/mol} \quad (32)$$

In order to obtain *100% liquid enthalpy* at this temperature, the following amount of heat must be added:

$$h_{\text{fusion}} := [.34458 \cdot (c_{p_m} \cdot T_m - h_{S_m})] \quad \text{cal/mol} \quad (33a)$$

$$h_{\text{fusion_SI}} := h_{\text{fusion}} \cdot \text{conv}_{\text{caltoJ}} \quad \text{J/mol} \quad (33b)$$

For hexane:

$$h_{\text{fusion_hexane}} := [.34458 \cdot (c_{p_m_hexane} \cdot T_{m_hexane} - h_{S_m})]$$

$$h_{\text{fusion_hexane}} = 1307.73355 \text{ cal/mol}$$

$$h_{\text{fusion_hexane_SI}} := h_{\text{fusion_hexane}} \cdot \text{conv}_{\text{caltoJ}}$$

$$h_{\text{fusion_hexane_SI}} = 5474.17264 \quad \text{J/mol}$$

Ref. [8], p. 143, indicates that the observed value is 13079 J/mol--which in this case is closer to the true heat of fusion.

For water:

$$h_{S_m} := 1458.720 \quad \text{cal/mol} \quad (\text{from the Reciprocal System Database})$$

$$1 - \Phi_m(T_{S_{H2O}}, T_{m_{H2O}}) = 0.46939 \quad 46.939\% \text{ solid at } T_{m_{H2O}}$$

$$h_{\text{fusion}_{H2O}} := [.46939 \cdot (c_{p_m_{H2O}} \cdot T_{m_{H2O}} - h_{S_m})]$$

$$h_{\text{fusion}_{H2O}} = 1608.02482 \quad \text{cal/mol}$$

$$h_{\text{fusion}_{H2O_SI}} := h_{\text{fusion}_{H2O}} \cdot \text{conv}_{\text{caltoJ}}$$

$$h_{\text{fusion}_{H2O_SI}} = 6731.19188 \quad \text{J/mol}$$

Ref. [8], p. 155, indicates that the observed value is 6002 J/mol. The discrepancy is understandable given the difficulty of measuring the true heat of fusion.

Ref. [7], p. 232 says flatly "It appears that there is no simple correlation between [heat of fusion] and melting point." So: there is no empirical equation with which we can use here to compare with the theory.

Now let's get back to the calculation of liquid enthalpy as a function of temperature, for hexane and water.

Enthalpy--Sample Calculations

For hexane:

Reciprocal System

$$n_{\text{LTG}} := 3 \quad n_{\text{StrG}} := 6 \quad c_{p_avg_StrG} := \frac{2}{3} \cdot R \quad n_{\text{int}} := 6 \quad n_{\text{initial}} := 1$$

$$c_{p_m_hexane} := c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, T_{m_hexane}) \quad c_{p_m_hexane} = 38.62122$$

At the critical point,

$$h_{c_hexane} := h_{\text{liq}}(c_{p_m_hexane}, T_{m_hexane}, T_{c_hexane}, n_{\text{int}}, n_{\text{LTG}}, c_{p_avg_StrG}, n_{\text{initial}}, n_{\text{StrG}}) \quad \text{cal/mol}$$

$$h_{c_hexane} = 23581.40449 \quad \text{cal/mol}$$

Yaws Regression

$$A_L := 78.848 \quad B_L := 8.8729 \cdot 10^{-1} \quad C_L := -2.9482 \cdot 10^{-3} \quad D_L := 4.1999 \cdot 10^{-6}$$

$$\Delta h_{\text{Yaws}}(A_L, B_L, C_L, D_L, T_1, T_2) := A_L \cdot (T_2 - T_1) + \left(\frac{B_L}{2}\right) \cdot (T_2^2 - T_1^2) + \left(\frac{C_L}{3}\right) \cdot (T_2^3 - T_1^3) + \left(\frac{D_L}{4}\right) \cdot (T_2^4 - T_1^4)$$

And here's the comparison graph:

$$\frac{(h_{\text{liq}}(c_{p_m_hexane}, T_{m_hexane}, TT, n_{\text{int}}, n_{\text{LTG}}, c_{p_avg_StrG}, n_{\text{initial}}, n_{\text{StrG}})) \cdot (1 - \text{frac_VG}(T_{c_hexane}, TT)) + (\text{frac_VG}(T_{c_hexane}, TT)) \cdot h_{c_he}}{\text{conv_caltoJ}} + c_{p_m_hexane} \cdot T_{m_hexane}$$

Figure 4a. Hexane Liquid Absolute Enthalpy

Let's repeat the above calculation for water.

Reciprocal System

$$T_{m_H2O} := 273.15 \quad T_{c_H2O} := 647.13 \quad n_{int} := 0 \quad n_{LTG} := 1.5 \quad c_{p_avg_StrG} := 3 \cdot R \quad n_{initial} := 0 \quad n_{StrG} := 1.5$$

$$(same\ as\ n_v) \quad c_{p_avg_StrG} = 5.9607 \quad (same\ as\ n_v)$$

$$h_{m_H2O} := h_{liq}(c_{p_m_H2O}, T_{m_H2O}, T_{m_H2O}, n_{int}, n_{LTG}, c_{p_avg_StrG}, n_{initial}, n_{StrG})$$

$$h_{m_H2O} = 4884.49561 \quad cal/mol$$

$$h_{c_H2O} := h_{liq}(c_{p_m_H2O}, T_{m_H2O}, T_{c_H2O}, n_{int}, n_{LTG}, c_{p_avg_StrG}, n_{initial}, n_{StrG}) cal/mol$$

$$h_{c_H2O} = 11572.04337 \quad cal/mol$$

Yaws Regression

$$A_L := 92.053 \quad B_L := -3.9953 \cdot 10^{-2} \quad C_L := -2.1103 \cdot 10^{-4} \quad D_L := 5.3469 \cdot 10^{-7}$$

And here's the graph comparing the two curves:

1.

1.

$$\frac{(h_{\text{liq}}(c_{p_m_H2O}, T_{m_H2O}, TT, n_{\text{int}}, n_{\text{LTG}}, c_{p_avg_StrG}, n_{\text{initial}}, n_{\text{StrG}})) \cdot (1 - \text{frac_VG}(T_{c_H2O}, TT)) + (\text{frac_VG}(T_{c_H2O}, TT)) \cdot h_{c_H2O}}{\text{conv_caltoJ}} + c_{p_m_H2O} \cdot T_{m_H2O}$$

Figure 4b. Water Liquid Absolute Enthalpy

Liquid Entropy

Reciprocal System

By definition:
$$s := s_i + \int_{T_i}^{T_f} \frac{c_p(T)}{T} dT \quad \blacksquare \quad (34a)$$

From above, we have the specific heat in functional form:

$$c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, T) := 3 \cdot R \cdot n_{\text{LTG}} + c_{p_avg_StrG} \cdot n_{\text{StrG}} \dots \\ + (3 \cdot R \cdot n_{\text{int}} + c_{p_avg_StrG} \cdot n_{\text{initial}}) \cdot \frac{T}{T_{\text{SL_u}}} \quad \text{cal/mol K}$$

$$s_L := s_{i_L} + \int_{T_i}^{T_f} \frac{3 \cdot R \cdot n_{\text{LTG}} + c_{p_avg_StrG} \cdot n_{\text{StrG}} \dots \\ + (3 \cdot R \cdot n_{\text{int}} + c_{p_avg_StrG} \cdot n_{\text{initial}}) \cdot \frac{T}{T_{\text{SL_u}}}}{T} dT \quad \blacksquare \quad (34b)$$

Carrying out the integration and putting into functional form:

$$s_L(T_i, T_f, n_{\text{LTG}}, c_{p_avg_StrG}, n_{\text{StrG}}, n_{\text{int}}, n_{\text{initial}}, s_{i_L}) := s_{i_L} + \frac{3 \cdot R \cdot T_f \cdot n_{\text{int}} - 3 \cdot R \cdot T_i \cdot n_{\text{int}} + T_f \cdot c_{p_avg_StrG} \cdot n_{\text{initial}} - T_i \cdot c_{p_avg_StrG} \cdot n_{\text{initial}}}{T_f - T_i} \quad (34c)$$

H2O

$$n_{\text{int}} := 0 \quad n_{\text{LTG}} := 1.5 \quad c_{p_avg_StrG} := 3 \cdot R \quad n_{\text{initial}} := 0 \quad n_{\text{StrG}} := 1.5$$

$$c_{p_avg_StrG} = 5.9607 \quad (3R) \quad T_i := T_{m_H2O} \quad T_f := T_{c_H2O} \quad s_{i_L} := 28.177 \quad \text{cal/mol K}$$

for absolute entropy at
 T_{m_H2O} from the Reciprocal
 System Database (includes
 entropy of fusion)

Yaws Regression

$$A_L := 92.053 \quad B_L := -3.9953 \cdot 10^{-2} \quad C_L := -2.1103 \cdot 10^{-4} \quad D_L := 5.3469 \cdot 10^{-7}$$

$$c_{p_Yaws_H2O} := \frac{A_L + (B_L) \cdot (T) + (C_L) \cdot (T)^2 + D_L \cdot (T)^3}{\text{conv}_{\text{caltoJ}}}$$

$$s_{L_Yaws}(T, A_L, B_L, C_L, D_L) := s_{i_L} + \int_{T_m}^T \frac{A_L + (B_L) \cdot (T) + (C_L) \cdot (T)^2 + D_L \cdot (T)^3}{\text{conv}_{\text{caltoJ}} \cdot T} dT$$

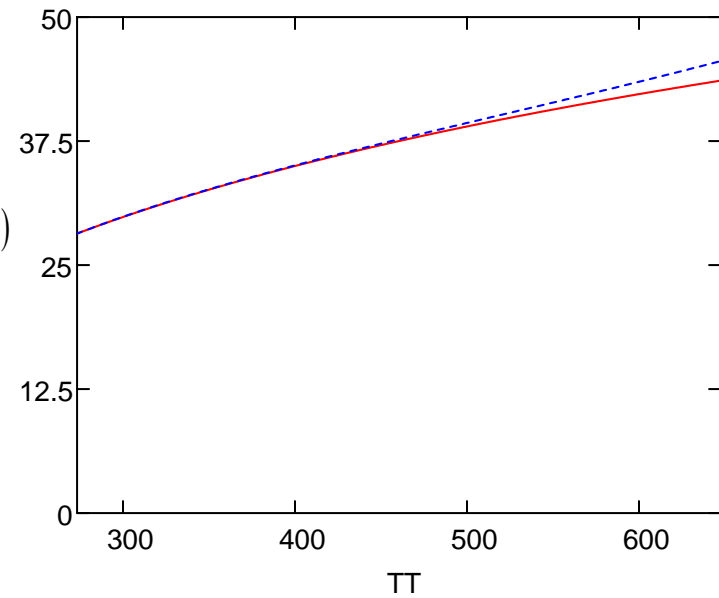
Carrying out the integration:

$$s_{L_Yaws}(T_i, T_f, A_L, B_L, C_L, D_L, s_i) := s_{i_L} + \frac{6 \cdot A_L \cdot \ln(T_f) - 6 \cdot A_L \cdot \ln(T_i) + 6 \cdot B_L \cdot T_f - 6 \cdot B_L \cdot T_i + 3 \cdot C_L \cdot T_f^2 - 3 \cdot C_L \cdot T_i^2 + 2 \cdot D}{6 \cdot \text{conv}_{\text{caltoJ}}}$$

cal/mol K

$s_L(T_i, TT, n_{LTG}, c_{p_avg_StrG}, n_{StrG}, n_{int}, n_{initial}, s_{i_L})$

$s_{L_Yaws}(T_i, TT, A_L, B_L, C_L, D_L, s_{i_L})$



K

Figure 5. Water Liquid Absolute Entropy

$$s_L(T_i, 516.35889, n_{LTG}, c_{p_avg_StrG}, n_{StrG}, n_{int}, n_{initial}, s_{i_L}) = 39.56398 \text{ cal/mol K}$$

for use for gas entropy calculation for water later.

4. Liquid Surface Tension

Reciprocal System

As stated in a previous section, the natural unit of pressure in the Reciprocal System is

$$P_{u_atm} := 15538642 \quad \text{atm}$$

Note that this is force over *two-dimensions*: it is force per unit *area*. Surface tension, by contrast, is defined as force per unit *length*: this property is therefore force over *one dimension*. The equation for it can be found by dimensionally transforming the above equation. As surface tension is commonly defined in the cgs units of dynes/cm, let's first convert the natural unit of pressure from atm to dynes/cm²:

$$P_{u_cgs} := P_{u_atm} \cdot \text{conv}_{\text{atmtodynescm2}}$$

$$P_{u_cgs} = 1.57406 \times 10^{13} \quad \text{dynes/cm}^2$$

To calculate the internal pressure of a solid we divide this number by the interregional ratio, I_R . For a liquid, we divide by the *square* of the interregional ratio. Because liquid cohesion is two-dimensional rather than three-dimensional we must multiply the expression by 2/3. Therefore,

$$P_{L_u_cgs} := \frac{2}{3} \cdot \frac{P_{u_cgs}}{I_R^2} \quad P_{L_u_cgs} = 4.28757 \times 10^8 \quad \text{dynes/cm}^2$$

The liquid internal pressure is then P_{L_u} multiplied by the effective number of atoms or molecular groups of the molecule acting against the pressure, n_p , and divided by the ratio of the base volume to 1, raised to the $2/3$ power.

$$P_{0_L_cgs} := \frac{P_{L_u_cgs} \cdot n_p}{\left(\frac{V_{00}}{1}\right)^{\frac{2}{3}}} \quad \text{dynes/cm}^2$$

In order to get the surface tension we must now transform the above equation into its *one-dimensional equivalent*. Therefore we multiply the equation for $P_{L_u_cgs}$ by the natural unit of space, s_u , and divide by another l_R , and replace the $2/3$ coefficient with $1/3$:

$$\gamma_{L_u_cgs} := \frac{1}{3} \cdot \frac{P_{u_cgs} \cdot s_u}{l_R^3} \quad \gamma_{L_u_cgs} = 6.24703 \quad \text{dynes/cm} \quad \text{(Reciprocal System natural unit of surface tension)} \quad (35)$$

Now to get the value of surface tension for a particular element or compound we must multiply the natural unit of surface tension by the number of pressure units, n_p , divide by the $1/3$ power of specific volume (not base volume) at temperature T (and dividing by 1 to make it non-dimensional), and multiply by the factor $\left(1 - \frac{T}{T_c}\right) \cdot n_T$ because the surface tension vanishes at T_c . So:

$$\gamma_L := \frac{\gamma_{L_u_cgs} \cdot n_P}{\left(\frac{V_L}{1}\right)^{\frac{1}{3}}} \cdot \left(1 - \frac{T}{T_C}\right) \cdot n_T \quad \text{dynes/cm (liquid surface tension)} \quad (36)$$

Note: n_p is the *same* as for the pressure calculations--but it is conceivable that it could change somewhat with temperature. Also note, again, that we must use V_L , not V_{00} , here. If $n_T = 0$, then that factor is not included in the equation.

For hexane:

$$n_P := 8 \quad T := 25 + 273.15 \quad T = 298.15 \quad (\text{room temperature for this calculation}) \quad \Delta V := .08$$

$$n_T := 1 \quad P := 1 \quad n_{s1} := 1 \quad n_{s2} := 2 \quad n_V := 8$$

$$V_{L_hexane} := V_{liq}(n_V, w_{hexane}, n_{s1}, T, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_hexane})$$

$$V_{L_hexane} = 1.52721 \quad \text{cm}^3/\text{g}$$

$$\gamma_{L_hexane} := \frac{\gamma_{L_u_cgs} \cdot n_P}{\left(\frac{V_{L_hexane}}{1}\right)^{\frac{1}{3}}} \cdot \left(1 - \frac{T}{T_{c_hexane}}\right) \cdot n_T \quad \gamma_{L_hexane} = 17.89843 \quad \text{dynes/cm}$$

Yaws Regression

Yaws, in Ref. [8], provides an empirical regression expression for surface tension. It is

$$\gamma_{L_Yaws} := A \cdot \left(1 - \frac{T}{T_c}\right)^n$$

For hexane, the table in Ref. [8] gives

$$A_{\text{hexane}} := 56.081 \quad n_{\text{hexane}} := 1.2843$$

$$\gamma_{L_Yaws_hexane} := A_{\text{hexane}} \cdot \left(1 - \frac{T}{T_{c_hexane}}\right)^{n_{\text{hexane}}} \quad \gamma_{L_Yaws_hexane} = 17.98092 \text{ dynes/cm}$$

This is $\frac{17.98092}{17.89843} = 1.00461$ or about .4% higher than that calculated by the Reciprocal System.

And here's the comparison graph:

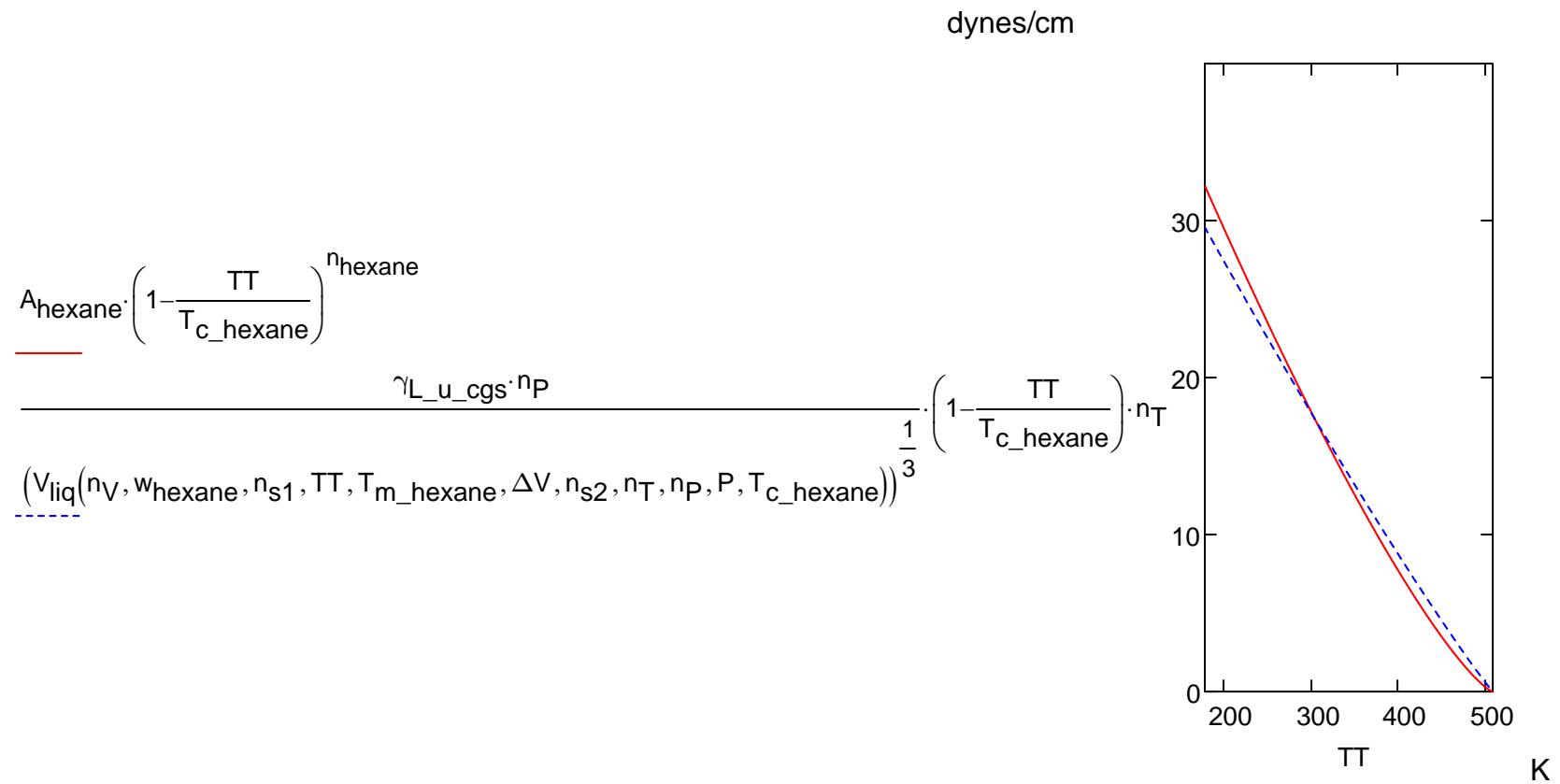


Figure 6a. Hexane Liquid Surface Tension

Hypothetically, n_p could vary with the mix of the liquid and vapor components in the liquid, but that doesn't seem to be the case here. Also, the solid molecules existing at the lower temperatures of the liquid aggregate could *raise* the surface tension somewhat, making the curves closer at the lower temperatures.

The Reciprocal System Database will handle all of these calculations for the elements and any compound entered. A user will be able to graphically compare the results from the Reciprocal System with those from the Yaws empirical regression equation. Because there is much more empirical data for surface tension than for the bulk modulus, the determination of n_p should be based on the surface tension calculation and then used for the bulk modulus calculation.

Let's repeat the calculation for the surface tension of water.

Reciprocal System

$$T_{m_H2O} := 273.15 \text{ K} \quad T_{c_H2O} := 647.13 \text{ K} \quad w_{H2O} := 18.015 \quad \Delta V := 0 \quad (\text{negligible})$$

$$n_V := 1.5 \quad n_T := 2 \quad n_{s1} := 1.77 \quad n_{s2} := 1.77 \quad P := 1 \quad n_P := 9 \quad n_{T_2} := 2.5 \quad \textit{provides much better fit--probably due to hydrogen bonding}$$

Yaws Regression

$$A_{H2O} := 132.674 \quad n_{H2O} := .9550$$

$$\frac{A_{H2O} \cdot \left(1 - \frac{TT}{T_{c_H2O}}\right)^{n_{H2O}}}{\gamma_{L_u_cgs} \cdot n_P} \cdot \frac{1}{\left(V_{liq}(n_V, w_{H2O}, n_{s1}, TT, T_{m_H2O}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_H2O})\right)^3} \cdot \left(1 - \frac{TT}{T_{c_H2O}}\right) \cdot n_T$$

$$\frac{\gamma_{L_u_cgs} \cdot n_P}{\left(V_{liq}(n_V, w_{H2O}, n_{s1}, TT, T_{m_H2O}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_H2O})\right)^3} \cdot \left(1 - \frac{TT}{T_{c_H2O}}\right) \cdot n_{T_2}$$

dynes/cm

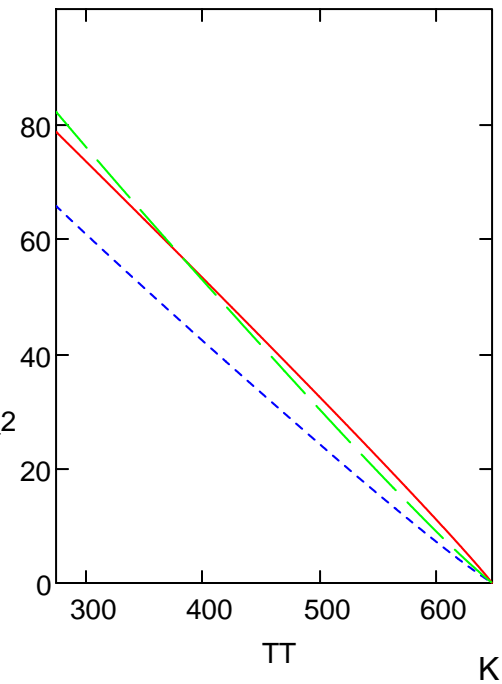


Figure 6b. Water Liquid Surface Tension

5. Liquid Viscosity

Reciprocal System

As with other properties of matter, the first step in the calculation of the viscosity of liquids is the determination of the Reciprocal System natural unit of viscosity. The usual unit of (dynamic) viscosity is the poise, with .01 of this, the cp (the centipoise) the usual unit found in the data tables of the handbooks. The poise is defined as

$$\text{poise} := \frac{\text{g}}{\text{sec} \cdot \text{cm}}$$

In Reciprocal System space-time dimensions:

$$[t^2/s^4] = [t^3/s^3] / ([t] \times [s])$$

But these are the dimensions of *momentum per area*. It's a two-dimensional property. The natural unit is then:

$$\eta_{L_u} := \frac{M_u}{s_u^2} \quad \eta_{L_u} = 0.00239 \quad \text{poise} \quad (37a)$$

However, it's more usual to use centipoise, cp, and so we will use the following:

$$\eta_{L_u_cgs} := 100 \cdot \eta_{L_u} \quad \eta_{L_u_cgs} = 0.23943 \quad \text{cp} \quad (37b)$$

Now we can express the liquid viscosity in a manner similar to that for surface tension. Of course, because the viscosity is a two-dimensional property, rather than one-dimensional, we must use the 2/3 power of specific volume, rather than the 1/3 power. And we will, of course, use the melting point, rather than the critical temperature. Therefore:

$$\eta_L := \frac{\eta_{u_cgs}}{\left(\frac{V_L}{1}\right)^{\frac{2}{3}} \cdot \left(\frac{T - T_m}{T_m}\right) \cdot n_T} \quad \text{cp} \quad (38a)$$

If we were dealing with molecules all at the same temperature and all liquid, with no solid or gas/vapor component, that equation would be correct. But actual liquid aggregates contain solid and gas/vapor molecules. The solid molecules have infinite viscosity or zero fluidity. The gas/vapor molecules have a different (lower) viscosity than the liquid and will be ignored for now. To account for the proportion of solid molecules, Eq. (38a) must be modified to

$$\eta_L := \frac{\eta_{L_u_cgs} \cdot \frac{1}{(1 - \text{frac}_S(T, T_m))}}{\left(\frac{V_L}{1}\right)^{\frac{2}{3}} \cdot \left(\frac{T - T_m}{T_m}\right) \cdot n_T} \quad \text{cp} \quad (38b)$$

where

$$\text{frac}_S(T, T_m) := \left| \begin{array}{l} z_S \leftarrow \frac{4 \cdot (T - T_m)}{T_m} + .4 \\ (1 - \Phi(z_S)) \end{array} \right. \quad (39)$$

The temperature factor in Eq. (37a/37b), $\frac{T - T_m}{T_m}$, needs some further explanation.

At the molecular level there is a sharp demarcation at T_m between solid and liquid--but not for an *aggregate*, as explained previously. At $.9 \times T_m$, not right at T_m , there are an equal number of solid and liquid molecules. So, perhaps $.9 \times T_m$ should replace T_m in the expression--however, numerical experiments show that this makes little difference in the results. Other choices have also been tested, and these also make little difference, so--until there is further clarification--we will stick with the use of T_m here. Also, note that if $n_T = 0$, then that factor is not included in the expression.

The fluidity is defined to be the reciprocal of the viscosity:

$$f_{L_u_cgs} := \frac{1}{\eta_{L_u_cgs}} \quad f_{L_u_cgs} = 4.17667 \quad \text{cp}^{-1} \quad (40)$$

$$f_L := f_{L_u_cgs} \cdot (1 - \text{frac}_S(T, T_{m_hexane})) \cdot \left(\frac{V_L}{1}\right)^{\frac{2}{3}} \cdot \left(\frac{T - T_m}{T_m}\right) \cdot n_T \quad \text{cp}^{-1} \quad (41)$$

The Reciprocal System Database will have calculations for both viscosity and fluidity.

Yaws Regression

Ref. [7], p. 470, says flatly "Many viscosity-correlating methods have been proposed, but few are predictive in nature." And it says this on p. 436: "Little theory has been shown to be applicable to estimating liquid viscosities." But Ref. [8] has, as usual, a practical regression equation:

$$\eta_{L_Yaws} := 10^{A + \frac{B}{T} + C \cdot T + D \cdot T^2} \quad \text{cp}$$

Let's compare the Reciprocal System viscosity calculation for hexane with that from Yaws. From the table in Ref. [8]:

$$A_{\text{hexane}} := -5.0715 \quad B_{\text{hexane}} := 6.5536 \cdot 10^2 \quad C_{\text{hexane}} := 1.2349 \cdot 10^{-2} \quad D_{\text{hexane}} := -1.5042 \cdot 10^{-5}$$

At $T := 298$ $n_P := 8$ $T := 25 + 273.15$ $T = 298.15$ (room temperature for this calculation) $\Delta V := .08$

$$n_T := 1 \quad P := 1 \quad n_{S1} := 1 \quad n_{S2} := 2 \quad n_V := 8$$

$$\eta_{L_hexane} := \frac{\eta_{L_u_cgs} \cdot \frac{1}{(1 - \text{frac}_S(T, T_{m_hexane}))}}{\left(\frac{V_{liq}(n_V, w_{hexane}, n_{S1}, T, T_{m_hexane}, \Delta V, n_{S2}, n_T, n_P, P, T_{c_hexane})}{1} \right)^{\frac{2}{3}} \cdot \left(\frac{T - T_{m_hexane}}{T_{m_hexane}} \right) \cdot n_T}$$

$$\eta_{L_hexane} = 0.26074 \text{ cp}$$

$$\eta_{Yaws_hexane} := 10 \left(A_{hexane} + \frac{B_{hexane}}{T} + C_{hexane} \cdot T + D_{hexane} \cdot T^2 \right)$$

$$\eta_{Yaws_hexane} = 0.29601 \text{ cp}$$

Here are the plots, assuming that external pressure is one atm: $P := 1$

Note: if $P > 1$, then viscosity would increase, as expected.

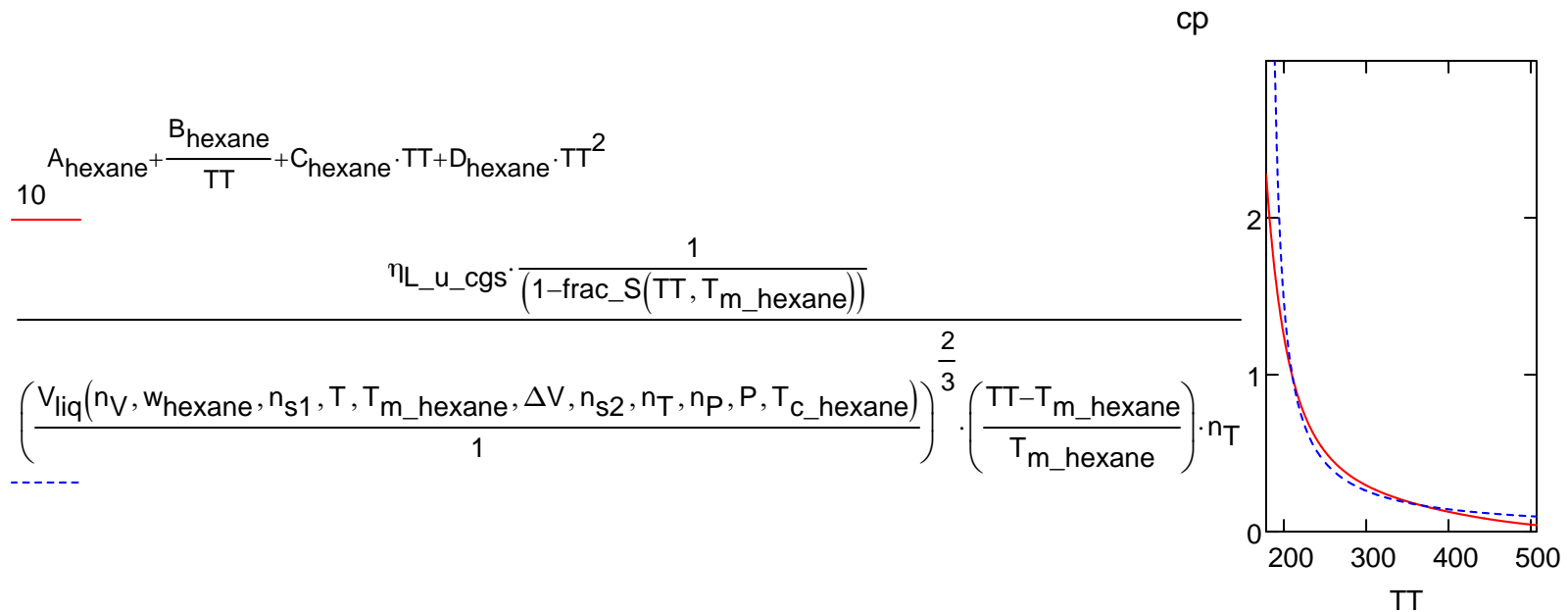


Figure 7a. Hexane Liquid Viscosity

K

Yaws says, Ref. [8], p. 478, "Very limited experimental data for liquid viscosities are available at temperatures in the region of the melting and critical point temperatures. Thus, the values in the regions of the melting and critical point temperatures should be considered rough approximations. The values in the intermediate region (above melting and below critical point) are more accurate." Obviously, the viscosity should approach infinity at the low end--so the Reciprocal System curve appears to be closer to reality here than the regression equation curve.

The Reciprocal System Database contains all of the elements and thousands of compounds. The viscosity and fluidity equations will be applied to all of them and compared with the corresponding regression equation. This will provide a thorough verification of Larson's statements (applicable to specific volume, specific heat, surface tension, and fluidity) in Ref. [14], p. 133: "...the temperature and pressure dependent properties of the fluid states of matter--liquid, vapor, and gas--are linear with respect to both temperature and pressure....In the new physical picture the deviations of the properties of an aggregate of any particular fluid state from the theoretical linear relation are due to the presence of certain specific proportions of molecules which are individually in other states. The observed non-linear curves then result from super-imposing the probability curves expressing the proportion of 'foreign' molecules upon the standard linear curves for the pure state."

Before continuing with the next liquid property, let's repeat the above calculation for water.

Reciprocal System

$$T_{m_H2O} := 273.15 \text{ K} \quad T_{c_H2O} := 647.13 \text{ K} \quad w_{H2O} := 18.015 \quad \Delta V := 0 \quad (\text{negligible})$$

$$n_V := 1.5 \quad n_T := 2 \quad n_{s1} := 1.77 \quad n_{s2} := 1.77 \quad P := 1 \quad n_P := 9$$

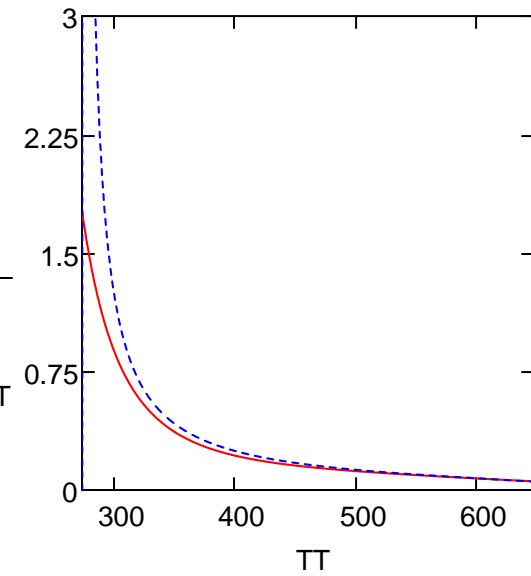
Yaws Regression

$$A_{H2O} := -10.2158 \quad B_{H2O} := 1.7925 \cdot 10^3 \quad C_{H2O} := 1.7730 \cdot 10^{-2} \quad D_{H2O} := -1.2631 \cdot 10^{-5}$$

The comparison graph follows.

cp

$$\frac{10 \cdot \left(A_{\text{H}_2\text{O}} + \frac{B_{\text{H}_2\text{O}}}{T} + C_{\text{H}_2\text{O}} \cdot T + D_{\text{H}_2\text{O}} \cdot T^2 \right)}{\eta_{\text{L_u_cgs}} \cdot \frac{1}{\left(1 - \text{frac_S}(T, T_{\text{m_H}_2\text{O}}) \right)}} \cdot \left(\frac{V_{\text{liq}}(n_{\text{V}}, w_{\text{H}_2\text{O}}, n_{\text{s1}}, T, T_{\text{m_H}_2\text{O}}, \Delta V, n_{\text{s2}}, n_{\text{T}}, n_{\text{P}}, P, T_{\text{c_H}_2\text{O}})}{1} \right)^{\frac{2}{3}} \cdot \left(\frac{T - T_{\text{m_H}_2\text{O}}}{T_{\text{m_H}_2\text{O}}} \right) \cdot n_{\text{T}}$$



K

Figure 7b. Water Liquid Viscosity

The regression equation does not go to infinity at T_m as it should.

6. Liquid Thermal Conductivity

Reciprocal System

Ref. [15] gives the author's Reciprocal System theory of electrical resistivity and conductivity for the solid state (both metallic and semiconductor), and Ref. [16] gives the author's Reciprocal System theory of thermal resistivity and conductivity for the solid state (both metallic and semiconductor). These equations can be adapted for use with liquids. But first a review:

The equation for solid thermal conductivity given in Ref. [16] is

$$\kappa_S := \frac{\frac{3}{2} \cdot (c_{p_e_mean})^2 \cdot T_{eff}}{\rho_{eff}} \quad \text{watt / cm K}$$

where $c_{p_e_mean}$ is the mean specific heat (at the mean temperature between the hot and cold sides) of the thermal electrons, T_{eff} is the effective temperature of the process, and ρ_{eff} is the effective electrical resistivity calculated at T_{eff} (not T). But, as shown in the paper,

$$c_{p_e_mean} := .5 \cdot c_{p_mean} \quad \text{eV/K}$$

This value of electron specific heat can be converted to the more usual value of cal/mol K:

$$c_{p_e_mean} := \frac{.5 \cdot c_p}{n_e \cdot Av} \quad \text{cal/mol K}$$

where c_p is the mean calculated value of specific heat for the conductor (in cal/mol K) and n_e is the number of massless, chargeless electrons per atom, normally one, and Av is Avogadro's number, of course.

For metallic elements: $T_{\text{eff}} := T + T_{\text{sc}} + 1 \text{ K}$ where T_{sc} is the superconducting temperature.

For semiconductor elements: $T_{\text{eff}} := T + T_{\text{bc}} + 1 \text{ K}$ where T_{bc} is the temperature when conduction begins.

As explained in Ref. [16], it's necessary to use the *effective* temperature for thermal conductivity, rather than T , because thermal resistance starts right after 0 K, whereas electrical resistivity starts right after T_{sc} for metallic elements, and electric current starts at T_{bc} for semiconductors.

The equation for solid state electrical resistivity, from Ref. [15], is

$$\rho_S := \rho_U \cdot \frac{(T - T_{\text{sc}})}{T_U} \cdot \frac{Z \cdot \frac{w}{1}}{V_{\text{uc}}} \cdot \frac{\frac{s_0}{s_{t_u}}}{\frac{d_{\text{atom}}}{d_U}} \cdot \frac{1}{\left[\frac{t_{e_mod}}{(t_p^2 \cdot t_s)^{\frac{1}{3}}} \right]^2} \quad \mu\text{-ohm-cm}$$

where ρ_S is solid resistivity here, not density, and Z is number of atoms in the crystal unit cell, not number of atoms in the molecule. V_{uc} is the volume of the crystal unit cell. The equation for semiconductor electrical resistivity is different, of course, but for thermal conductivity, we use the *same* expression for the semiconductor elements; see Ref. [16] for a discussion of this point.

Now, we must transform the above equation to work for liquids. Obviously, with liquids, we must replace V_{uc} with V_{molec} , the volume taken up by the molecule. Also, in a liquid, there is no preferred crystalline axis or direction, so there is no s_0/s_{t_u} term. We can generalize the above equation, as transformed, to n number of elements in a liquid compound:

$$\rho_{L_1_n} := \frac{\rho_u \cdot d_u}{\frac{V_{molec}}{(s_{t_u})^3}} \cdot \frac{1}{T_u} \cdot \sum_{i=1}^n \left[\frac{Z_i \cdot w_i \cdot (T - T_{sc_i})}{d_{atom_i}} \cdot \frac{1}{\left[\frac{t_{e_mod_i}}{(t_{p_i}^2 \cdot t_{s_i})^{\frac{1}{3}}} \right]^2} \right]^{\blacksquare} \quad (42a)$$

But, as discussed above, we must replace T with T_{eff} in order to use the expression in the thermal conductivity equation.:

$$T - T_{sc} = (T + T_{sc} + 1) - T_{sc} \quad \text{or} \quad T - T_{sc} = T + 1 \quad \text{as given above} \quad (\text{metallic elements})$$

$$T - T_{bc} = (T + T_{bc} + 1) - T_{bc} \quad \text{or} \quad T - T_{bc} = T + 1 \quad \text{as given above} \quad (\text{semiconductor elements})$$

$$\rho_{L_1_n} := \frac{\rho_u \cdot d_u}{\frac{V_{molec}}{(s_{t_u})^3}} \cdot \frac{1}{T_u} \cdot \sum_{i=1}^n \left[\frac{Z_i \cdot w_i \cdot (T + 1)}{d_{atom_i}} \cdot \frac{1}{\left[\frac{t_{e_mod_i}}{(t_{p_i}^2 \cdot t_{s_i})^{\frac{1}{3}}} \right]^2} \right]^{\blacksquare} \quad (42b)$$

In liquid thermal conduction, *not only are the massless, chargeless electrons moving from hot to cold, but so are the hot liquid atoms!* We must therefore multiply the 3/2 coefficient by 2. Also, just as in other cases when going from solid to liquid properties, we must divide by the inter-regional ratio, l_R . So:

$$\kappa_L := \frac{3 \cdot \left(\frac{.5 \cdot c_p}{n_e \cdot Av} \right)^2 \cdot T_{\text{eff_L}}}{\frac{\rho_u \cdot d_u}{\frac{V_{\text{molec}}}{(s_{t_u})^3}} \cdot \frac{l_R}{T_u} \cdot \sum_{i=1}^n \left[\frac{Z_i \cdot w_i \cdot (T+1)}{d_{\text{atom_i}}} \cdot \frac{1}{\left[\frac{t_{e_mod_i}}{(t_{p_i}^2 \cdot t_{s_i})^{\frac{1}{3}}} \right]^2} \right]} \quad \text{watt / cm K} \quad (43)$$

Another difference: liquids have a *different temperature zero point than solids*. Here, for liquid organic compounds,

$$T_{\text{eff_L_0}} := (T_c - T + T_{\text{offset}}) \cdot n_T \quad (44a)$$

where T_{offset} is necessary to account for the thermal conductivity when $T = T_c$. Eq. (43a) applies to those liquids which have thermal conductivities which *decrease* with temperature. Inorganic compounds and elements, however, have thermal conductivities which at first *increase* with temperature to a maximum and then *decrease* (usually). Here, based on numerical experiments, $T_{\text{eff_L}}$ for the first segment is given by

$$T_{\text{eff_L_1}} := (T - T_m + T_{\text{offset}}) \cdot n_T \cdot \frac{T}{T_m} \quad T \leq T_{\text{midpoint}} \quad \text{(semi-theoretical)} \quad (44b)$$

For the second segment:

$$T_{\text{eff_L_2}} := (T_c - T + T_{\text{offset}}) \cdot n_T \cdot \frac{T_c}{T} \quad T > T_{\text{midpoint}} \quad (\text{semi-theoretical}) \quad (44c)$$

Eq. (43b) and Eq. (43c) are *semi-theoretical* at this stage in the development of the theory.

The volume taken up by a liquid molecule, in cm³, can be easily calculated as follows:

$$V_{\text{molec}} := V_L \cdot w \cdot \text{conv}_{\text{utog}} \quad \text{cm}^3 \quad (45)$$

The number of volumetric units, n_V , is then simply V_{molec} divided by $s_{t_u}^3$ and rounded up or down to an integer (or half-integer in the case of H₂O).

For hexane, C_6H_{14} :

$T := 298$ K (room temperature)

$Z_C := 6$ $Z_H := 14$ $w_C := 12.011$ $w_H := 1.0079$ $Z := Z_C + Z_H$ $Z = 20$ atoms/molecule

$t_{p_H} := 2$ $t_{s_H} := 1$ $t_{e_H} := -1$ (no modification necessary)

$t_{p_C} := 2$ $t_{s_C} := 2$ $t_{e_C} := -4$ (no modification necessary)

$d_{atom_H} := 2$ fm $d_{atom_C} := 2$ fm (from Reciprocal System Database)

$n_P := 8$ $\Delta V := .08$ $n_T := 1$ $P := 1$ $n_{s1} := 1$ $n_{s2} := 2$ $n_V := 8$

$n_{LTG} := 3$ $n_{StrG} := 6$ $c_{p_avg_StrG} := \frac{2}{3} \cdot R$ $n_{int} := 6$ $n_{initial} := 1$

$V_{L_hexane} := V_{liq}(n_V, w_{hexane}, n_{s1}, T, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P, T_{C_hexane})$

$V_{L_hexane} = 1.5269$ cm³/g

$w_{hexane} := 86.175$ $V_{molec} := V_{L_hexane} \cdot w_{hexane} \cdot conv_{utog}$ $V_{molec} = 0$ cm³

$\frac{V_{molec}}{s_{t_u}^3} = 8.8261$ (rounded down, it's clearly 8 volumetric units, verifying previous assertion that $n_V = 8$)

$$\rho_{L_hexane} := \frac{\rho_u \cdot d_u}{\left[\frac{V_{molec}}{(s_{t_u})^3} \right]} \cdot \frac{1}{T_u} \cdot \frac{1}{l_R} \cdot \left[\frac{Z_C \cdot w_C \cdot (T+1)}{d_{atom_C}} \cdot \frac{1}{\left[\frac{t_{e_C}}{\left(t_{p_C}^2 \cdot t_{s_C} \right)^{\frac{1}{3}}} \right]^2} + \frac{Z_H \cdot w_H \cdot (T+1)}{d_{atom_H}} \cdot \frac{1}{\left[\frac{t_{e_H}}{\left(t_{p_H}^2 \cdot t_{s_H} \right)^{\frac{1}{3}}} \right]^2} \right] \cdot 10^{-6}$$

$$\rho_{L_hexane} = 6.965355 \times 10^{-8} \quad \text{ohm-cm} \quad (\text{note: must use ohm-cm here, rather than } \mu\text{-ohm-cm})$$

(This is the *effective* electrical resistivity for use in the thermal conductivity expression, not the *actual* electrical resistivity at T.)

Now the specific heat must be expressed in eV/electron or eV/atom. In this molecule

$$n_{e_hexane} := Z \quad n_{e_hexane} = 20 \quad \text{assuming one massless, chargeless electron per atom} \quad n_T := 1$$

$$c_{p_e} := c_p(n_{LTG}, n_{StrG}, c_{p_avg_StrG}, n_{int}, n_{initial}, T) \cdot \frac{\text{conv}_{caltoev}}{n_{e_hexane} \cdot A_v} \cdot .5 \quad c_{p_e} = 0.000051 \quad \text{V/K}$$

$$T_{offset} := 44 \quad \text{K} \quad (\text{from iteration to obtain the correct thermal conductivity at } T_c, \text{ based on the gas calculation, to be given later})$$

$$T_{eff_L} := T_{c_hexane} - T + T_{offset} \quad T_{eff_L} = 253.43 \quad (\text{using Eq. (43a) because hexane is an organic compound})$$

$$\kappa_{L_hexane} := \frac{3 \cdot c_{p_e}^2 \cdot (T_{eff_L})}{\rho_u \cdot d_u} \cdot \frac{1}{T_u} \cdot I_R \cdot \left[\frac{Z_C \cdot w_C}{d_{ato}} \right]$$

$$\left[\frac{V_{liq}(n_V, w_{hexane}, n_{s1}, T, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_hexane}) \cdot w_{hexane} \cdot conv_{utog}}{(s_{t_u})^3} \right]$$

$$\kappa_{L_hexane} = 0.00118 \text{ watt / cm K}$$

Yaws Regression

Yaws (Ref. [8], p. 531) gives the empirical regression equation for thermal conductivity for organic compounds, with the coefficients for hexane, as follows:

$$A_{hexane} := -1.8389 \quad B_{hexane} := 1.1860 \quad C_{hexane} := 507.43 \quad (\text{which is the same as } T_c)$$

$$\kappa_{L_Yaws_hexane} := \frac{10}{100} \frac{A_{hexane} + B_{hexane} \cdot \left(1 - \frac{T}{C_{hexane}}\right)^{\frac{2}{7}}}{100} \quad \kappa_{L_Yaws_hexane} = 0.00120818 \text{ watt / cm K}$$

$$\frac{\kappa_{L_hexane}}{\kappa_{L_Yaws_hexane}} = 0.97777 \quad \text{so about a 2\% difference, which is within the experimental error}$$

Now let's plot the two equations:

$$\frac{A_{\text{hexane}} + B_{\text{hexane}} \cdot \left(1 - \frac{T}{C_{\text{hexane}}}\right)^{\frac{2}{7}}}{100}$$

$$\frac{3 \cdot \left(c_p(n_{\text{LTG}}, n_{\text{StrG}}, c_{p_avg_StrG}, n_{\text{int}}, n_{\text{initial}}, T) \cdot \frac{\text{conv}_{\text{caltoev}}}{n_{e_hexane} \cdot Av} \cdot 5 \right)^2 \cdot (T_{c_hexane} - T + T_{\text{offset}}) \cdot n_T}{\rho_u \cdot d_u}$$

$$\left[\frac{V_{\text{liq}}(n_V, w_{\text{hexane}}, n_{s1}, T, T_{m_hexane}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_hexane}) \cdot w_{\text{hexane}} \cdot \text{conv}_{\text{utog}}}{(s_{t_u})^3} \right] \cdot \frac{1}{T_u} \cdot I_R \cdot \left[\frac{Z_C \cdot w_C \cdot (T+1)}{d_{\text{atom_C}}} \cdot \frac{1}{\left[\frac{t_{e_C}}{(t_{p_C}^2 \cdot t_{s_C})^{\frac{1}{3}}} \right]^2} \right]^{\frac{Z_t}{2}}$$

Figure 8a. Hexane Liquid Thermal Conductivity

The results are remarkably close.

Now we'll do an element, mercury, Hg.

Reciprocal System

$$Z_{\text{Hg}} := 1 \quad w_{\text{Hg}} := 200.59$$

$$t_{\text{p_Hg}} := 4 \quad t_{\text{s_Hg}} := 4 \quad t_{\text{e_Hg}} := -6 \quad (\text{no modification})$$

$$d_{\text{atom_Hg}} := 5.830 \quad \text{fm} \quad (\text{from Reciprocal System Database})$$

V_{uc} must be replaced by the volume of the molecule in cm^3

$$T_{\text{m_Hg}} := 234.26 \quad T_{\text{c_Hg}} := 1735 \quad \text{K} \quad (\text{from Yaws}) \quad T = 298 \quad \text{K} \quad P := 1$$

$$n_{\text{V}} := 1 \quad n_{\text{s1}} := 1 \quad n_{\text{s2}} := 1 \quad \Delta V := 0 \quad (\text{assumed}) \quad n_{\text{P}} := 1 \quad n_{\text{T}} := 2 \quad (\text{see below})$$

$$V_{\text{L_Hg}} := V_{\text{liq}}(n_{\text{V}}, w_{\text{Hg}}, n_{\text{s1}}, T, T_{\text{m_Hg}}, \Delta V, n_{\text{s2}}, n_{\text{T}}, n_{\text{P}}, P, T_{\text{c_Hg}})$$

$$V_{\text{L_Hg}} = 0.06046 \quad \text{cm}^3/\text{g}$$

$$V_{\text{Hg_molec}} := V_{\text{L_Hg}} \cdot w_{\text{Hg}} \cdot \text{conv}_{\text{utog}} \quad V_{\text{Hg_molec}} = 0 \quad \text{cm}^3$$

$$\frac{V_{\text{Hg_molec}}}{s_{\text{t_u}}^3} = 0.81354 \quad \text{rounded up, it's clearly 1 volumetric unit}$$

$$T_{c_RS_Hg} := \frac{T_{SL_u} \cdot n_T}{2} \cdot \left[\left(\frac{w_{Hg}}{1} \right)^{\frac{1}{4}} - 1 \right] + 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{Hg}}{1}} \quad T_{c_RS_Hg} = 1421.71712 \quad K$$

(This is rather low compared with that observed--so we'll use the observed value, pending clarification.)

$$\rho_{L_Hg} := \frac{\rho_u \cdot d_u}{\left[\frac{V_{Hg_molec}}{(s_{t_u})^3} \right]} \cdot \frac{1}{T_u} \cdot \frac{1}{lR} \cdot \left[\frac{Z_{Hg} \cdot w_{Hg} \cdot (T + 1)}{d_{atom_Hg}} \cdot \frac{1}{\left[\frac{t_{e_Hg}}{\left(t_{p_Hg}^2 \cdot t_{s_Hg} \right)^{\frac{1}{3}}} \right]^2} \right] \cdot 10^{-6} \quad \text{ohm-cm}$$

$$\rho_{L_Hg} = 4.313974 \times 10^{-7} \quad \text{ohm-cm} \quad (\text{note--must use ohm-cm here, rather than } \mu\text{-ohm-cm})$$

(This is the *effective* electrical resistivity for use in the thermal conductivity expression, not the actual electrical resistivity at T.)

Now the specific heat must be expressed in eV/electron K and eV/atom K. For this atom,

$$n_{e_Hg} := Z_{Hg} \quad n_{e_Hg} = 1 \quad \text{one massless, chargeless electron per atom of Hg}$$

The liquid specific heat for elements is basically constant. For Hg, the value is:

$$c_{p_Hg} := 3 \cdot R + \frac{1}{3} \cdot R \quad c_{p_Hg} = 6.623 \quad \text{cal/mol K}$$

$$c_{p_e} := c_{p_Hg} \cdot \frac{\text{conv}_{\text{caltoev}}}{n_{e_Hg} \cdot Av} \cdot .5 \quad \text{V/K}$$

$$c_{p_e} = 0.000144 \quad \text{V/K}$$

$$T_{\text{offset}} := 5400 \quad (\text{based on graph below})$$

$$T_{\text{eff_L}} := (T - T_{m_Hg} + T_{\text{offset}}) \cdot n_T \quad (\text{the alternative equation for } T_{\text{eff}}, \text{ because thermal conductivity increases with } T)$$

$$\kappa_{L_Hg} := \frac{3 \cdot c_{p_e}^2 \cdot (T_{\text{eff_L}}) \cdot \frac{T}{T_{m_Hg}}}{\rho_u \cdot d_u} \cdot \frac{1}{T_u} \cdot lR \cdot \left[\frac{Z_{Hg} \cdot w_{Hg} \cdot (T + 1)}{d_{\text{atom_Hg}}} \cdot \frac{1}{\left[\frac{t_{e_Hg}}{(t_{p_Hg})^2 \cdot t_s} \right]} \right]$$

$$\kappa_{L_Hg} = 0.08147 \quad \text{watt / cm K}$$

Yaws Regression

$$A_{\text{Hg}} := .9230 \quad B_{\text{Hg}} := 2.8887 \cdot 10^{-2} \quad C_{\text{Hg}} := -1.5499 \cdot 10^{-5}$$

$$\kappa_{\text{L_Yaws_Hg}} := (A_{\text{Hg}} + B_{\text{Hg}} \cdot T + C_{\text{Hg}} \cdot T^2) \cdot .01 \quad \kappa_{\text{L_Yaws_Hg}} = 0.08155 \quad \text{watt / cm K}$$

$$\frac{\kappa_{\text{L_Hg}}}{\kappa_{\text{L_Yaws_Hg}}} = 0.99902$$

Now let's plot the comparison graph:

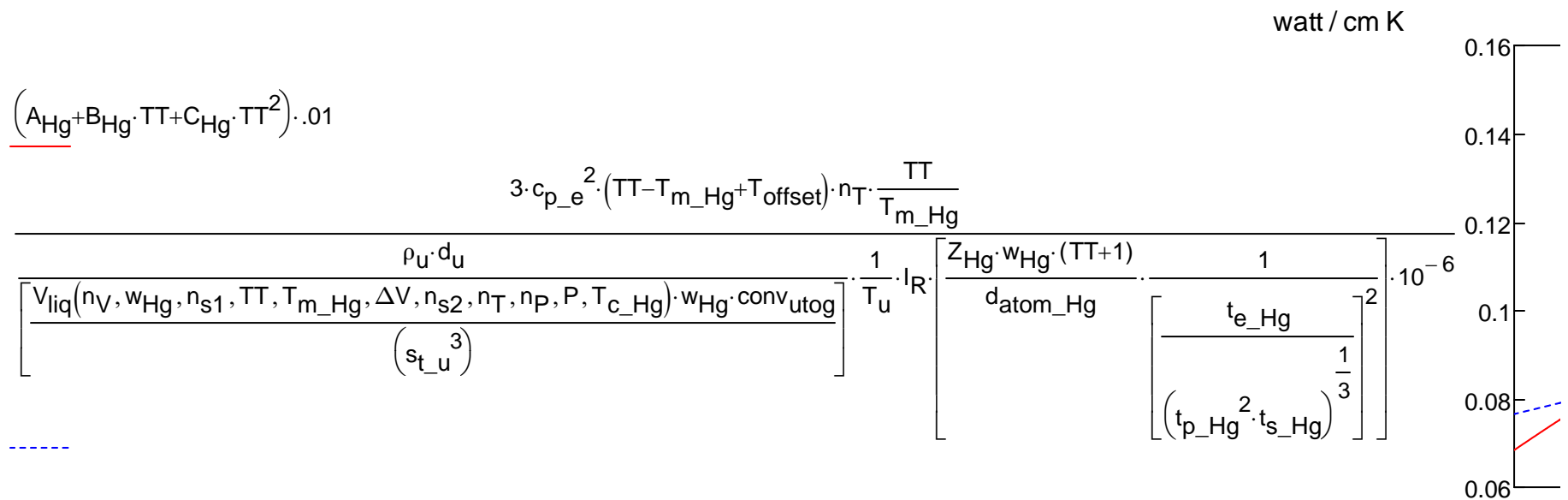


Figure 8b. Mercury Liquid Thermal Conductivity (tentative)--Up to Midpoint

Now we plot the thermal conductivity after the midpoint, using Eq. (43c) for T_{eff} .

watt / cm K

$T_{\text{offset}} := 12000$ (not the same as for the first segment)

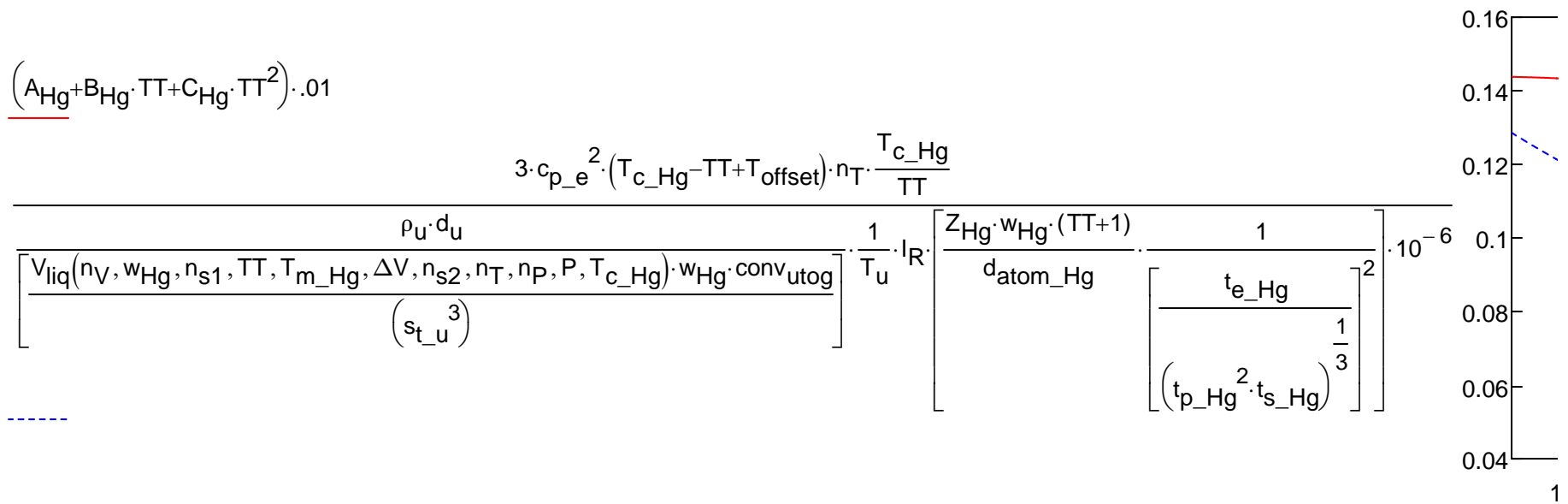


Figure 8c. Mercury Liquid Thermal Conductivity (tentative)--From Midpoint

All liquid properties in the Reciprocal System are essentially linear, up or down, with temperature--thus there *cannot* be any quadratic curve with T.

Yaws himself says (Ref. [8], p. 531), "Very limited experimental data for liquid thermal conductivities are available at temperatures in the region of the melting point. Also, there are very few reliable data at temperatures above a reduced temperature of $T_r = 0.65$. [$T_r = T/T_c$] Thus, the values in the regions of the melting point and reduced temperatures above 0.65 should be considered rough approximations. The values in the intermediate region (above melting point and below reduced temperature of 0.65) are more accurate." There is certainly a divergence between the Reciprocal System calculation and the empirical regression equation for $T_r > .65$.

The equations for liquid thermal conductivity will be thoroughly tested using the Reciprocal System Database. It's possible that n_T changes with temperature past the midpoint--which accounts for the use of the ratio T/T_c for the second segment.

The electrical resistivity and conductivity could be calculated for liquids, with the equations given above, but there is relatively little experimental data for electrical resistivity and conductivity compared with that for thermal resistivity and conductivity, so we will leave that for later work.

We'll do one more liquid thermal conductivity calculation--for water.

Reciprocal System

$$Z_H := 2 \quad Z_O := 1 \quad w_H = 1.0079 \quad w_O := 15.9994 \quad n_{e_H2O} := 3 \quad (\text{one per atom})$$

$$t_{p_H} := 2 \quad t_{s_H} := 1 \quad t_{e_H} := -1 \quad (\text{no modification})$$

$$t_{p_O} := 2 \quad t_{s_O} := 2 \quad t_{e_O} := -2$$

$$d_{\text{atom_H}} := 2 \quad d_{\text{atom_O}} := 2 \quad \text{fm} \quad (\text{from Reciprocal System Database})$$

$$T_{m_H2O} = 273.15 \quad T_{c_H2O} = 647.13 \text{ K} \quad T = 298 \text{ K} \quad P := 1$$

$$n_V := 1.5 \quad n_{s1} := 1.77 \quad n_{s2} := 1.77 \quad \Delta V := 0 \quad (\text{assumed}) \quad n_P := 9 \quad n_T := 2$$

$$n_{\text{int}} := 0 \quad n_{\text{LTG}} := 1.5 \quad c_{p_avg_StrG} := 3 \cdot R \quad c_{p_avg_StrG} = 5.9607 \quad n_{\text{initial}} := 0 \quad n_{\text{StrG}} := 1.5$$

$$V_{L_H2O} := V_{\text{liq}}(n_V, w_{H2O}, n_{s1}, T, T_{m_H2O}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_H2O})$$

$$V_{L_H2O} = 0.98783 \quad \text{cm}^3/\text{g}$$

$$V_{H2O_molec} := V_{L_H2O} \cdot w_{H2O} \cdot \text{conv}_{\text{utog}} \quad V_{H2O_molec} = 0 \quad \text{cm}^3$$

$$\frac{V_{H2O_molec}}{s_{t_u}^3} = 1.19369 \quad \text{slightly rounded up, it's clearly 1.5 volumetric unit, as asserted previously}$$

$$T_{\text{offset}} := 200 \quad (\text{by iteration with graph below})$$

Yaws Regression

$$A_{H2O} := -.2758 \quad B_{H2O} := 4.6120 \cdot 10^{-3} \quad C_{H2O} := -5.5391 \cdot 10^{-6}$$

The graph comparing the two curves follows.

$$\left(A_{H_2O} + B_{H_2O} \cdot TT + C_{H_2O} \cdot TT^2 \right) \cdot .01$$

$$\frac{3 \cdot \left(c_p(n_{LTG}, n_{StrG}, c_{p_avg_StrG}, n_{int}, n_{initial}, TT) \cdot \frac{conv_{caltoev}}{n_{e_H_2O} \cdot Av} \cdot .5 \right)^2 \cdot (TT - T_{m_H_2O} + T_{offset}) \cdot n_T \cdot \frac{TT}{T_{m_H_2O}}}{\rho_u \cdot d_u} \cdot \frac{1}{T_u} \cdot R \cdot \left[\frac{Z_O \cdot w_O \cdot (TT + 1)}{d_{atom_O}} \cdot \frac{1}{\left[\frac{t_{e_O}}{(t_{p_O}^2 \cdot t_{s_O})^{\frac{1}{3}}} \right]^2} + \frac{Z_H \cdot w_H \cdot (T}{d_{atom_}}$$

Figure 8d. Water Liquid Thermal Conduct

Obviously not very close. Clearly more research is needed here.

$$\frac{(A_{H2O} + B_{H2O} \cdot TT + C_{H2O} \cdot TT^2) \cdot 0.01}{3 \cdot \left(c_p(n_{LTG}, n_{StrG}, c_{p_avg_StrG}, \rho_u \cdot d_u) \right)} \cdot \frac{V_{liq}(n_V, w_{H2O}, n_{s1}, TT, T_{m_H2O}, \Delta V, n_{s2}, n_T, n_P, P, T_{c_H2O}) \cdot w}{(s_{t_u})^3}$$

Figure 8e. Water Liquid Thermal Conductivity--from midpoint (

This is a little closer than the first segment, but obviously more study is needed.

7. The Vapor State

Some definitions:

vapor: The Reciprocal System agrees with the standard definition of a vapor (Ref. [17], Vol. 7, p. 586)--"A vapor is a non-liquid fluid. Unlike a gas, a vapor can be liquefied by the application of a sufficient pressure. The vapor state is thus possible only below the critical temperature of the substance. If any liquid or solid is put into an evacuated enclosure, molecules escape from it until the enclosure contains vapor whose pressure is a function of the temperature only."

saturated vapor: (Ref. [17], Vol. 6, p. 384)--"A saturated vapor at any temperature is a vapor in equilibrium with its liquid at that temperature, vapor being defined as a substance in the gaseous state at a temperature below its critical temperature."

single phase vapor volume: This is the volume per unit mass of the *unsaturated* normal vapor under an external pressure.

saturated vapor pressure: (Ref. [19], p. 1913, "[This is] the vapor pressure of a thermodynamic system, measured at a specified temperature, in which the vapor phase and the liquid or solid phase exist in equilibrium."

saturated vapor volume: This is the volume per unit mass of the vapor, in a two-phase system, when the pressure is the saturated vapor pressure.

superheated vapor volume: (Ref. [17], Vol. 7, p. 114)--"A vapor whose temperature exceeds the saturation temperature corresponding to the vapor pressure is said to be superheated. The addition of heat to a saturated vapor will not result in superheating until all traces of liquid have been evaporated. The properties of highly superheated vapors approach those of a perfect gas."

The most important vapor is, of course, water vapor, and this substance is what we'll focus on for all vapor properties. The equations may, of course, also be utilized for other vapors in the Reciprocal System Database.

Note: Ref. [21] is an excellent reference work for steam science and engineering.

8. Critical Liquid, Vapor, and Gas Volumes and Critical Vapor Pressure (Water)

Observed value of critical pressure (Ref. [10], p.6-5) is

$$P_{c_H2O_obs} := 22064000 \cdot 9.869 \cdot 10^{-6} \quad P_{c_H2O_obs} = 217.74962 \quad \text{atm} \quad (\text{see below for calc.})$$

$$V_{c_L_H2O} := V_{liq}(n_V, w_{H2O}, n_{s1}, T_{c_H2O}, T_{m_H2O}, \Delta V, n_{s2}, n_T, n_P, P_{c_H2O_obs}, T_{c_H2O}) \quad (46a)$$

$$V_{c_L_H2O} = 2.10246 \quad \text{cm}^3/\text{g} \quad (\text{critical volume of liquid water at } T_{c_H2O} \text{ and } P = P_c) \quad \text{cm}^3/\text{g}$$

In terms of moles, rather than grams:

$$V_{c_L_H2O_mol} := V_{c_L_H2O} \cdot w_{H2O} \quad V_{c_L_H2O_mol} = 37.87588 \quad \text{cm}^3/\text{mol} \quad (46b)$$

From Ref. [3], p. 206, Larson says: "The critical vapor volume is therefore twice the critical liquid volume. For *equal proportions* of vapor and liquid the average volume is $(1/2)(1+2) = 1.50$, but as indicated in Chapter XVIII there is an initial vapor level of .167 which has no corresponding volume and we therefore subtract half of this amount from 1.50 which gives us the a value of 1.417 [1.4165] for the critical volume, or volume of the *combined liquid-vapor aggregate* at the critical temperature, on the basis of the critical liquid volume as unity."

$$V_{c_LV_H2O} := V_{c_L_H2O} \cdot 1.4165 \quad V_{c_LV_H2O} = 2.97814 \quad \text{cm}^3/\text{g} \quad (47)$$

$$V_{c_LV_H2O_obs} := 3.11 \quad \text{cm}^3/\text{g} \quad (\text{Ref. [10], p.6-5})$$

In terms of moles, rather than grams:

$$V_{c_LV_H2O_mol} := V_{c_L_H2O_mol} \cdot 1.4165 \quad V_{c_LV_H2O_mol} = 53.65119 \quad \text{cm}^3/\text{mol}$$

$$V_{c_LV_H2O_mol_obs} := 56.0 \quad (\text{Ref. [8], p. 26}) \quad (\text{approx. 3\% larger than computed})$$

Now the *critical gas volume* is a 2/3 of the ideal gas volume at T_c and P_c . Observed value P_{c_H2O} :

$$P_{c_H2O} := 217.7496 \quad \text{atm} \quad V_{c_G_H2O} := \frac{2}{3} \cdot 1244.178 \cdot \frac{\frac{T_{c_H2O}}{273.15}}{\frac{P_{c_H2O}}{1}} \quad V_{c_G_H2O} = 9.02452 \quad \text{cm}^3/\text{gm} \quad (48)$$

$$\text{The gas multiple } k, \text{ or "gas coefficient", is then } k := \frac{V_{c_G_H2O}}{V_{c_L_H2O}} \quad k = 4.29236 \quad (49)$$

The *critical vapor volume* is simply twice the critical liquid volume:

$$V_{c_V_H2O} := 2 \cdot V_{c_L_H2O} \quad V_{c_V_H2O} = 4.20493 \quad \text{cm}^3/\text{g} \quad (50)$$

We may now apply the ideal gas equation to the critical gas volume to calculate the *critical pressure*.

$$R_{atm} := 82.057 \quad \text{atm} \times \text{cm}^3 / \text{mol} \text{ K} \quad (\text{the gas constant})$$

$$\rho_{c_G_H2O} := \frac{1}{V_{c_G_H2O} \cdot \frac{3}{2}} \quad \rho_{c_G_H2O} = 0.07387 \quad \text{g/cm}^3 \quad (51)$$

$$P_{c_H2O} := \frac{\rho_{c_G_H2O} \cdot R_{atm}}{w_{H2O}} \cdot T_{c_H2O} \quad P_{c_H2O} = 217.74963 \quad \text{atm} \quad (52)$$

which is what we used above.

9. Sequence of Volume Changes Along the Critical Isotherm as Pressure Changes

a. as pressure *decreases* while temperature stays at T_c :

critical liquid --> critical liquid/vapor aggregate --> critical vapor --> critical gas

b. as pressure *increases* while temperature stays at T_c :

critical gas --> critical vapor --> critical liquid/vapor aggregate --> critical liquid

Note: Ref. [20], Vol. III, p. 246 explains clearly, if a bit too simply, what happens: "The critical point, in physics, [is] the set of conditions under which a liquid and its vapor become identical....For each substance, the conditions defining the critical point are the critical temperature, the critical pressure, and the critical density. This is best understood by observing a simple experiment. If a closed vessel is filled with a pure substance, partly liquid and partly vapor, so that the average density equals the critical density, the critical conditions can be achieved. As the temperature is raised, the vapor pressure increases, and the gas phase becomes denser. The liquid expands and becomes less dense until, at the critical point, the densities of liquid and vapor become equal, eliminating the boundary between the two phases. If the average density at the start is too low, all the liquid will evaporate before the critical temperature is reached. If the initial average density is too high, the liquid will expand to fill the container."

Larson explains, Ref. [3], p. 206, "The critical liquid-vapor mixture only exists in the immediate vicinity of the critical temperature. We have already seen that in the liquid phase the volume reverts to the critical liquid value at once when the temperature falls below the critical point. Similarly in the vapor phase the volume makes an immediate transition to the critical vapor value as the temperature begins to drop."

As can be seen by inspection from Eqs. 13 and 14, the liquid endpoint is

$$T_L := T_c + \frac{T_{SL_u}^2}{2} \quad (53)$$

Beyond that point, the substance transforms to a 3D ideal gas.

10. Vapor Specific Heat, Enthalpy, and Entropy--Single Phase, Not Within Enclosed Container (Water)

Reciprocal System

In the Reciprocal System, the liquid water specific heat is constant; likewise the liquid vapor specific heat is constant:

$$c_{p_V_H2O} := 4 \cdot R \quad c_{p_V_H2O} = 7.9476 \quad \text{cal/mol K} \quad (54)$$

Yaws Regression (using the values for gas--there are no separate values for vapor)

$$A_V := 33.933 \quad B_V := -8.4186 \cdot 10^{-3} \quad C_V := 2.9906 \cdot 10^{-5} \quad D_V := -1.7825 \cdot 10^{-8} \quad E_V := 3.6934 \cdot 10^{-12}$$

$$c_{p_V_Yaws} := \frac{A_V + B_V \cdot T + C_V \cdot T^2 + D_V \cdot T^3 + E_V \cdot T^4}{\text{conv}_{\text{caltoJ}}} \quad \text{cal/mol K}$$

Here's the comparison graph:

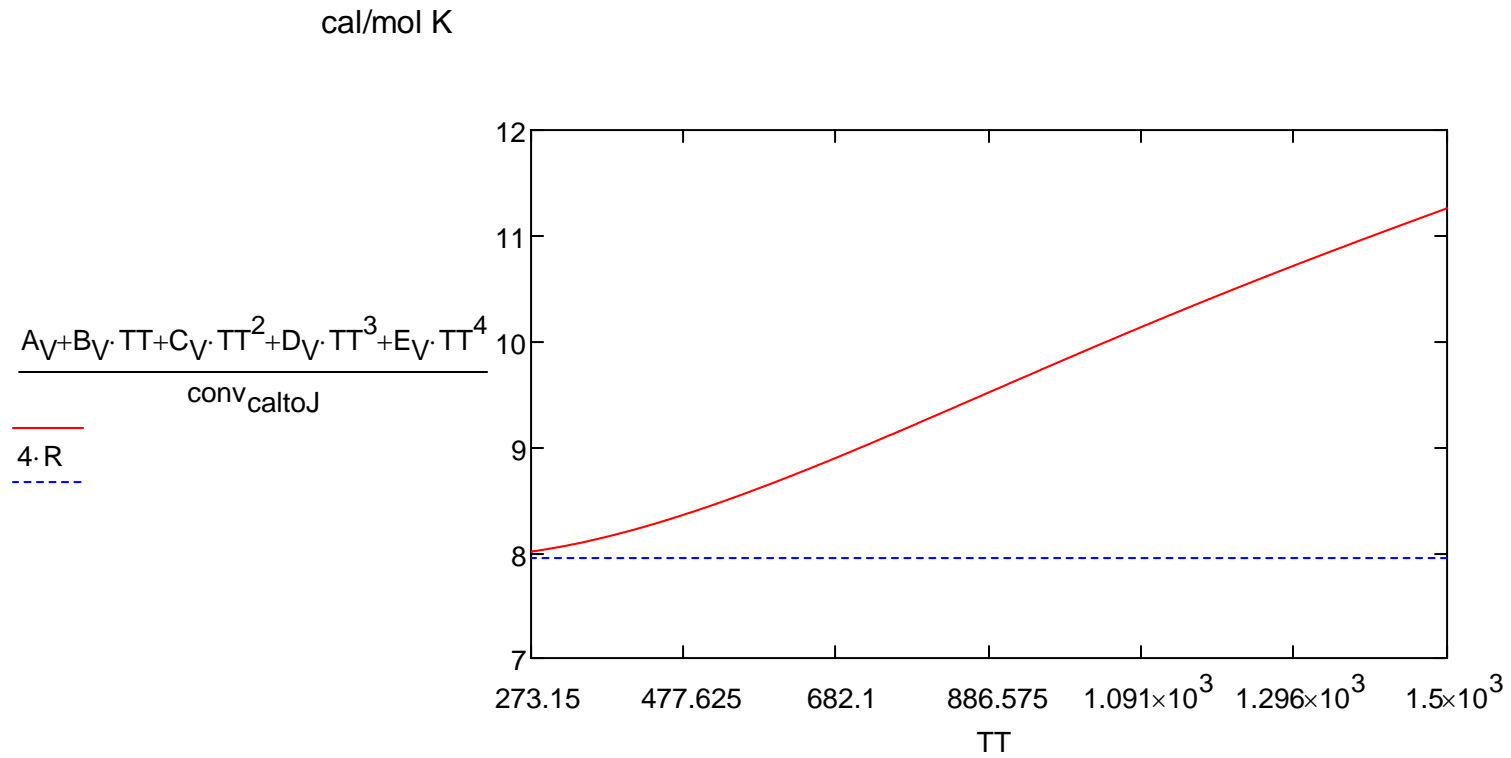


Figure 9. Water Vapor Specific Heat

Obviously the Yaws regression equation is formulated to be used for the enthalpy calculation.

Now let's do the enthalpy calculation.

Reciprocal System

$$h_{V_H2O} := 4 \cdot R \cdot (T - T_{m_H2O}) \quad (55)$$

Yaws Regression

$$\Delta h_{\text{steam_Yaws}}(T_1, T_2) := A_V \cdot (T_2 - T_1) + \left(\frac{B_V}{2}\right) \cdot (T_2^2 - T_1^2) + \left(\frac{C_V}{3}\right) \cdot (T_2^3 - T_1^3) + \left(\frac{D_V}{4}\right) \cdot (T_2^4 - T_1^4) + \left(\frac{E_V}{5}\right) \cdot (T_2^5 - T_1^5)$$

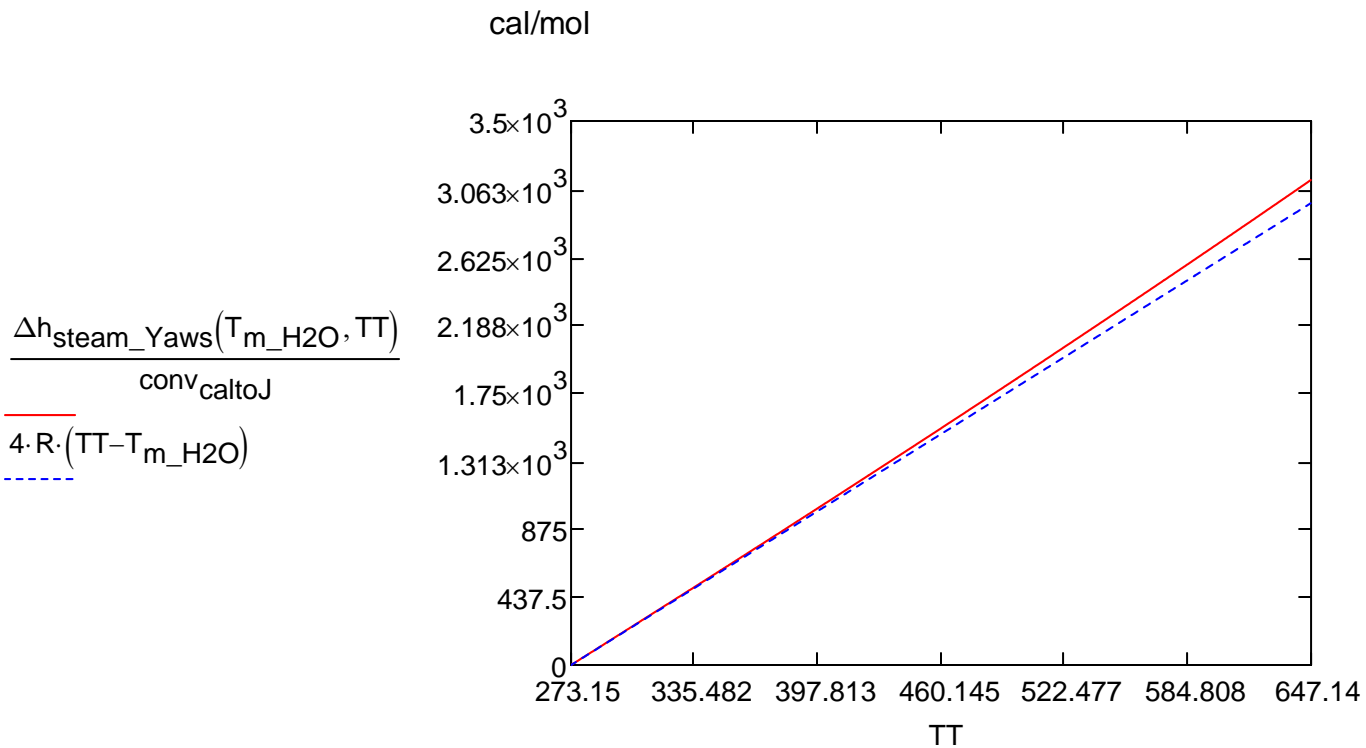


Figure 10. Water Vapor Relative Enthalpy (Single Phase)

Note: this does *not* include the enthalpy of vaporization at T_m , $h_{V,m}$, which is discussed below.

Water Specific Heat Summary

liquid:	$9 \cdot R = 17.8821$	cal/mol K	(within liquid)
vapor	$4 \cdot R = 7.9476$		(in space above liquid)
condensed vapor:	$3 \cdot R = 5.9607$		(on surface of liquid)

Water Vapor Entropy

Reciprocal System

Assume constant specific heat for most vapors, especially water, H₂O.

By definition, and assuming constant c_p : $c_{p,H_2O} := 4 \cdot R$

$$s_V(T_i, T_f, c_p, s_{i,V}) := s_{i,V} + \int_{T_i}^{T_f} \frac{c_p}{T} dT \quad \text{cal/mol K} \quad (56a)$$

$$s_V(T_i, T_f, c_p, s_{i,V}) := s_{i,V} + c_p \cdot (\ln(T_f) - \ln(T_i)) \quad \text{cal/mol K} \quad (56b)$$

From the Reciprocal System Database at T_m , $s_{i,V} := 66.3544$ cal/mol K (includes entropy of vap. at T_m)

Yaws Regression

$$s_{V_Yaws}(T_i, T_f, A_V, B_V, C_V, D_V, E_V, s_{i_V}) := \int_{T_i}^{T_f} \frac{\frac{A_V}{T} + B_V + C_V \cdot TT + D_V \cdot T^2 + E_V \cdot T^3}{\text{conv}_{\text{caltoJ}}} dT$$

Carrying out the integration:

$$s_{V_Yaws}(T_i, T_f, A_V, B_V, C_V, D_V, E_V, s_{i_V}) := s_{i_V} + \frac{12 \cdot A_V \cdot \ln(T_f) - 12 \cdot A_V \cdot \ln(T_i) + 12 \cdot B_V \cdot T_f - 12 \cdot B_V \cdot T_i + 6 \cdot C_V \cdot T_f^2 - 6 \cdot C_V \cdot T_i^2 - 2 \cdot D_V \cdot T_f^3 + 2 \cdot D_V \cdot T_i^3 - E_V \cdot T_f^4 + E_V \cdot T_i^4}{12 \cdot \text{conv}_{\text{caltoJ}}}$$

cal/mol K

$$\frac{s_V(T_{m_H2O}, TT, c_{p_H2O}, s_{i_V})}{s_{V_Yaws}(T_{m_H2O}, TT, A_V, B_V, C_V, D_V, E_V, s_{i_V})}$$

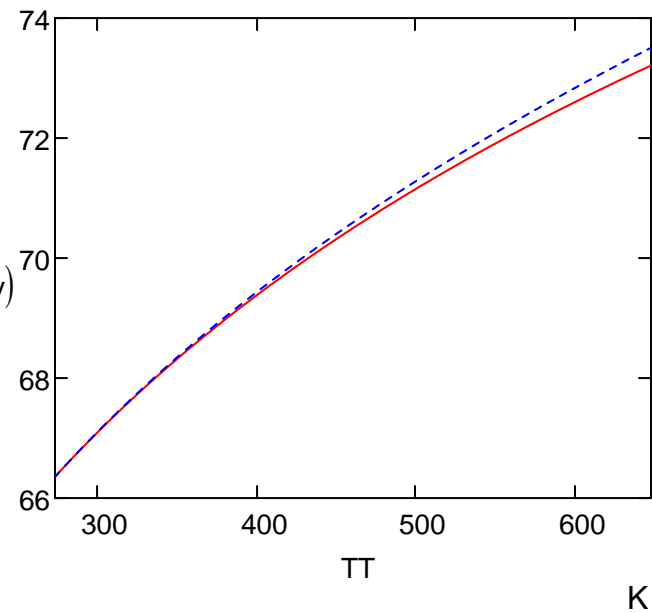


Figure 11. Water Vapor Absolute Entropy (Single Phase)

11. Liquid-Vapor Aggregate--Two-Phases Within Enclosed Container (Water)

Let's recall the functional forms to calculate the proportion of critical molecules in a liquid or vapor:

$$z_{c1}(T_c, T) := \frac{9 \cdot (T_c - T)}{T_c + \frac{T_{SL_u}}{2}} \quad \Phi_T(T_c, T) := \text{cnorm}(z_{c1}(T_c, T))$$

$$z_{c2}(T_c, T) := \frac{27 \cdot (T_c - T)}{T_c + \frac{T_{SL_u}}{2}} \quad \Phi_{3T}(T_c, T) := \text{cnorm}(z_{c2}(T_c, T))$$

Then the proportion of vapor which has *not* recondensed back to liquid is given by:

$$x := 1 - .167 \quad x = 0.833 \quad (\text{initial level})$$

$$n_{\text{Vap}}(T_c, T) := \left[\frac{x - (1 - \Phi_{3T}(T_c, T))}{x + (1 - \Phi_{3T}(T_c, T))} \right] \quad (57)$$

For water, the graph for this function is

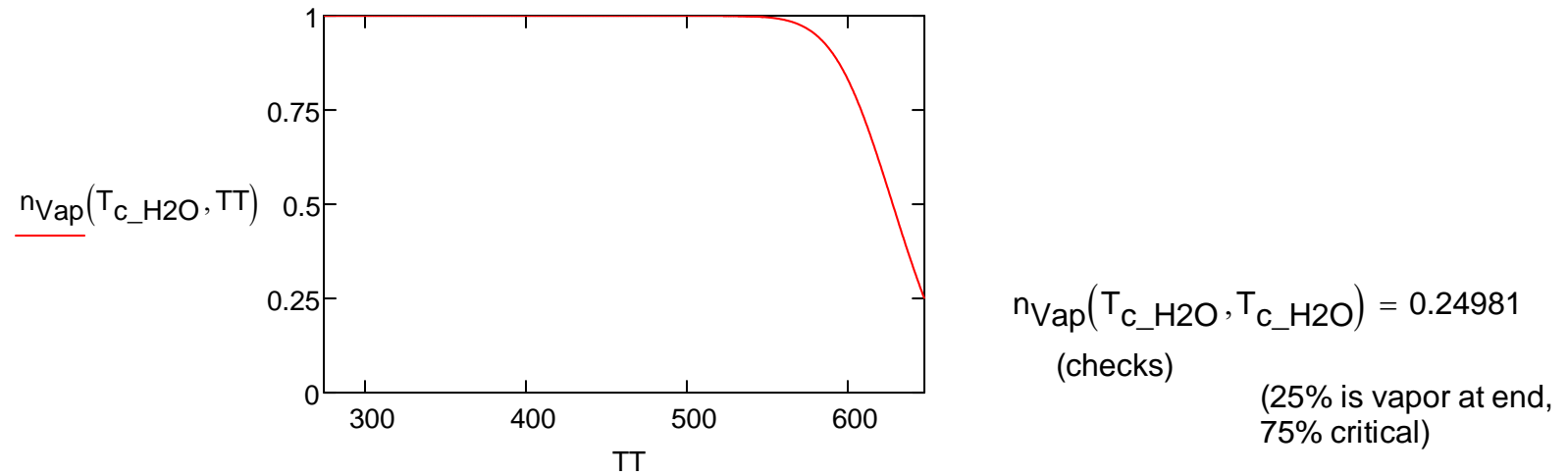


Figure 12. Proportion of Water Vapor Which Has *Not Recondensed*

Upon recondensation to surface of liquid, the *vapor molecules give up 1 R of specific heat*. The vapor and the condensed vapor continually trade molecules: the proportion of vapor is given by n_{Vap} and so the proportion of condensed vapor is $1 - n_{\text{Vap}}$.

12. Enthalpy of Vaporization for Liquid-Vapor Aggregate--Two-Phases Within Enclosed Container (Water)

Reciprocal System

assumption: initial enthalpy of vaporization (at T_m) = $h_{c_H2O} + \text{const}$

$$h_{V_m} := h_{c_H2O} + 930 \quad h_{V_m} = 12502.04337 \quad \text{cal/mol} \quad (\text{the constant is empirical; see below}) \quad (58)$$

Yaws Regression

Ref. [8], pp. 109, ff.

$$\Delta h_{Vap} := A_V \cdot \left(1 - \frac{T}{T_C}\right)^n \quad A_V := 52.053 \quad n := .321 \quad T_C := T_{c_H2O}$$

$$A_V \cdot \left(1 - \frac{T_{m_H2O}}{T_{c_H2O}}\right)^n \cdot \frac{1000}{\text{conv}_{\text{caltoJ}}} = 10428.03757 \quad \text{cal/mol}$$

By itself, the Yaws calculation has a lower starting point than the RS calculation, so a constant of

$$h_{V_m} - A_V \cdot \left(1 - \frac{T_{m_H2O}}{T_{c_H2O}}\right)^n \cdot \frac{1000}{\text{conv}_{\text{caltoJ}}} = 2074.0058 \quad \text{cal/mol}$$

has been added to the Yaws calculation. The constant for the Reciprocal System expression and that for the Yaws expression take care of the uncertainty in the enthalpy at the melting point. The enthalpy at the melting point cancels from both sides in the RS equation and so is not included.

$$\frac{A_V \cdot \left(1 - \frac{TT}{T_{c_H2O}}\right)^n \cdot 1000}{\text{conv_caltoJ}} + 2074$$

$$\left[\left[4 \cdot R \cdot (TT - T_{m_H2O}) \right] \cdot n_{\text{Vap}}(T_{c_H2O}, TT) + h_{V_m} - \left[(h_{\text{liq}}(0, T_{m_H2O}, TT, n_{\text{int}}, n_{\text{LTG}}, c_{p_avg_StrG}, n_{\text{initial}}, n_{\text{StrG}})) \cdot (1 - \text{frac_VG}(T_{c_H2O}, TT)) \right] \right] +$$

At T_c , the enthalpy of vaporization should be zero:

$$\left[4 \cdot R \cdot (T_{c_H2O} - T_{m_H2O}) \right] \cdot n_{\text{Vap}}(T_{c_H2O}, T_{c_H2O}) + h_{V_m} - \left[(h_{\text{liq}}(0, T_{m_H2O}, T_{c_H2O}, n_{\text{int}}, n_{\text{LTG}}, c_{p_avg_StrG}, n_{\text{initial}}, n_{\text{StrG}})) \cdot (1 - \text{frac_VG}(T_{c_H2O}, T_{c_H2O})) \right]$$

Close enough. However, pending theoretical clarification, the Reciprocal System Database will use the empirical value of enthalpy of vaporization, which will be added to the calculated liquid enthalpy at that temperature, to give the vapor enthalpy. Also: the empirical value of enthalpy of vaporization divided by the temperature will be added to the liquid entropy at that temperature to give the vapor entropy. This avoids the necessity of determining vapor specific heats for the two-phase situation. (59)

13. Single Phase Vapor Volume (Water)

Reciprocal System

There are three components of the vapor volume: 1) the critical molecules, 2) the simple vapor molecules, and 3) the gas molecules

1) critical vapor molecules at temperature T

$$V_{V_crit_H2O}(T) := (1 - \Phi_{3T}(T_{c_H2O}, T)) \cdot V_{c_V_H2O} \quad (60)$$

2) simple vapor molecules (free translatory motion in two dimensions)

$$V_{V_simple_H2O}(T) := 2 \cdot (1 - \Phi_T(T_{c_H2O}, T))^5 \cdot \Phi_{3T}(T_{c_H2O}, T) \cdot V_{c_V_H2O} \quad (61)$$

3) gas molecules (free translatory motion in three dimensions)

$$V_G(T, P) := 1244.178 \cdot \frac{T}{\frac{P}{1}} \quad \text{cm}^3/\text{g} \quad (62)$$

$$V_{V_gas_H2O}(T, P) := \Phi_T(T_{c_H2O}, T) \cdot (\Phi_{3T}(T_{c_H2O}, T)) \cdot V_G(T, P) \quad (63)$$

Sum:

$$V_{V_ortho}(T_c, T, P) := (1 - \Phi_{3T}(T_{c_H2O}, T)) \cdot V_{c_V_H2O} + 2 \cdot (1 - \Phi_T(T_{c_H2O}, T))^5 \cdot \Phi_{3T}(T_{c_H2O}, T) \cdot V_{c_V_H2O} \dots \\ + \Phi_T(T_{c_H2O}, T) \cdot (\Phi_{3T}(T_{c_H2O}, T)) \cdot V_G(T, P) \quad \text{cm}^3/\text{g} \quad (64)$$

Yaws Regression

$$T_c := 647.13 \text{ K} \quad P_c := 220.55 \text{ bar} \quad V_c := 56.0 \text{ cm}^3/\text{mol} \quad \rho_c := .3220 \text{ g/cm}^3$$

$$\omega := .345 \quad R_{\text{bar}} := 83.144 \text{ bar} \times \text{cm}^3 / (\text{mol K})$$

$$P_{\text{bar}} := \frac{1}{1.01325} \text{ bar} \quad P_{\text{bar}} = 0.98692 \text{ bar} \quad (\text{one atm})$$

Virial coefficients from Reid, et. el. (Ref. [7])

$$B_0(T) := .083 - \frac{.422}{\left(\frac{T}{T_c}\right)^{1.6}} \quad B_1(T) := .139 - \frac{.172}{\left(\frac{T}{T_c}\right)^{4.2}}$$

$$B(T) := \frac{R_{\text{bar}} \cdot T_c}{P_c} \cdot (B_0(T) + \omega \cdot B_1(T))$$

$$Z(T) := 1 + \frac{B(T) \cdot P_{\text{bar}}}{R_{\text{bar}} \cdot T}$$

$$P := 1 \text{ atm}$$

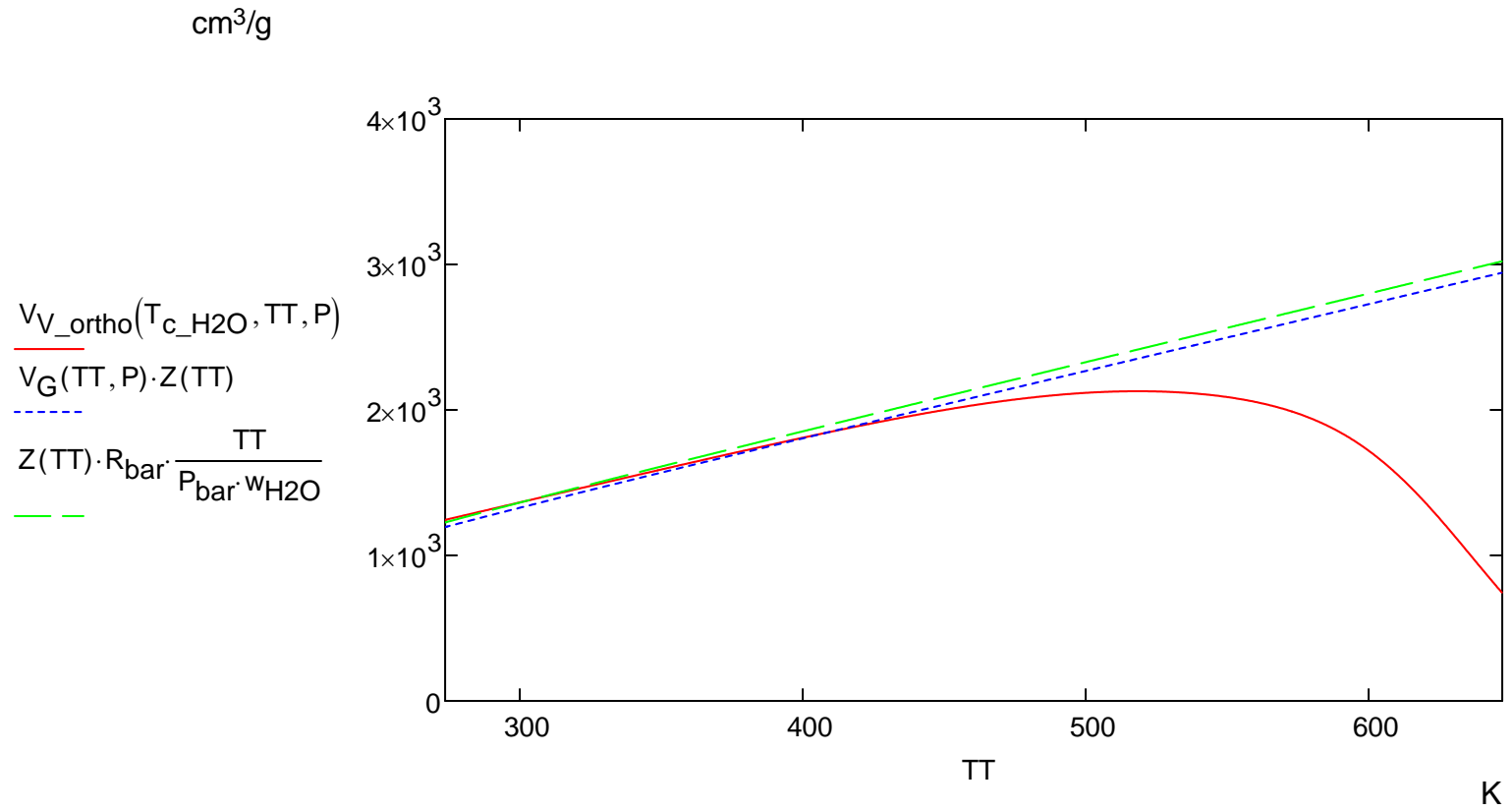


Figure 13. Single Phase Specific Volume of Water Vapor at 1 Atm

The equations match until critical molecules begin to dominate.

14. Vapor Pressure (Water)

Reciprocal System

The critical liquid molecules have 3 times the energy of the critical vapor molecules, $9RT$ vs. $3RT$, and pressure is proportional to energy. Obviously, at T_c , $P_{\text{vap_RS}} = P_{c_H2O}$. Solid molecules cannot contribute to vapor pressure.

We must add another random variable to indicate the *number of liquid molecules over $y \times T_c$ which can contribute to vapor pressure* because *not all* liquid molecules are capable of making the "jump."

$$y := .5$$

$$z_3(T_c, T, y) := \frac{9 \cdot (T_c \cdot y - T)}{T_c \cdot y + \frac{T_{SL_u}}{2}} \quad \Phi_u(T_c, T, y) := \text{cnorm}(z_3(T_c, T, y)) \quad (65)$$

$$\underline{3 \cdot (1 - \Phi_T(T_{c_H2O}, TT)) \cdot (1 - \Phi_u(T_{c_H2O}, TT, y))}$$

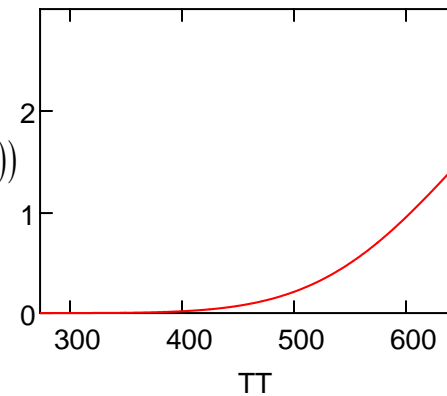


Figure 14. Proportion of Liquid Molecules Which Can Contribute to Vapor Pressure x 3 (Energy Basis)

Therefore the vapor pressure is

$$P_{\text{Vap}}(T_c, T, T_m, y) := P_{c_H2O} \cdot \frac{1}{2} \cdot \left[3 \cdot (1 - \Phi_T(T_c, T)) \cdot ((1 - \Phi_u(T_c, T, y))) + (1 - \Phi_{3T}(T_c, T)) \right] \cdot (1 - \text{frac}_S(T, T_m)) \quad (66)$$

Yaws Regression

For H2O: $A := 29.8605$ $B := -3.1522 \cdot 10^3$ $C := -7.3037 \cdot 10^0$ $D := 2.4247 \cdot 10^{-9}$ $E := 1.8090 \cdot 10^{-6}$

$$P_{\text{Vap_Yaws}}(T, A, B, C, D, E) := 10^{\left(A + \frac{B}{T} + C \cdot \log(T) + D \cdot T + E \cdot T^2 \right)} \cdot 1.316 \cdot 10^{-3} \quad \text{atm (converted from mm Hg)}$$

$$P_{\text{Vap_Yaws}}(T_{c_H2O}, A, B, C, D, E) = 216.5911 \quad \text{atm} \quad \text{vs.} \quad P_{c_H2O} = 217.74963 \quad \text{atm}$$

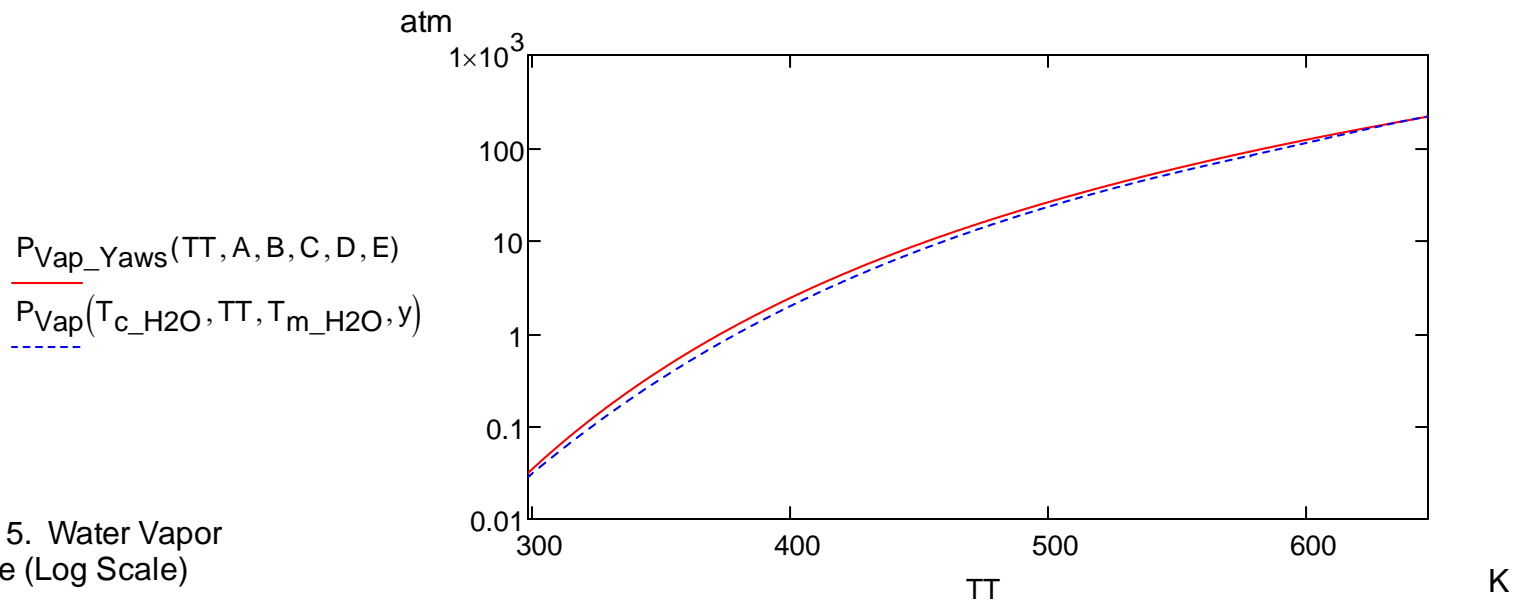


Figure 15. Water Vapor Pressure (Log Scale)

15. Saturated Specific Vapor Volume of H2O (P = Saturated Vapor Pressure at T) (Water)

Presumably we can put the vapor pressure at any value of T into the equation for the single phase volume to calculate the dual phase saturated volume (although using V_{c_LV} , instead of V_{c_V} as the critical volume and also multiplying the result by .5):

$$V_{V_ortho_sat}(T_c, T, T_m, P_c, V_{c_LV}) := (1 - \Phi_{3T}(T_{c_H2O}, T)) \cdot V_{c_LV} + 2 \cdot (1 - \Phi_T(T_{c_H2O}, T))^{.5} \cdot \Phi_{3T}(T_{c_H2O}, T) \\ + \Phi_T(T_{c_H2O}, T) \cdot (\Phi_{3T}(T_{c_H2O}, T)) \cdot V_G\left[T, P_c \cdot \frac{1}{2} \cdot \left[3 \cdot (1 - \Phi_T(T_c, T))\right] \cdot ((1 - \right.$$

$$V_{V_sat_H2O}(T_c, T, T_m, y, P_c, V_{c_LV}) := V_{V_ortho_sat}(T_{c_H2O}, T, T_m, P_c, V_{c_LV}) \cdot .5 \quad (67)$$

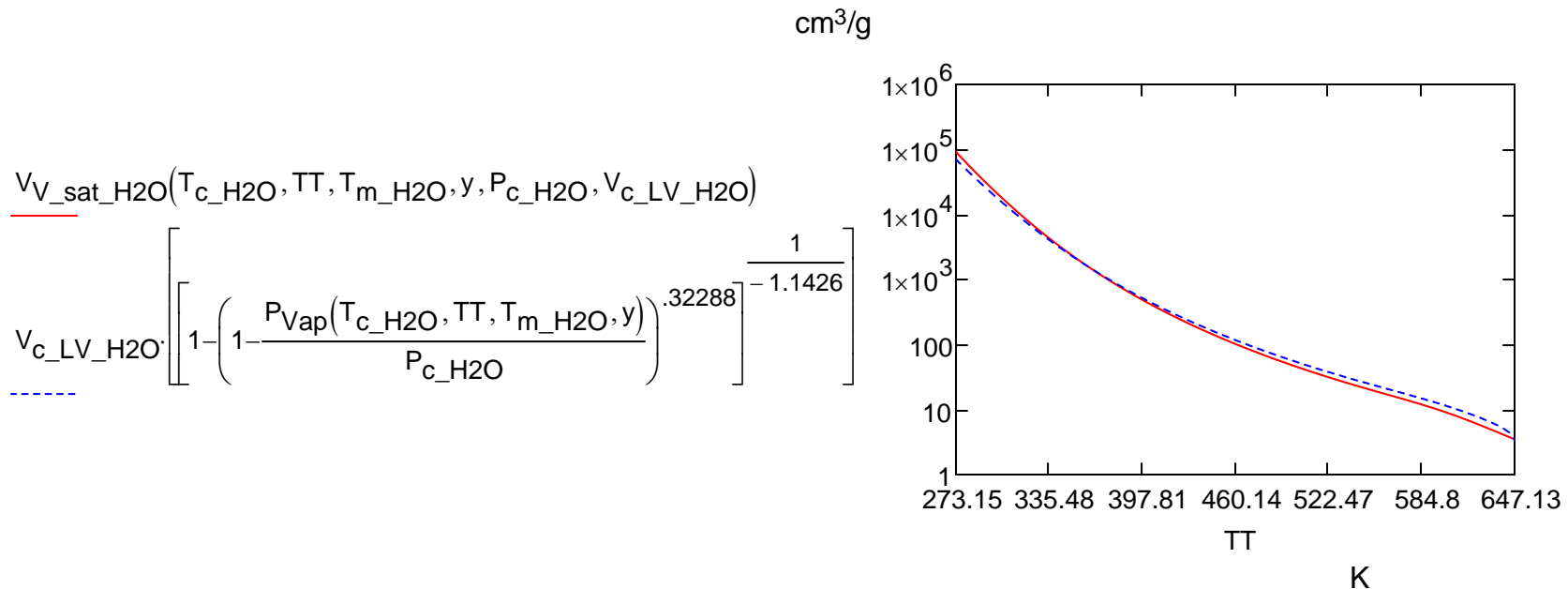


Figure 16. Saturated Water Vapor Specific Volume (Log Scale)

The second equation graphed is the empirical Thompson-Sullivan equation for water, discussed on p. 225 of Ref. [7]. The Reciprocal System Database will calculate both values for every vapor. The numerical values for the Thompson-Sullivan equation (such as .32288 and 1.1426 for water) are computed from the acentric factor, which has to be input.

A further refinement can be made for compounds, such as water, which have hydrogen bonding. The calculated value of V_{V_sat} at the critical temperature and pressure is higher than the known value of V_{c_LV} . This difference can then be subtracted from V_{V_sat} so that it is in agreement with V_{c_LV} . The Reciprocal System Database will include this refinement.

16. Superheated Vapor Volume (Water)

Reciprocal System

From Larson in Ref. [3], p. 209: "...the volume of the superheated vapor at saturation temperature and pressure is not the same as the volume of the saturated vapor as there is an isobaric change in the proportion of critical molecules in the aggregate in passing from one condition to the other. This results in a volume *increase* which is similar to the isothermal increase which we have noted in the transition from critical vapor to saturated vapor. At zero pressure and low temperatures, the critical component is entirely absent from the superheated vapor and the theoretical volume at saturation under these conditions is therefore the volume of $1-\Phi$ gas molecules [Φ in our notation] and Φ [$1-\Phi$ in our notation] simple vapor molecules." Continuing with water as our example vapor:

$$V_{V_SH_sat_H2O}(T) := \Phi_T(T_{c_H2O}, T) \cdot V_G(T, P_{Vap}(T_{c_H2O}, T, T_{m_H2O}, y)) + 2 \cdot (1 - \Phi_T(T_{c_H2O}, T))^5 \cdot V_{c_V_H2O} \quad (68)$$

"The difference between this volume and that of the saturated vapor is a function of both temperature and pressure as saturation may be attained either by decreasing the temperature or by increasing the pressure. Since the two are equally effective we may attribute half of the volume difference to pressure and half to temperature. At the critical temperature, where the difference is limited to pressure only, the zero pressure volume is necessarily halfway between that of the superheated and saturated vapors. Below this temperature the proportion of molecules which are individually at the critical temperature is Φ_{3T} [$1-\Phi_{3T}$ in our notation] along the saturation line but the probability along the zero pressure line is a compound function involving both temperature and pressure, with the value Φ_{3T}^2 [$(1-\Phi_{3T})^2$ in our notation]. The volume of the superheated vapor aggregate at zero pressure is therefore the superheated vapor volume computed [from the equation above] less Φ_{3T}^2 [$(1-\Phi_{3T})^2$ in our notation] times half the difference between the saturated and superheated volumes:"

$$V_{V_SH_aggr_P_0_H2O}(T) := V_{V_SH_sat_H2O}(T) - \frac{1}{2} \cdot (1 - \Phi_{3T}(T_{c_H2O}, T))^2 \cdot (V_{V_SH_sat_H2O}(T) - V_{V_sat_H2O}(T_{c_H2O})) \quad (P = 0) \quad (69)$$

"If we apply the critical pressure to the superheated vapor aggregate at the critical temperature, the volume is again decreased by an amount equal to half of the difference between the saturated and superheated volumes, which brings it down to the critical volume. However, if the critical state is approached along the saturation line this volume decrement follows the probability relation Φ_{3T} [$1-\Phi_{3T}$ in our notation] and the volume is $(1/2) \times \Phi_{3T} \times (V_{SH} - V_{sat})$ [$(1/2) \times (1-\Phi_{3T}) \times (V_{V_SH} - V_{V_sat})$] less than the zero pressure volume at the same temperature. This may be expressed as"

$$V_{V_SH_aggr_P_sat_H2O}(T) := V_{V_SH_sat_H2O}(T) - \left[\frac{1}{2} \cdot (1 - \Phi_{3T}(T_{c_H2O}, T))^2 - \frac{1}{2} \cdot (1 - \Phi_{3T}(T_{c_H2O}, T)) \right] \cdot (V_{V_SH_sat_} - V_{V_sat_}) \quad (70)$$

(P=P_{Vap})

"The pressure effect on the vapor volume is linear hence the volume at any intermediate pressure is

$$V_{V_SH_aggr_P_H2O}(T, P) := V_{V_SH_aggr_P_sat_H2O}(T) + \left(1 - \frac{P}{P_{Vap}(T_{c_H2O}, T, T_{m_H2O}, y)} \right) \cdot (V_{V_SH_aggr_P_0_H2O}(T) - V_{V_SH_aggr_P_sat_H2O}(T)) \quad (71)$$

(any P between 0 and
P_{Vap})

Please note that the above expression is for the specific volume of the superheated vapor *aggregate*, not the superheated vapor volume only. So we must subtract this aggregate value from the the normal gas volume at the *saturation temperature and pressure*. This gives the deviation:

$$\text{Dev}_{\text{SH}}(T, P) := V_{\text{G}}(T, P_{\text{Vap}}(T_{\text{c_H2O}}, T, T_{\text{m_H2O}}, y)) - V_{\text{V_SH_aggr_P_H2O}}(T, P) \quad \text{cm}^3/\text{g} \quad (72)$$

Finally:

$$V_{\text{V_SH_H2O}}(T, P) := V_{\text{G}}(T, P) - \text{Dev}_{\text{SH}}(T, P) \quad \text{cm}^3/\text{g} \quad (73)$$

Al-Hamdi Regression Equation (Ref. [18], p.110--for Temperature and Pressure Far from Critical)

$$C_1 := .015461 \quad C_2 := -.000005 \quad C_3 := 3.136615 \quad C_4 := 0 \quad C_5 := .000278 \quad C_6 := .126073$$

$$C_7 := -.629711 \quad C_8 := .595804 \quad C_9 := -3.13669 \quad C_{10} := -.999999 \quad C_{11} := .000461$$

note: the regression equation uses T in deg. C and P in MPa, and V is in m³/kg

$$V_{\text{V_SH_H2O_Al_Hamdi}}(T, P) := C_1 + C_2 \cdot T + C_3 \cdot P + C_4 \cdot (T \cdot P) + \frac{C_5}{T \cdot P^2} + \frac{C_6}{P} + \frac{C_7}{T} + C_{11} \cdot \frac{T}{P}$$

We will convert this to work with our units, T in K and P in atm and V in cm³/g:

$$V_{\text{V_SH_H2O_Al_Hamdi}}(T, P) := 1000 \cdot \left[C_1 + C_2 \cdot (T - 273.15) + C_3 \cdot (P \cdot .1013) + C_4 \cdot [(T - 273.15) \cdot P \cdot .1013] + \frac{C_5}{(T - 273.15) \cdot (P \cdot .1013)^2} + \frac{C_6}{P} + \frac{C_7}{T} + C_{11} \cdot \frac{T}{P} \right]$$

Here is a graph comparing the two curves:

$T := 900 \text{ K}$

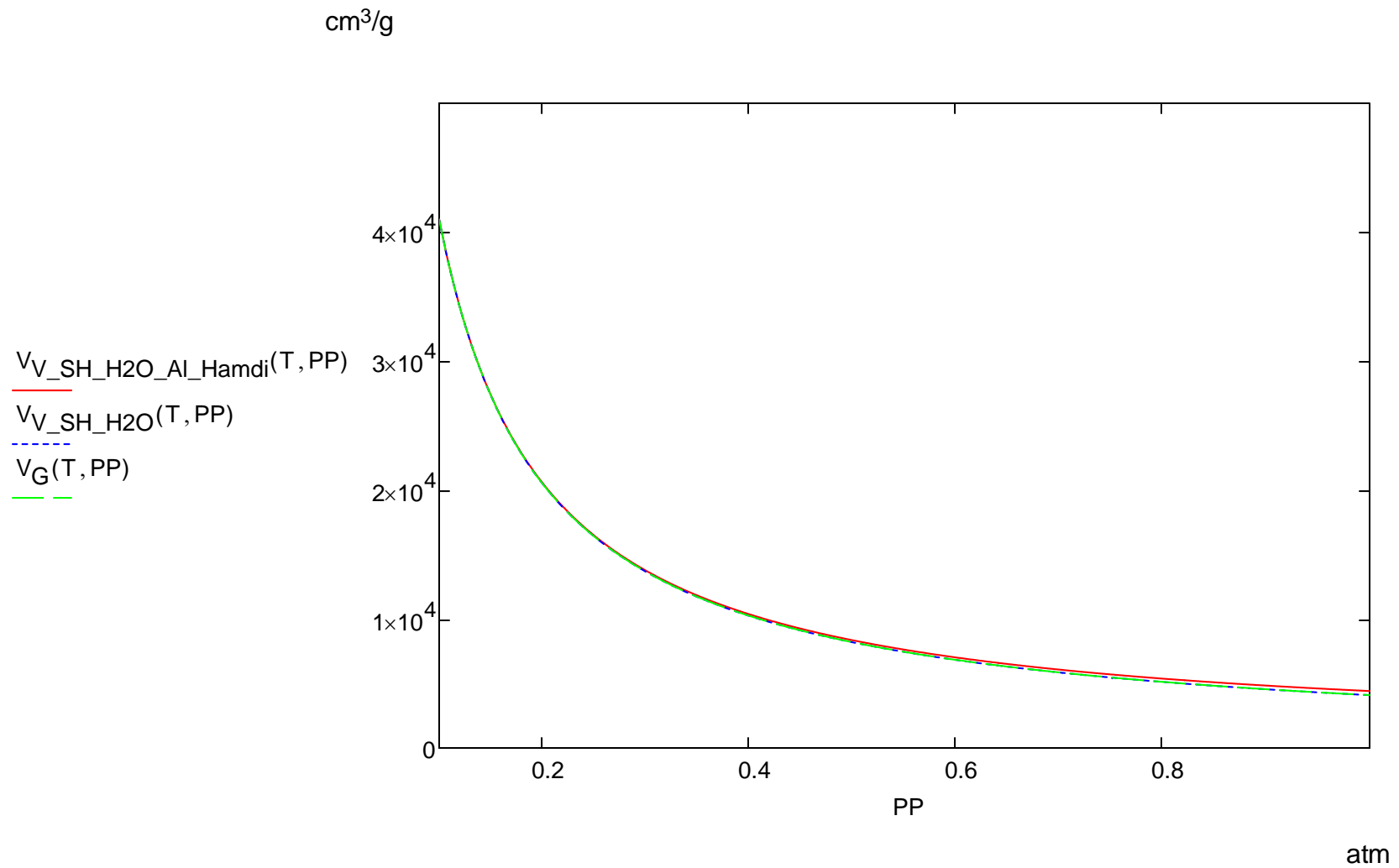


Figure 17. Specific Volume of Superheated Water Vapor, $T = 900 \text{ K}$

Here is another graph comparing the two curves: $P := .5 \text{ atm}$

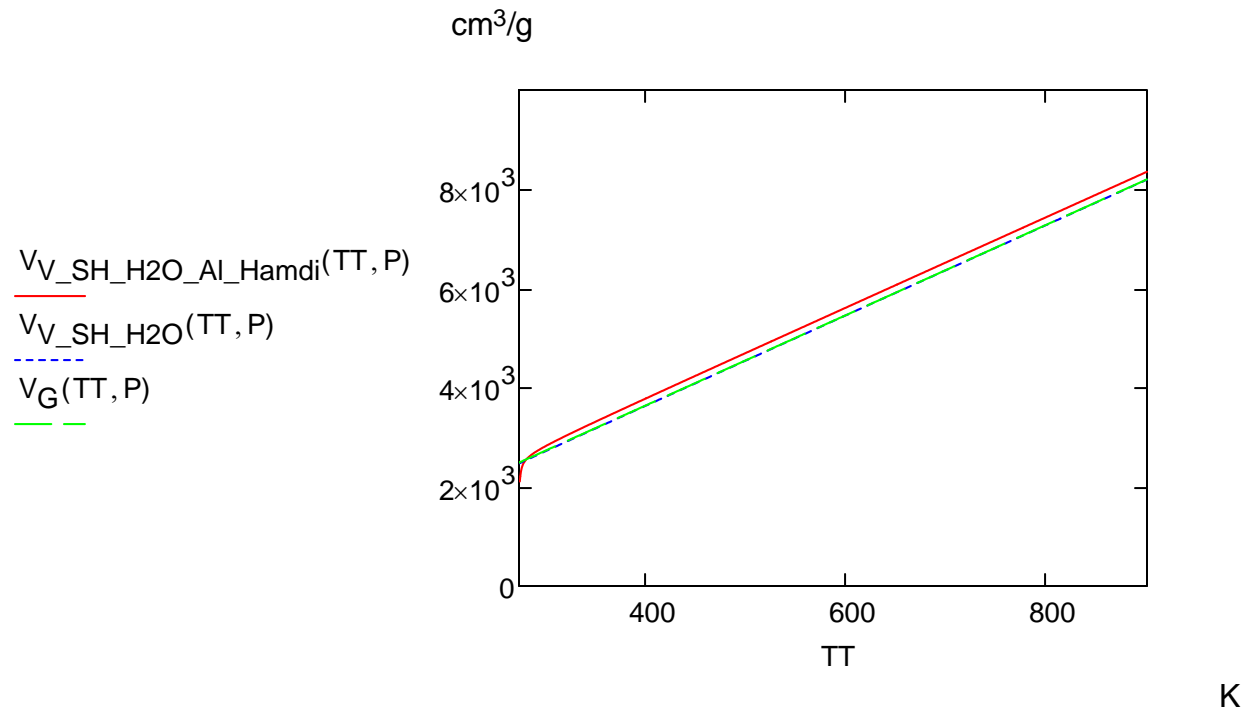


Figure 18. Specific Volume of Superheated Water Vapor, $P = .5 \text{ atm}$

Clearly, for both graphs, there is little deviation from the ideal gas law.

Now let's plot the superheated vapor volume at T_{c_H2O} over the whole range of pressures; here, the regression equation cannot be used.

$$T := T_{c_H2O} \quad P < P_{c_H2O}$$

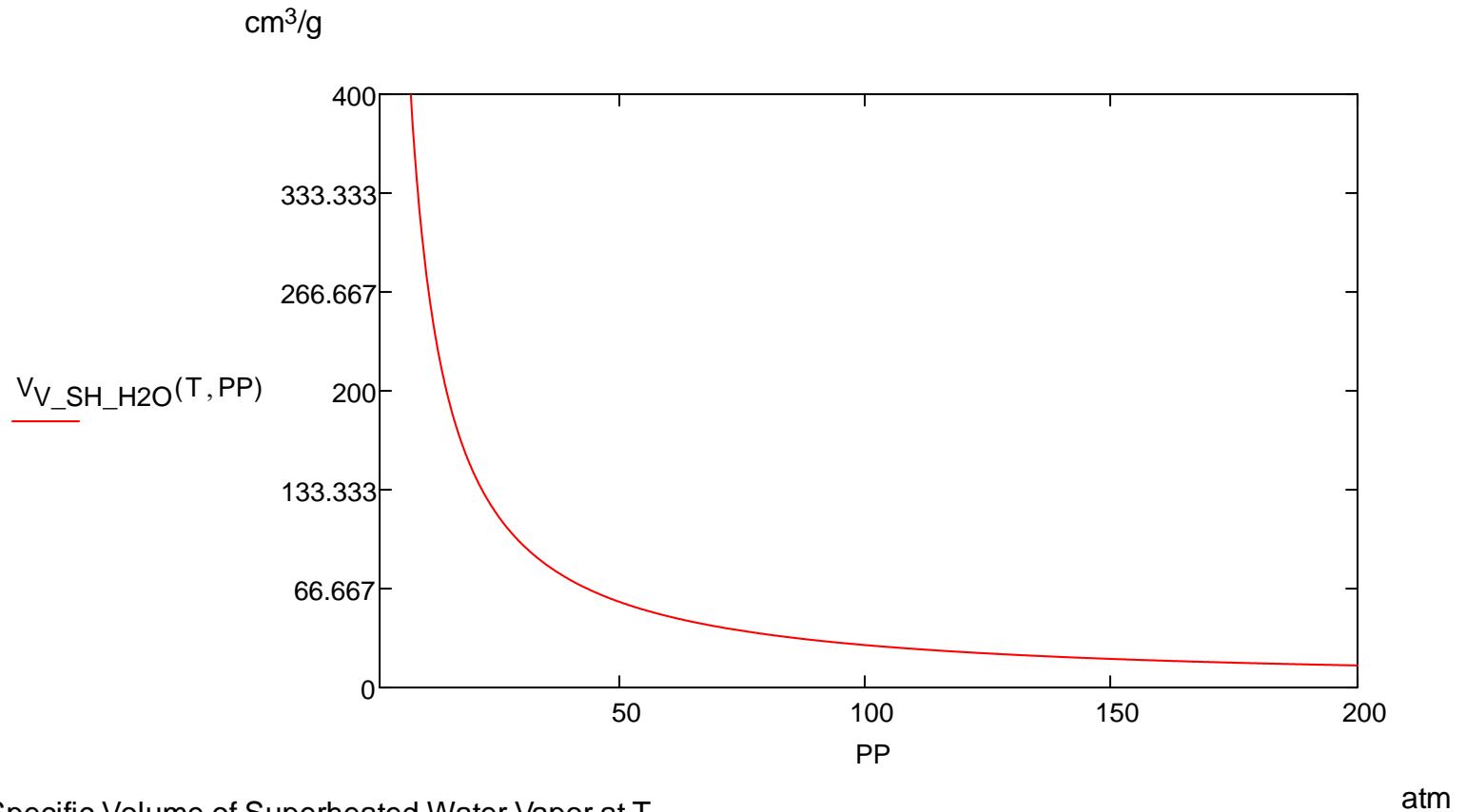


Figure 19. Specific Volume of Superheated Water Vapor at T_{c_H2O}

atm

$$V_{V_SH_H2O}(T_{c_H2O}, P_{c_H2O}) = 13.86824 \text{ cm}^3/\text{g} \quad \text{which is greater than} \quad V_{c_G_H2O} = 9.02452 \text{ cm}^3/\text{g}$$

17. Real Gas Volume ($T > T_c$)

Reciprocal System

From the critical temperature to the liquid end-point, the gas changes from two dimensions of free translational motion to three dimensions. Therefore, this transition occurs within the temperature range

$$T_c \leq T \leq T_c + \frac{1}{2} \cdot T_{SL_u} \quad (\text{transition from 2-D gas to 3-D gas})$$

Of course, if the pressure is too high, the gas will not make the transition. The volume of the gas, as a function of both temperature and pressure, is

$$V_{RG}(T, P, x) := V_G(T, P) - \text{Dev}(T, P, x) \quad (74)$$

where $\text{Dev}(T, P, x)$ represents the deviation from the ideal gas law and RG means "real gas". The factor x is discussed below. Because the gas in this region is two-dimensional, the first component of the deviation is 1/3 of the ideal gas volume multiplied by the appropriate temperature fraction.

$$\text{Dev}_1(T, P, x) := \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{V_G(T, P)}{3} \quad (75a)$$

This is the time-space region deviation. When the liquid endpoint temperature is reached, this component becomes zero. The second component of the deviation from ideality represents the time region deviation due to the cohesion in one dimension: it is the fraction of two-dimensional gas molecules at T multiplied by the appropriate volume.

$$\text{Dev}_2(T, P, x) := \left[\left(1 - \Phi_{3T}(T_{c_H2O}, T) \right)^{.5} \right] \cdot x \cdot V_{c_L_H2O} \quad (75b)$$

where x is an integer or half-integer or an integer plus or minus a simple fraction to be determined. Therefore the real gas volume is

$$V_{RG}(T, P, x) := V_G(T, P) - \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{V_G(T, P)}{3} - \left[\left(1 - \Phi_{3T}(T_{c_H2O}, T) \right)^{.5} \right] \cdot x \cdot V_{c_L_H2O} \quad (76)$$

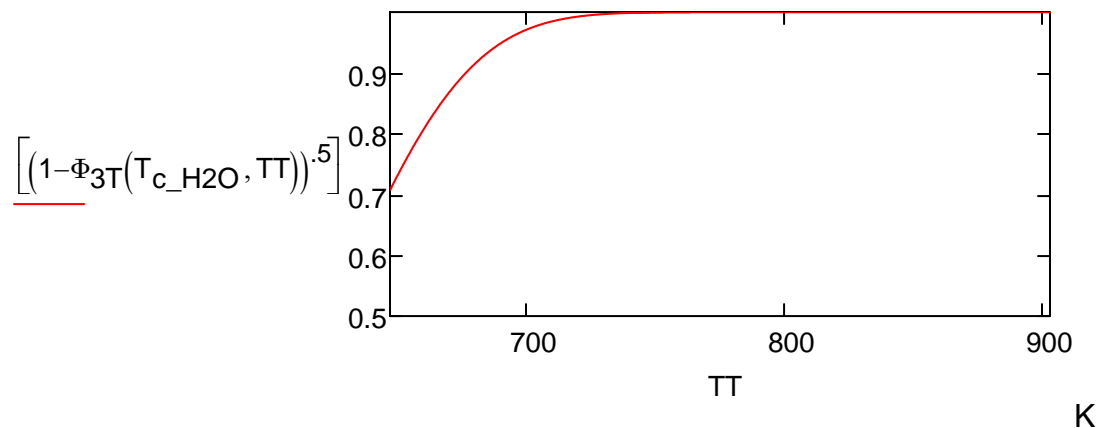


Figure 20. Probability Function for Specific Volume Deviation from Ideality

The sequence of critical specific volumes (with decreasing pressure) is:

$$V_{c_L}, V_{c_LV}, V_{c_V}, V_{c_G}$$

The corresponding pressures on the two-dimensional gas to get these specific volumes will be symbolized by

$$P_L, P_{LV}, P_V, P_G$$

The corresponding values of x will be symbolized by

$$x_L, x_{LV}, x_V, x_G$$

The pressure P_L is that needed to cause the *gas volume to be equal to the critical liquid volume* at T_c .

$$V_{c_L} = 1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_L}{1}} - \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_L}{1}}}{3} - \left[(1 - \Phi_{3T}(T_c, T))^{.5} \right] \cdot (x_L) \cdot V_{c_L}$$

$$P_L(x_L, T_c, T, V_{c_L}) := \frac{3.0366172432729269632 \cdot T^2 - 3.0366172432729269632 \cdot T \cdot T_c + 3.0366172432729269632 \cdot T \cdot T_{SL_u}}{1.0 \cdot T_{SL_u} \cdot V_{c_L} + 1.0 \cdot T_{SL_u} \cdot V_{c_L} \cdot x_L \cdot \sqrt{1.0 - 1.0 \cdot \Phi_{3T}(T_c, T)}}$$

(77)

$$x_L := \frac{1}{2} \quad (\text{for H2O}) \quad (\text{see below for a discussion of how to select the } x \text{ values})$$

$$P_L(x_L, T_{c_H2O}, T_{c_H2O}, V_{c_L_H2O}) = 690.52231 \quad \text{atm} \quad (\text{for H2O})$$

The pressure P_{LV} is that needed to cause the *volume of the gas to be equal to that of the critical liquid/vapor aggregate*.

$$V_{c_LV} = 1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_{LV}}{1}} - \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_{LV}}{1}}}{3} - \left[(1 - \Phi_{3T}(T_c, T))^{.5} \right] \cdot (x_{LV}) \cdot V_{c_L}$$

$$P_{LV}(x_{LV}, T_c, T, V_{c_L}, V_{c_LV}) := \frac{3.0366172432729269632 \cdot T^2 - 3.0366172432729269632 \cdot T \cdot T_c + 3.0366172432729269632 \cdot T}{1.0 \cdot T_{SL_u} \cdot V_{c_LV} + 1.0 \cdot T_{SL_u} \cdot V_{c_L} \cdot x_{LV} \cdot \sqrt{1.0 - 1.0 \cdot \Phi_{3T}(T_c, T)}}$$

(78)

$$x_{LV} := \frac{2}{3} \quad (\text{for H2O})$$

$$P_{LV}(x_{LV}, T_{c_H2O}, T_{c_H2O}, V_{c_L_H2O}, V_{c_LV_H2O}) = 495.07738 \quad \text{atm}$$

The pressure P_V is that needed to cause the *volume of the gas to be equal to that of the critical vapor*.

$$V_{c_V} = 1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_V}{1}} - \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_V}{1}}}{3} - \left[(1 - \Phi_{3T}(T_c, T))^5 \right] \cdot (x_V) \cdot V_{c_L}$$

$$P_V(x_V, T_c, T, V_{c_L}, V_{c_V}) := \frac{3.0366172432729269632 \cdot T^2 - 3.0366172432729269632 \cdot T \cdot T_c + 3.0366172432729269632 \cdot T \cdot T}{1.0 \cdot T_{SL_u} \cdot V_{c_V} + 1.0 \cdot T_{SL_u} \cdot V_{c_L} \cdot x_V \cdot \sqrt{1.0 - 1.0 \cdot \Phi_{3T}(T_c, T)}}$$

$$x_V := \frac{1}{2} \quad (\text{for H}_2\text{O}) \quad (79)$$

$$P_V(x_V, T_{c_H2O}, T_{c_H2O}, V_{c_L_H2O}, V_{c_V_H2O}) = 397.12667 \text{ atm}$$

The pressure P_G is that needed to cause the *volume of the gas to be equal to that of the critical gas*.

$$V_{c_G} = 1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_G}{1}} - \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{1244.178 \cdot \frac{\frac{T}{273.15}}{\frac{P_G}{1}}}{3} - \left[(1 - \Phi_{3T}(T_c, T))^5 \right] \cdot (x_{SH}) \cdot V_{c_L}$$

$$P_G(x_G, T_c, T, V_{c_L}, V_{c_G}) := \frac{3.0366172432729269632 \cdot T^2 - 3.0366172432729269632 \cdot T \cdot T_c + 3.0366172432729269632 \cdot T \cdot T_s}{1.0 \cdot T_{SL_u} \cdot V_{c_G} + 1.0 \cdot T_{SL_u} \cdot V_{c_L} \cdot x_G \cdot \sqrt{1.0 - 1.0 \cdot \Phi_{3T}(T_c, T)}} \quad (80)$$

$$x_G := \frac{1}{9} \quad (\text{for H}_2\text{O})$$

$$P_G(x_G, T_{c_H2O}, T_{c_H2O}, V_{c_L_H2O}, V_{c_G_H2O}) = 213.83555 \quad \text{atm} \quad (\text{for H}_2\text{O}) \quad (\text{must be close to } P_c)$$

Now we can form several deviation functions to calculate the deviation from ideality for each pressure range.

$$\text{Dev}_0(T, T_c, P) := \left[1 - \left(\frac{T - T_c}{\frac{1}{2} \cdot T_{SL_u}} \right) \right] \cdot \frac{V_G(T, P)}{3}$$

$$\text{Dev}_G(T, T_c, P, x_G, V_{c_L}) := (1 - \Phi_{3T}(T_c, T))^{.5} \cdot V_{c_L} \cdot x_G + \text{Dev}_0(T, T_c, P)$$

$$\text{Dev}_V(T, T_c, P, x_V, V_{c_L}) := (1 - \Phi_{3T}(T_c, T))^{.5} \cdot V_{c_L} \cdot x_V + \text{Dev}_0(T, T_c, P)$$

$$\text{Dev}_{LV}(T, T_c, P, x_{LV}, V_{c_L}) := (1 - \Phi_{3T}(T_c, T))^{.5} \cdot V_{c_L} \cdot x_{LV} + \text{Dev}_0(T, T_c, P)$$

$$\text{Dev}_L(T, T_c, P, x_L, V_{c_L}) := (1 - \Phi_{3T}(T_c, T))^{.5} \cdot V_{c_L} \cdot x_L + \text{Dev}_0(T, T_c, P)$$

$$\text{Dev}_{0\text{toG}}(T, T_c, P, x_G, V_{c_L}, V_{c_G}) := \text{Dev}_0(T, T_c, P) + \frac{P}{P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G})} \cdot (\text{Dev}_G(T, T_c, P, x_G, V_{c_L}) - \text{Dev}_0(T, T_c, P))$$

$$\text{Dev}_{G\text{toV}}(T, T_c, P, x_G, x_V, V_{c_L}, V_{c_V}, V_{c_G}) := \text{Dev}_G(T, T_c, P, x_G, V_{c_L}) + \frac{(P - P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G}))}{P_V(x_V, T_c, T_c, V_{c_L}, V_{c_V}) - P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G})}$$

$$\text{Dev}_{V\text{toLV}}(T, T_c, P, x_G, x_V, x_{LV}, V_{c_L}, V_{c_LV}, V_{c_V}) := \text{Dev}_V(T, T_c, P, x_V, V_{c_L}) + \frac{(P - P_V(x_V, T_c, T_c, V_{c_L}, V_{c_V}))}{P_{LV}(x_{LV}, T_c, T_c, V_{c_L}, V_{c_LV}) - P_V(x_V, T_c, T_c, V_{c_L}, V_{c_V})}$$

$$\text{Dev}_{LV\text{toL}}(T, T_c, P, x_L, x_{LV}, V_{c_L}, V_{c_LV}) := \text{Dev}_{LV}(T, T_c, P, x_{LV}, V_{c_L}) + \frac{(P - P_{LV}(x_{LV}, T_c, T_c, V_{c_L}, V_{c_LV}))}{P_L(x_L, T_c, T_c, V_{c_L}) - P_{LV}(x_{LV}, T_c, T_c, V_{c_L}, V_{c_LV})}$$

The *Mathcad* internal programming function to calculate the real gas volume ($T \geq T_c$) is then:

$$V_{RG}(T, T_c, P, x_G, x_V, x_{LV}, x_L, V_{c_L}, V_{c_LV}, V_{c_V}, V_{c_G}) := \begin{cases} (V_G(T, P) - \text{Dev}_{0\text{toG}}(T, T_c, P, x_G, V_{c_L}, V_{c_G})) & \text{if } P \leq P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G}) \\ (V_G(T, P) - \text{Dev}_{G\text{toV}}(T, T_c, P, x_G, x_V, V_{c_L}, V_{c_V}, V_{c_G})) & \text{if } P > P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G}) \\ (V_G(T, P) - \text{Dev}_{V\text{toLV}}(T, T_c, P, x_G, x_V, x_{LV}, V_{c_L}, V_{c_LV}, V_{c_V})) & \text{if } P > P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G}) \text{ and } P > P_V(x_V, T_c, T_c, V_{c_L}, V_{c_V}) \\ (V_G(T, P) - \text{Dev}_{LV\text{toL}}(T, T_c, P, x_L, x_{LV}, V_{c_L}, V_{c_LV})) & \text{if } P > P_G(x_G, T_c, T_c, V_{c_L}, V_{c_G}) \text{ and } P > P_V(x_V, T_c, T_c, V_{c_L}, V_{c_V}) \text{ and } P > P_{LV}(x_{LV}, T_c, T_c, V_{c_L}, V_{c_LV}) \end{cases}$$

(81)

Beyond P_L , the pressure acts on the *individual components* of the aggregate, and so we're back to the liquid calculations. Larson refers to a substance above the critical temperature but below the critical liquid volume as a "condensed gas."

Peng-Robinson Regression Equation

There are zillions of empirical regression equations for PVT calculations in the scientific literature, but *there is no other theory with which to compare the Reciprocal System*. One of the best known and accurate PVT regression equations is called the Peng-Robinson, after the engineers who devised it. Based on Ref. [7], pp. 42-43, here it is, as a *Mathcad* internal program:

$$V_{\text{Peng_Robinson}}(T, P, P_C, T_C, mw, \omega) := \left| \begin{array}{l} R \leftarrow 82.05746 \\ T_r \leftarrow \frac{T}{T_C} \\ f\omega \leftarrow .37464 + 1.54226 \cdot \omega - .26992 \cdot \omega^2 \\ a \leftarrow \frac{.457235 \cdot R^2 \cdot T_C^2}{P_C} \cdot \left[1 + f\omega \cdot (1 - T_r^{.5}) \right]^2 \\ b \leftarrow \frac{.077796 \cdot R \cdot T_C}{P_C} \\ A \leftarrow \frac{a \cdot P}{R^2 \cdot T^2} \\ B \leftarrow \frac{b \cdot P}{R \cdot T} \\ u \leftarrow 2 \\ w \leftarrow -1 \end{array} \right.$$

$$Z \leftarrow \frac{B}{3} - \frac{B \cdot u}{3} + \left(\frac{B}{9} - \frac{A}{6} + \frac{B^2 \cdot u}{9} + \frac{B^3 \cdot u}{18} + \frac{B^2 \cdot w}{3} + \frac{B^3 \cdot w}{3} + \frac{B^2}{9} + \frac{B^3}{27} + \frac{A \cdot B}{3} - \frac{B^2 \cdot u^2}{18} \right)$$

$$V \leftarrow \frac{R \cdot T \cdot Z}{P \cdot m w}$$

$$V$$

The Peng-Robinson regression equation will serve as a proxy for the experimental data. Notice how much simpler is the Reciprocal System function.

Sample Calculations for 2-D Water Gas, Fixed P, Varying T

$P1 := P_{c_H2O}$ $P1 = 217.74963$ $\omega_{H2O} := .345$ (acentric factor, from Ref. [8] for use with the Peng-Robinson regression)

$$\underline{V_{RG}}(TT, T_{c_H2O}, P1, x_G, x_V, x_{LV}, x_L, V_{c_L_H2O}, V_{c_LV_H2O}, V_{c_V_H2O}, V_{c_G_H2O})$$

$$\underline{V_{Peng_Robinson}}(TT, P1, P_{c_H2O}, T_{c_H2O}, \omega_{H2O}, \omega_{H2O})$$

$$\underline{V_G}(TT, P1)$$

cm³/g

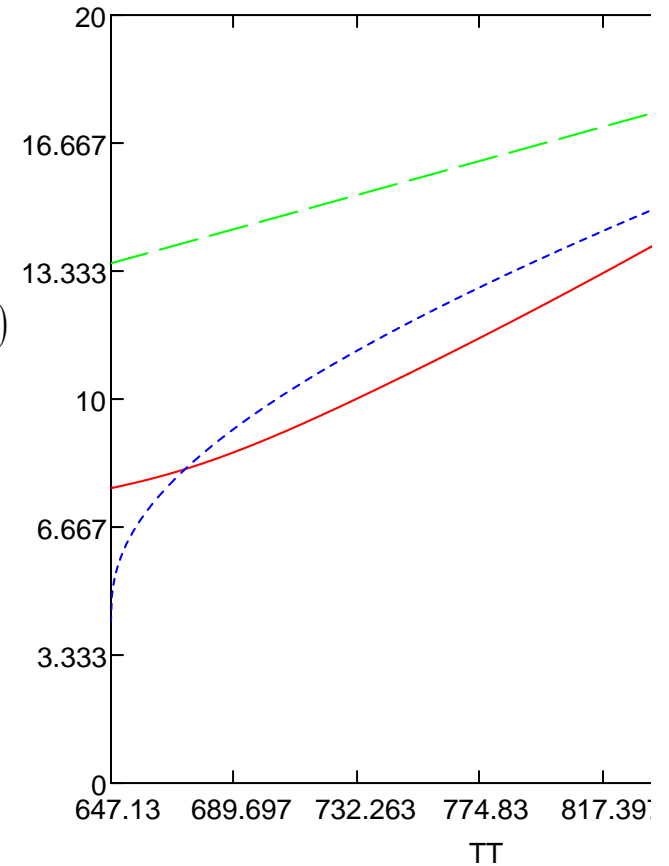


Figure 21. Water Gas Specific Volume at Critical Pressure

Note: Close to the critical temperature, a portion of the gas molecules condense and so reduce the volume; this explains the discrepancy between the theoretical and empirical calculations in that region. The RS calculation is for gas only. It's also known that *none of the empirical PVT regression equations works well in the critical region.*

P2 := 400 atm

cm³/g

$V_{RG}(TT, T_{c_H2O}, P2, x_G, x_V, x_{LV}, x_L, V_{c_L_H2O}, V_{c_LV_H2O}, V_{c_V_H2O}, V_{c_G_H2O})$

$V_{Peng_Robinson}(TT, P2, P_{c_H2O}, T_{c_H2O}, w_{H2O}, \omega_{H2O})$

$V_G(TT, P2)$

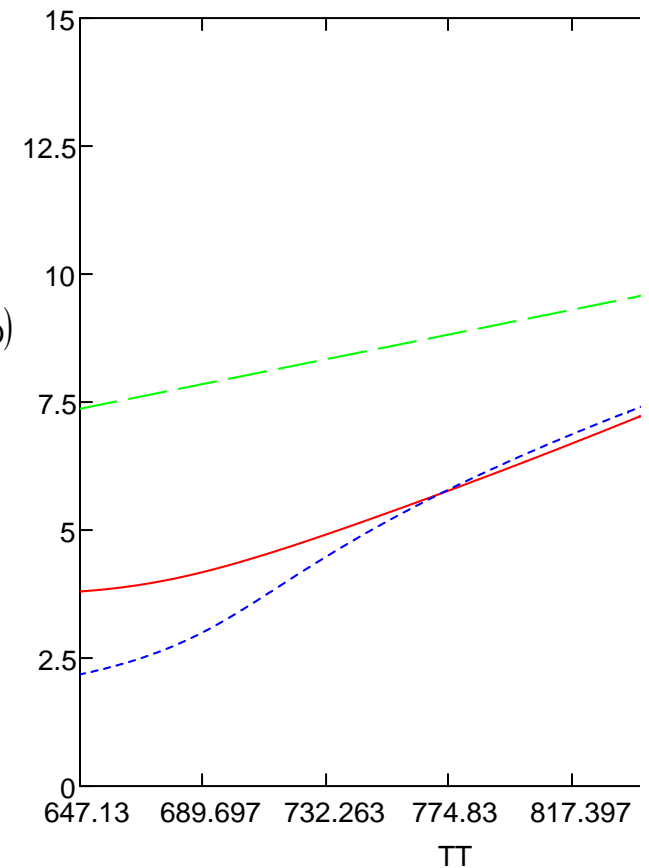


Figure 22. Water Gas Specific Volume at 400 atm

See the note above. The RS calculation is for gas only.

P3 := 500 atm

cm³/g

$V_{RG}(TT, T_{c_H2O}, P3, x_G, x_V, x_{LV}, x_L, V_{c_L_H2O}, V_{c_LV_H2O}, V_{c_V_H2O}, V_{c_G_H2O})$

$V_{Peng_Robinson}(TT, P3, P_{c_H2O}, T_{c_H2O}, w_{H2O}, \omega_{H2O})$

$V_G(TT, P3)$

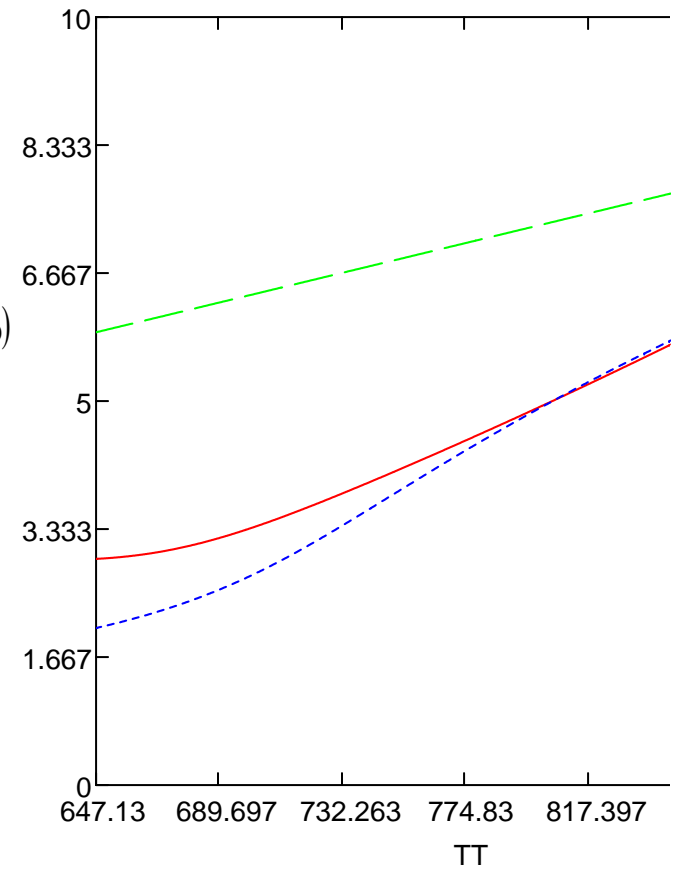


Figure 23. Water Gas Specific Volume at 500 atm

Sample Calculation for 2-D Water Gas, Fixed T, Varying P

$$T1 := T_{c_H2O} + \frac{T_{SL_u}}{2} \quad T1 = 902.53 \quad K \quad T2 := 750 \quad K \quad \text{cm}^3/\text{g}$$

$$\underline{V_{RG}}(T1, T_{c_H2O}, PP, x_G, x_V, x_{LV}, x_L, V_{c_L_H2O}, V_{c_LV_H2O}, V_{c_V_H2O}, V_{c_G_H2O})$$

$$\underline{V_{Peng_Robinson}}(T1, PP, P_{c_H2O}, T_{c_H2O}, w_{H2O}, \omega_{H2O})$$

$$\underline{V_G}(T1, PP)$$

$$\underline{V_{RG}}(T2, T_{c_H2O}, PP, x_G, x_V, x_{LV}, x_L, V_{c_L_H2O}, V_{c_LV_H2O}, V_{c_V_H2O}, V_{c_G_H2O})$$

$$\underline{V_{Peng_Robinson}}(T2, PP, P_{c_H2O}, T_{c_H2O}, w_{H2O}, \omega_{H2O})$$

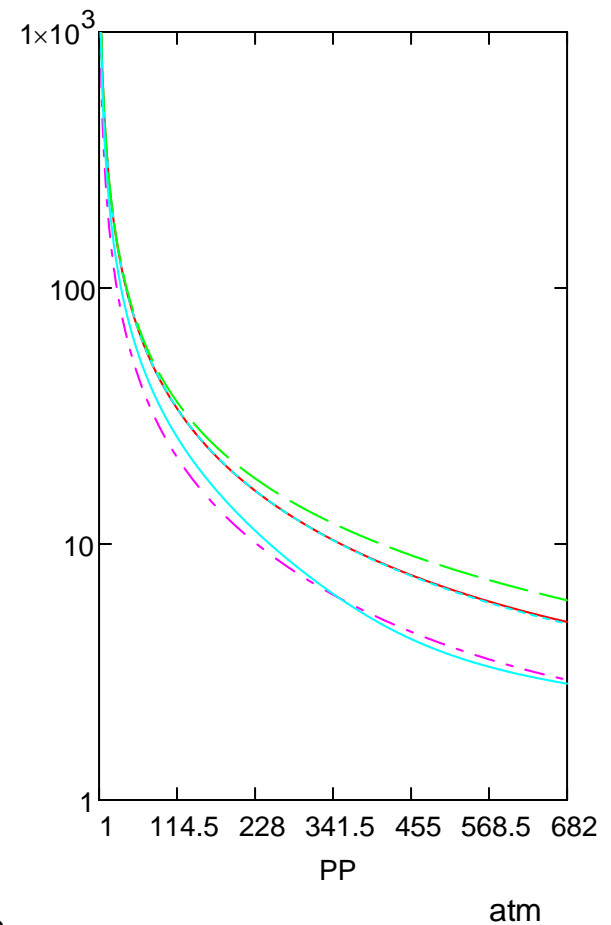


Figure 24. Water Gas Specific Volume at T1 and T2 Over Whole Pressure Range

This figure was useful in determining the correct values of x_G , x_V , x_{LV} , and x_L to use for H₂O.

Sample Calculation for 2-D Nitrogen, Fixed T, Varying P

$$n_T := 6 \quad w_{N2} := 28.0134 \quad T_{c_N2} := \left[\frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{N2}}{1} \right)^{\frac{1}{4}} - 1 \right] \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{N2}}{1}} \quad T_{c_N2} = 113.36413$$

$$P_{c_N2_obs} := 33.45591$$

$$T_{c_N2_obs} := 126.21 \text{ K} \quad (\text{we'll use this value, pending clarification}) \quad T_{c_N2} := T_{c_N2_obs}$$

$$T_{m_N2} := 63.15 \text{ K} \quad n_V := 3 \quad n_{s1} := 1 \quad n_{s2} := 1 \quad n_P := 3 \quad \Delta V := 0 \quad P := 1 \text{ atm} \quad T := T_{c_N2} \text{ K}$$

(assumed hexagonal close-packing)

$$V_{c_L_N2} := V_{liq}(n_V, w_{N2}, n_{s1}, T, T_{m_N2}, \Delta V, n_{s2}, n_T, n_P, P_{c_N2_obs}, T_{c_N2}) \quad V_{c_L_N2} = 2.26 \text{ cm}^3/\text{g}$$

$$V_{c_LV_N2} := 1.4165 \cdot V_{c_L_N2} \quad V_{c_LV_N2} = 3.20129 \text{ cm}^3/\text{g}$$

$$V_{c_V_N2} := 2 \cdot V_{c_L_N2} \quad V_{c_V_N2} = 4.52 \text{ cm}^3/\text{g} \quad V_{c_G_N2} := \frac{2}{3} \cdot 1244.178 \cdot \frac{T_{c_N2_obs}}{273.15} \cdot \frac{1}{P_{c_N2_obs}}$$

$$V_{c_G_N2} = 11.45542 \text{ cm}^3/\text{g} \quad \rho_{c_G_N2} := \frac{1}{V_{c_G_N2}} \quad \rho_{c_G_N2} = 0.08729 \text{ g/cm}^3$$

$$x_G := \frac{1}{6} \quad x_V := \frac{1}{6} \quad x_{LV} := \frac{1}{6} \quad x_L := \frac{1}{9} \quad (\text{by iteration with graph below})$$

$$P_{L_N2} := P_L(x_L, T_{c_N2}, T_{c_N2}, V_{c_L_N2})$$

$$P_{L_N2} = 157.22742$$

$$P_{LV_N2} := P_{LV}(x_{LV}, T_{c_N2}, T_{c_N2}, V_{c_L_N2}, V_{c_LV_N2})$$

$$P_{LV_N2} = 110.52253$$

$$P_{V_N2} := P_V(x_V, T_{c_N2}, T_{c_N2}, V_{c_L_N2}, V_{c_V_N2})$$

$$P_{V_N2} = 80.0719$$

$$P_{G_N2} := P_G(x_G, T_{c_N2}, T_{c_N2}, V_{c_L_N2}, V_{c_G_N2})$$

$$P_{G_N2} = 32.69572$$

$$T1 := T_{c_N2} + \frac{T_{SL_u}}{2} \quad T1 = 381.61 \quad K \quad T2 := 300 \quad K \quad \omega_{N2} := .040 \quad (\text{Ref. 8, p. 27})$$

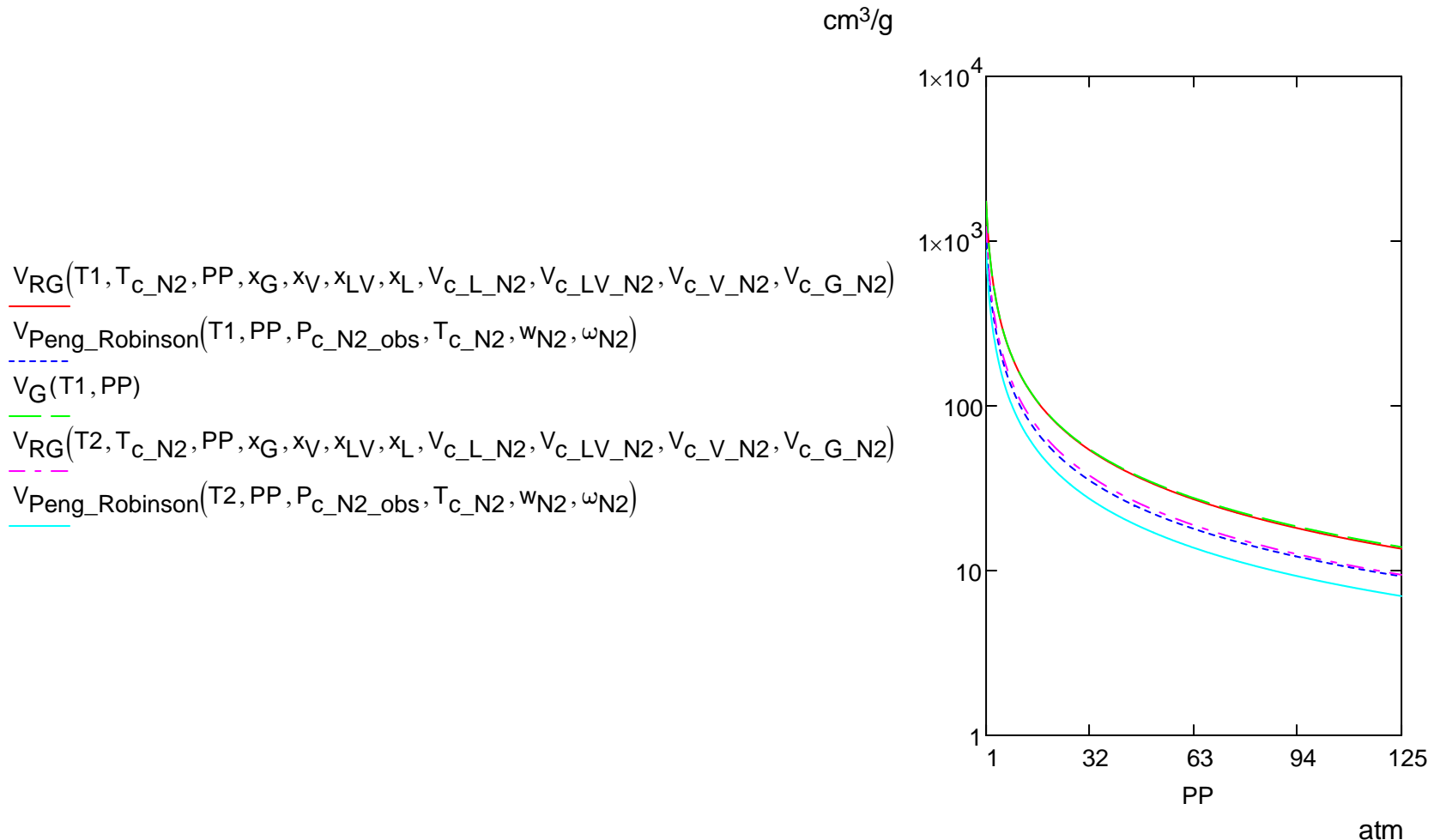


Figure 25. Nitrogen Gas Specific Volume at T1 and T2 Over Whole Pressure Range

The equations given above may be applied to any gas. The Reciprocal System Database will handle all the calculations automatically; of course, the appropriate values of x_G , x_V , x_{LV} , and x_L have to be entered; the values range from 1/9 to 6. Of course, we must have $P_L > P_{LV} > P_V > P_G$. Please note that these are *physical* parameters, not empirical regression coefficients, and must make sense physically. Unfortunately, the Peng-Robinson equation is too complicated to use in the the Reciprocal System Database, so a four-term Virial expansion of the Redlich-Kwong equation will be used as a means of comparison.

18. Idea Gas Volume ($P \ll P_c$ or $T > T_c + 1/2 T_{SL_U}$), Specific Heat, Enthalpy, and Entropy

Basic Properties of Ideal Gas

In Ref. [3], pp. 196-197, Larson says: "The usual method of analyzing this situation is to consider an example in which n gas particles of mass m are enclosed in a cubical container s units of length in each dimension. The direction of motion of the gas particles is governed entirely by the probability of the result of random collisions, hence by the General Probability Law the velocities will be distributed equally in all directions. If we resolve the total motion into components parallel to the three perpendicular axes we have $n/3$ particles which can collide with face A. Each of these particles will do so every $2s$ units of travel and at velocity v the collisions will happen $v/2s$ times per unit of time.

"Each collision changes the momentum of the particle from mv to $-mv$, a total change of $2mv$ and since there are $v/2s$ collisions per unit of time the total change of momentum per particle per unit of time will be $v/2s \times 2mv = mv^2/s$. But the change of momentum per unit of time is force and we can multiply mv^2/s by the number of particles $n/3$ and divide by the area s^2 of face A to obtain the pressure

$$P = \frac{n}{3} \cdot \frac{m \cdot v^2}{s} \cdot \frac{1}{s^2} \quad (17.1)$$

"Since s^3 is the volume V we may express this as

$$P = \frac{n}{3} \cdot \frac{m \cdot v^2}{V} \quad (17.2)$$

"or

$$P \cdot V = \frac{1}{3} \cdot n \cdot m \cdot v^2 \quad (17.3)$$

"But $1/2 mv^2$ is the kinetic or heat energy and we can therefore rewrite equation 17.3 in terms of energy

$$P \cdot V = \frac{2}{3} \cdot n \cdot H \quad (17.4)$$

"When applied to a single particle or any other constant mass this becomes

$$P \cdot V = \frac{2}{3} \cdot H \quad (17.5)$$

"which tells us that the effective pressure energy PV of this confined gas is $2/3$ of the total thermal energy H ."

But:

$$P \cdot V = R \cdot T$$

so

$$\frac{2}{3} \cdot H = RT$$

or

$$H = \frac{3}{2} \cdot R \cdot T \quad (17.9)$$

.

.

From this we obtain by differentiation the *specific heat at constant volume*:

$$\frac{d}{dT}H = \frac{3}{2} \cdot R \quad \text{or} \quad c_v := \frac{3}{2} \cdot R \quad (17.10)$$

"Because of the linear relation between energy and temperature in the time-space region this gaseous specific heat is a constant and does not vary with the temperature.

"It is also desirable for many purposes to know the specific heat under constant pressure. Heating a gas under constant pressure is equivalent to heating it at constant volume and then expanding it back to the original pressure. The total specific heat therefore includes the specific heat at constant volume and the increment of energy required to increase the volume. The volume increase requires energy because it takes place against pressure and therefore decreases the product PV. The magnitude of the energy is measured by the change in this quantity. But equation 12.10 tells us that $PV = T$, or $PV = RT$ in conventional units, and the derivative of PV with respect to T is R. The *specific heat at constant pressure* is therefore

$$\frac{d}{dT}H = \frac{3}{2} \cdot R + R \quad \text{or} \quad c_p := \frac{5}{2} \cdot R \quad (17.11)$$

For compounds, Larson says, Ref. [3], p. 229: "At the two-dimensional initial point the specific heat is R per unit of internal motion less than the maximum and since each thermal group which is active in the temperature range under consideration constitutes a unit of thermal motion a molecule with n [n_a] atoms and m [n_{GTG}] thermal groups has a specific heat of $(2 + 1/2 R)(n_a - n_{GTG})$."

When n_{GTG} goes to zero, the molecule is *dissociated* and each atom goes its own independent way.

Gram-Molecular Ideal Gas Volume

Recall that

$$A_v = 6.02486 \times 10^{23} \quad T_u = 7.20423 \times 10^{12} \text{ K} \quad s_u^3 = 9.4745 \times 10^{-17} \text{ cm}^3 \quad P_{u_atm} := 15538642 \text{ atm}$$

Under natural unit conditions

$$V_{\text{mol}_u} := A_v \cdot s_u^3 \quad V_{\text{mol}_u} = 5.70825 \times 10^7 \text{ cm}^3 / \text{mol} \quad (81)$$

This is the gram-molecular volume under unit conditions of P_{u_atm} and T_u

Under standard conditions

$P := 1 \text{ atm}$ $T := 273.15 \text{ K}$ Recall that R is 2/3 of the Reciprocal System natural unit of specific heat.

$$V_{\text{mol}} := V_{\text{mol}_u} \cdot \frac{P_{u_atm}}{P} \cdot \frac{T}{T_u} \cdot \frac{2}{3} \quad V_{\text{mol}} = 22420.15385 \text{ cm}^3 / \text{mol} \quad (82)$$

This is the gram-molecular volume at standard conditions

The accepted value is 22413.996 cm³/mol. Therefore ratio of calculated to observed is $\frac{22420.153141}{22413.996} = 1.00027$

Symbols for Real / Ideal Gas Properties

Let

$T_{G_3D_0}$ = temperature of 3D gas at initial point, K (when *internal motion* reaches the three-dimensional state)

$T_{G_2D_0}$ = temperature of 2D gas at initial point, K (when *internal motion* leaves the liquid state and assumes the status of a two-dimensional gas)

$T_{G_2.5D_0}$ = temperature intermediate between $T_{G_3D_0}$ and $T_{G_2D_0}$, K

T_{L_0} = temperature of liquid at very beginning of transition to gas, K

n_{GTG_0} = number of thermal groups in gas (integer or half integer) at 2D gas initial point

n_{GTG_1} = number of thermal groups in gas (integer or half-integer) just *before* going to zero at 3D gas initial point or thereafter

n_a = number of atoms per molecule

c_{p_G} = specific heat of gas (from *both* internal and external motion), cal/mol K

l_T = initial level in terms of natural temperature unit for 2D and 3D gas temperatures (fraction)

T_{diss} = temperature of dissociation

Gas Specific Heat

Water Specific Heat, H₂O

Reciprocal System (using $T_{G_2D_0}$ and $T_{G_3D_0}$)

$$T_{c_H2O} = 647.13$$

$$T_{L_0} := T_{c_H2O} - \frac{T_{SL_u}}{2} \quad I_T := \frac{2}{9} \quad n_a := 3 \quad n_{GTG_0} := 1.3 \quad (\text{apparently an average of 1 and 1.5})$$

$$T_{L_0} = 391.73 \text{ K}$$

$$n_{GTG_1} := 1$$

$$T_{G_3D_0} := 3 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad (84)$$

$$T_{G_3D_0} = 1027.15889 \text{ K}$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad (85)$$

$$T_{G_2D_0} = 516.35889 \text{ K}$$

$$c_{p_G} := \frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) \quad (86)$$

$$c_{p_G} = 8.44432 \text{ cal/mol K} \quad (\text{at } T_{G_2D_0})$$

Variation of specific heat from $T_{G_2D_0}$ to $T_{G_3D_0}$

$$\frac{5}{2} \cdot R \cdot (n_a - n_{GTG_1}) - \frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) = m \cdot (T_{G_3D_0} - T_{G_2D_0}) \quad (m \text{ is slope of line here})$$

$$n_{GTG_1} := 1 \quad (\text{just before going to zero after } T_{G_3D_0})$$

$$m := \frac{5 \cdot R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_3D_0} - T_{G_2D_0})}$$

$$\text{Therefore: } c_{p_G} := \frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) + \frac{5 \cdot R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_3D_0} - T_{G_2D_0})} \cdot (T - T_{G_2D_0}) \quad (87)$$

Yaws Regression (Ref. [8])

$$A := 33.933 \quad B := -8.4186 \cdot 10^{-3} \quad C := 2.9906 \cdot 10^{-5} \quad D := -1.7825 \cdot 10^{-8} \quad E := 3.6934 \cdot 10^{-12}$$

$$c_{p_G_H2O} := A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^4$$

cal/mol K

$$\frac{\frac{5}{2} \cdot R \cdot (n_a - n_{\text{GTG}_0}) + \frac{5 \cdot R \cdot (n_{\text{GTG}_0} - n_{\text{GTG}_1})}{2(T_{\text{G}_3\text{D}_0} - T_{\text{G}_2\text{D}_0})} \cdot (TT - T_{\text{G}_2\text{D}_0})}{\frac{A + B \cdot TT + C \cdot TT^2 + D \cdot TT^3 + E \cdot TT^4}{\text{conv}_{\text{caltoJ}}}}$$

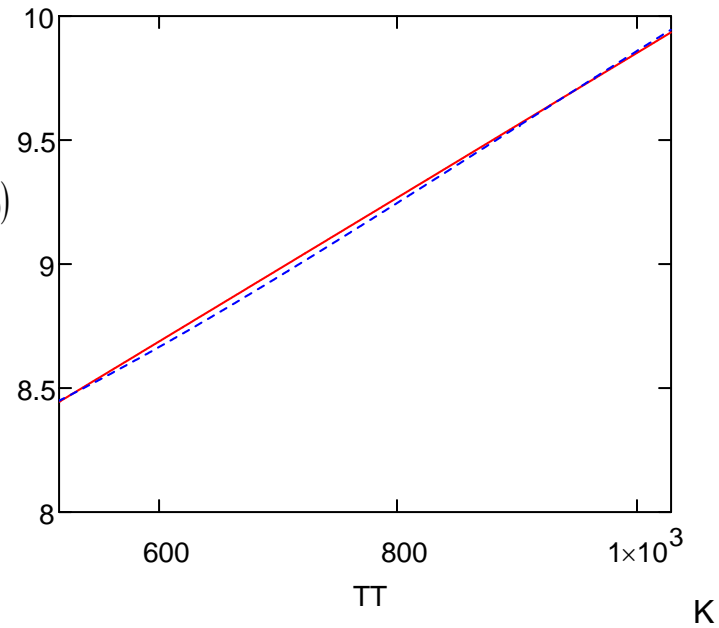


Figure 26. Water Gas Specific Heat

Note: the dissociation temperature is that which results in each atom having $5/2 R$ of energy. For water:

$$T_{\text{diss}} := -\frac{T_{\text{G}_2\text{D}_0} \cdot n_{\text{GTG}_1} - T_{\text{G}_3\text{D}_0} \cdot n_{\text{GTG}_0}}{n_{\text{GTG}_0} - n_{\text{GTG}_1}} \quad T_{\text{diss}} = 2729.82556 \quad \text{K}$$

Hexane Specific Heat, C₆H₁₄**Reciprocal System** (using T_{G_2D_0} and T_{G_3D_0})

$$T_{c_hexane} = 507.43$$

$$T_{L_0} := T_{c_hexane} - \frac{T_{SL_u}}{2} \quad T_{L_0} = 252.03 \quad K \quad n_a := 20 \quad n_{GTG_0} := 7 \quad n_{GTG_1} := 3$$

$$T_{G_3D_0} := 3 \cdot T_{SL_u} - T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1166.85889 \quad K$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 656.05889 \quad K$$

$$c_{p_G} := \frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) + \frac{5 \cdot R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_3D_0} - T_{G_2D_0})} \cdot (T - T_{G_2D_0})$$

Yaws Regression (Ref. [8])

$$A := 25.924 \quad B := 4.1927 \cdot 10^{-1} \quad C := -1.2491 \cdot 10^{-5} \quad D := -1.5916 \cdot 10^{-7} \quad E := 5.8784 \cdot 10^{-11}$$

$$c_{p_G_hexane} := A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^4$$

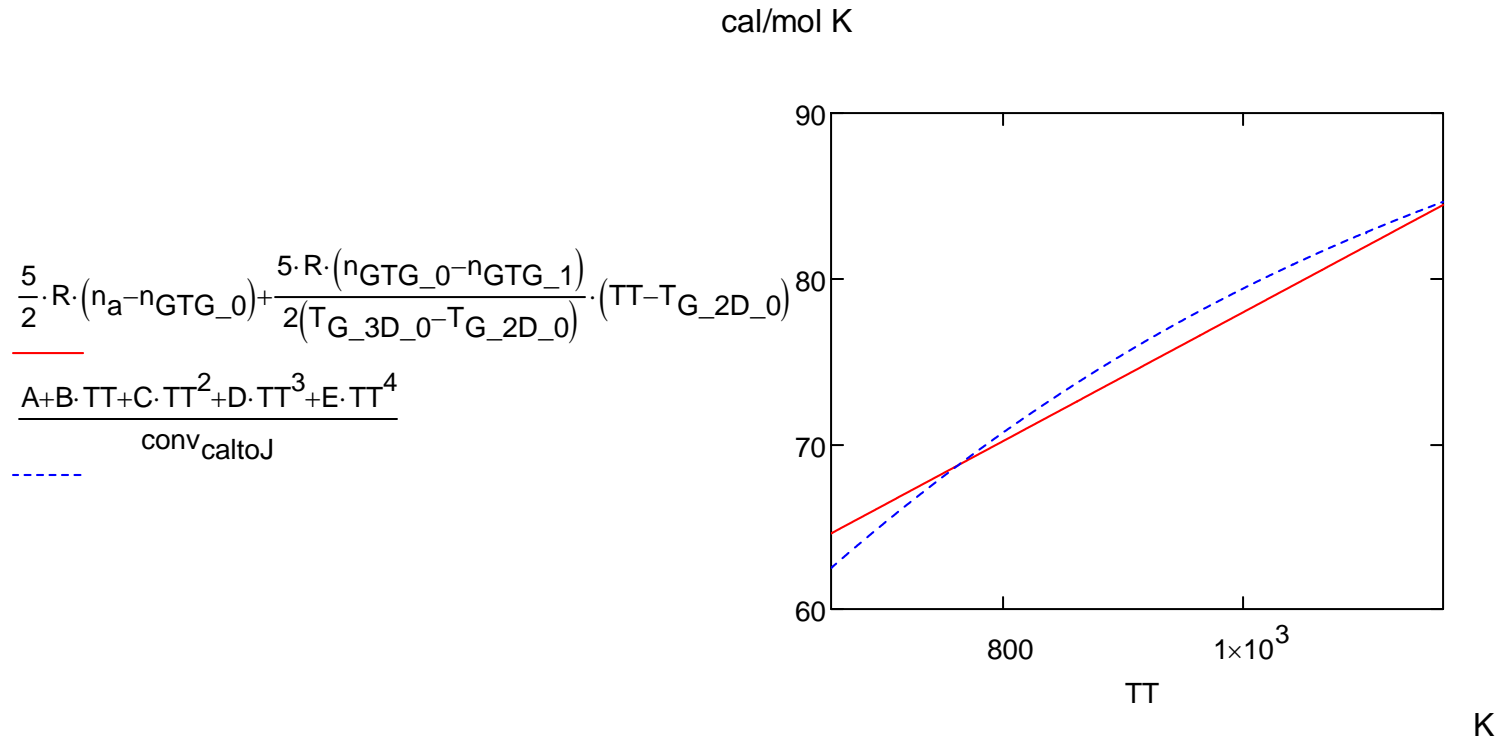


Figure 27. Hexane Gas Specific Heat

$$T_{\text{diss}} := -\frac{T_{G_2D_0} \cdot n_{GTG_1} - T_{G_3D_0} \cdot n_{GTG_0}}{n_{GTG_0} - n_{GTG_1}} \quad T_{\text{diss}} = 1549.95889 \text{ K}$$

Nitrogen Specific Heat, N₂**Reciprocal System** (using T_{G_3D_0})

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{N2} := 28.0134 \quad n_T := 5.5 \quad T_{c_N2} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{N2}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{N2}}{1}} \quad T_{c_N2} = 131.59826$$

$$T_{c_N2_obs} := 126.21 \quad K \quad (\text{we'll use this value, pending clarification}) \quad T_{c_N2} := T_{c_N2_obs}$$

$$T_{L_0} := T_{c_N2} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -129.19 \quad K \quad T_{L_0} := T_{c_N2} \quad \text{We cannot have anything below 0 K.}$$

$$T_{G_3D_0} := 3 \cdot T_{SL_u} - n_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1292.67889 \quad K$$

There is no T_{G_2D_0} for N₂. The specific heat at T_{L_0} is R for the internal motion and 2.5 R for the external motion, for a total of 3.5 R for the molecule. There is a linear increase to 4 R at T_{G_3D_0}. The full specific heat of 5/2 R for *each* of the two atoms is reached considerably *after* T_{G_3D_0}

Yaws Regression (Ref. [8])

$$A := 29.342 \quad B := -3.5395 \cdot 10^{-3} \quad C := 1.0076 \cdot 10^{-5} \quad D := -4.3116 \cdot 10^{-9} \quad E := 2.5935 \cdot 10^{-13}$$

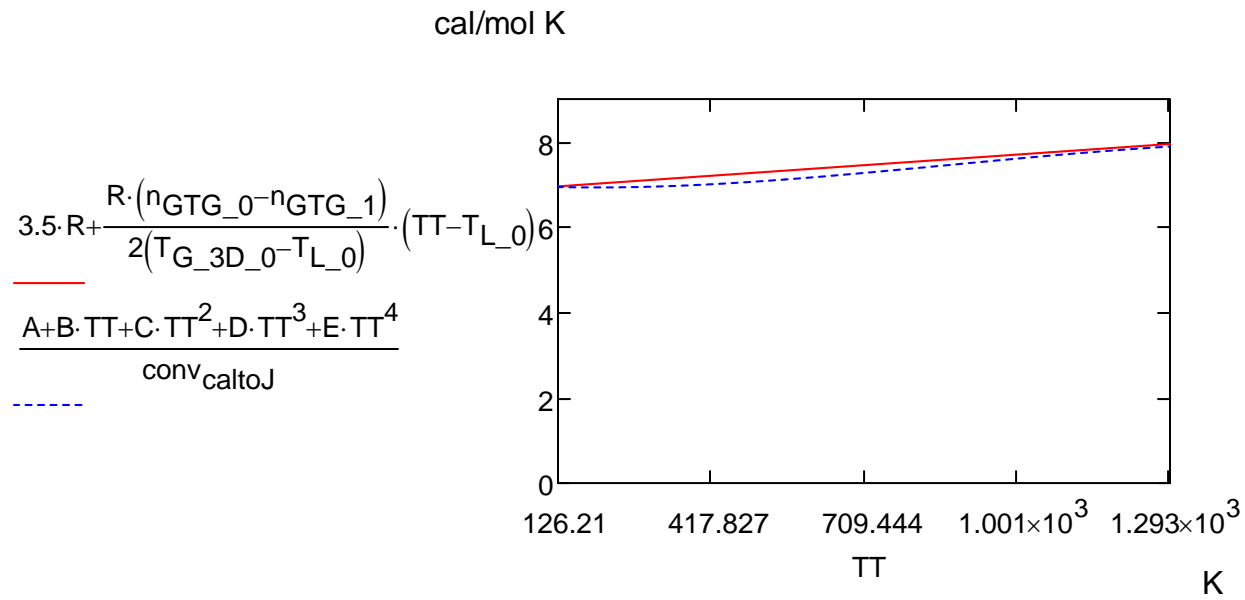


Figure 28. Nitrogen Gas Specific Heat

$$T_{\text{diss}} := \frac{7.0 \cdot T_{\text{L}_0} - 7.0 \cdot T_{\text{G}_3\text{D}_0} - 5.0 \cdot T_{\text{L}_0} \cdot n_a + 5.0 \cdot T_{\text{G}_3\text{D}_0} \cdot n_a + T_{\text{L}_0} \cdot n_{\text{GTG}_0} - 1.0 \cdot T_{\text{L}_0} \cdot n_{\text{GTG}_1}}{n_{\text{GTG}_0} - 1.0 \cdot n_{\text{GTG}_1}}$$

$$T_{\text{diss}} = 3625.61667 \quad \text{K}$$

Nitric Oxide Specific Heat, NO**Reciprocal System** (using $T_{G_2D_0}$)

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{NO} := 30.006 \quad n_T := 5 \quad T_{c_NO} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{NO}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{NO}}{1}} \quad T_{c_NO} = 172.12197$$

$$T_{c_NO_obs} := 180 \quad \text{we'll use this pending clarification} \quad T_{c_NO} := T_{c_NO_obs}$$

$$T_{L_0} := T_{c_NO} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -75.4 \quad K \quad T_{L_0} := T_{c_NO} \quad \text{We cannot have anything below 0 K.}$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - n_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 728.08889 \quad K$$

There is no $T_{G_3D_0}$ for NO. The specific heat at T_{L_0} is R for the internal motion and 2.5 R for the external motion, for a total of 3.5 R for the molecule. There is a linear increase to 4 R at $T_{G_2D_0}$. The full specific heat of 5/2 R for *each* of the two atoms is reached considerably *after* $T_{G_2D_0}$ here.

Yaws Regression (Ref. [8])

$$A := 33.227 \quad B := -2.3626 \cdot 10^{-2} \quad C := 5.3156 \cdot 10^{-5} \quad D := -3.7858 \cdot 10^{-8} \quad E := 9.1197 \cdot 10^{-12}$$

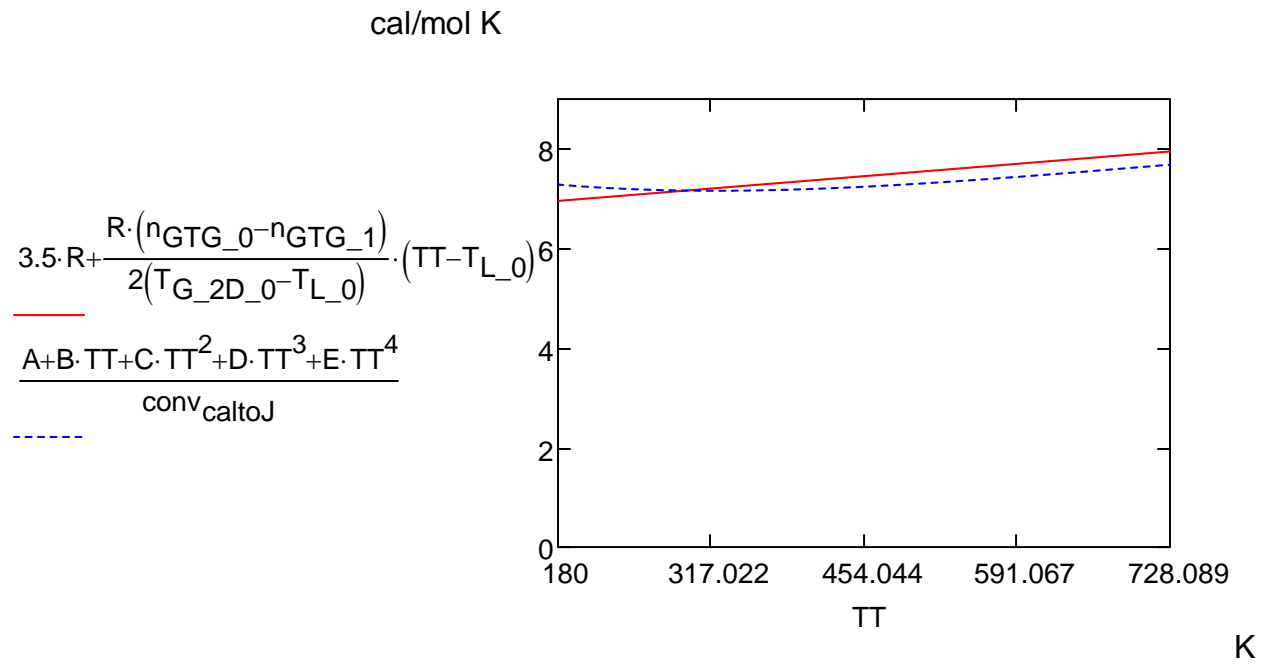


Figure 29. Nitric Oxide Gas Specific Heat

$$T_{\text{diss}} := \frac{7.0 \cdot T_{\text{L}_0} - 7.0 \cdot T_{\text{G}_2\text{D}_0} - 5.0 \cdot T_{\text{L}_0} \cdot n_{\text{a}} + 5.0 \cdot T_{\text{G}_2\text{D}_0} \cdot n_{\text{a}} + T_{\text{L}_0} \cdot n_{\text{GTG}_0} - 1.0 \cdot T_{\text{L}_0} \cdot n_{\text{GTG}_1}}{n_{\text{GTG}_0} - 1.0 \cdot n_{\text{GTG}_1}}$$

$$T_{\text{diss}} = 1824.26667 \quad \text{K}$$

Carbon Monoxide Specific Heat, CO**Reciprocal System** (using $T_{G_2.5D_0}$)

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{CO} := 28.01 \quad n_T := 5.5 \quad T_{c_CO} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{CO}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{CO}}{1}} \quad T_{c_CO} = 131.55609$$

$$T_{c_CO_obs} := 132.86$$

$$T_{L_0} := T_{c_CO} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -123.84391 \quad K \quad T_{L_0} := T_{c_CO} \quad \text{We cannot have anything below 0 K.}$$

$$T_{G_2.5D_0} := 2.5 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad (88)$$

$$T_{G_2.5D_0} = 1031.9328$$

The specific heat at T_{L_0} is R for the internal motion and 2.5 R for the external motion, for a total of 3.5 R for the molecule. There is a linear increase to 4 R at $T_{G_2.5D_0}$. The full specific heat of 5/2 R for *each* of the two atoms is reached considerably *after* $T_{G_2.5D_0}$ here.

Yaws Regression (Ref. [8])

$$A := 29.556 \quad B := -6.5807 \cdot 10^{-3} \quad C := 2.0130 \cdot 10^{-5} \quad D := -1.2227 \cdot 10^{-8} \quad E := 2.2617 \cdot 10^{-12}$$

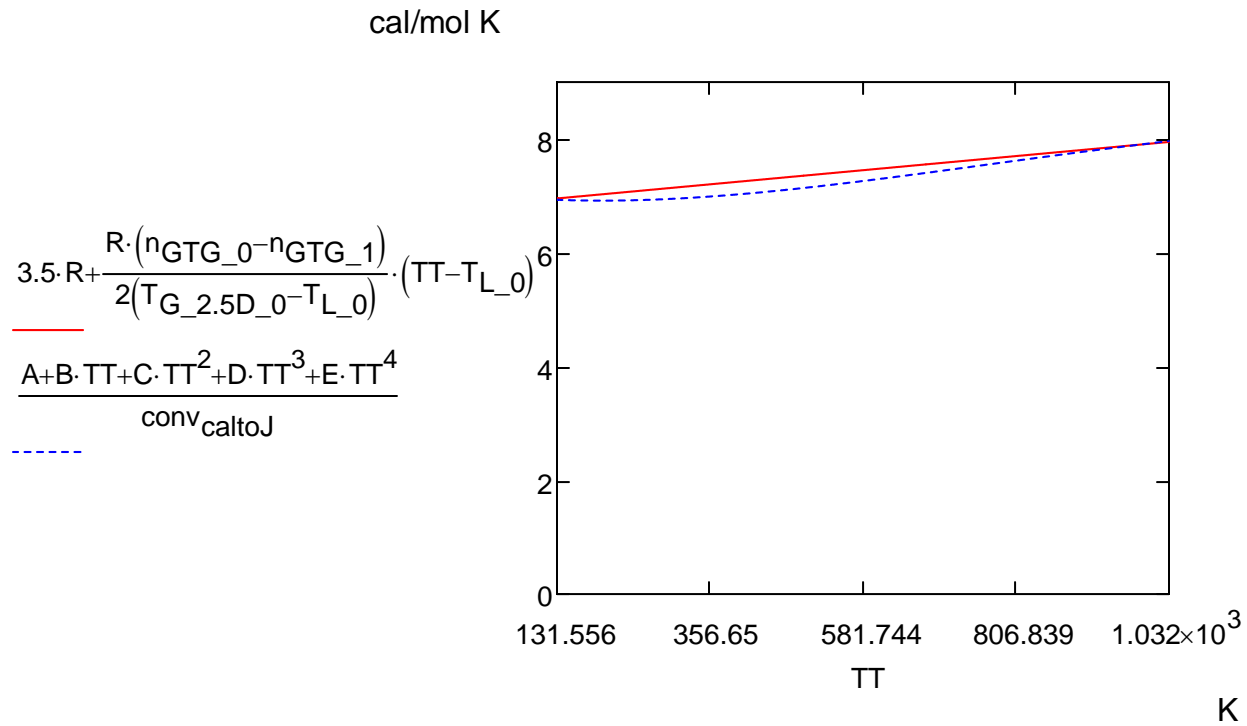


Figure 30. Carbon Monoxide Gas Specific Heat

$$T_{\text{diss}} := \frac{7.0 \cdot T_{\text{L}_0} - 7.0 \cdot T_{\text{G}_2.5\text{D}_0} - 5.0 \cdot T_{\text{L}_0} \cdot n_a + T_{\text{L}_0} \cdot n_{\text{GTG}_0} - 1.0 \cdot T_{\text{L}_0} \cdot n_{\text{GTG}_1} + 5.0 \cdot T_{\text{G}_2.5\text{D}_0} \cdot n_a}{n_{\text{GTG}_0} - 1.0 \cdot n_{\text{GTG}_1}}$$

$$T_{\text{diss}} = 2832.68624 \quad \text{K}$$

Oxygen Specific Heat, O₂

Reciprocal System (using T_{G_2D_0})

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{O2} := 31.9988 \quad n_T := 6 \quad T_{c_O2} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{O2}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{O2}}{1}} \quad T_{c_O2} = 160.48412$$

$$T_{c_O2_obs} := 154.59 \quad \text{We'll use this pending clarification.} \quad T_{c_O2} := T_{c_O2_obs}$$

$$T_{L_0} := T_{c_O2} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -100.81 \quad K \quad T_{L_0} := T_{c_O2} \quad \text{cannot have anything below 0 K}$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - |T| \cdot T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 753.49889$$

The specific heat at T_{L_0} is R for the internal motion and 2.5 R for the external motion, for a total of 3.5 R for the molecule. There is a linear increase to 4 R at T_{G_2.5D_0}. The full specific heat of 5/2 R for *each* of the two atoms is reached considerably *after* T_{G_2D_0} here.

Yaws Regression (Ref. [8])

$$A := 29.526 \quad B := -8.8999 \cdot 10^{-3} \quad C := 3.8083 \cdot 10^{-5} \quad D := -3.2629 \cdot 10^{-8} \quad E := 8.8607 \cdot 10^{-12}$$

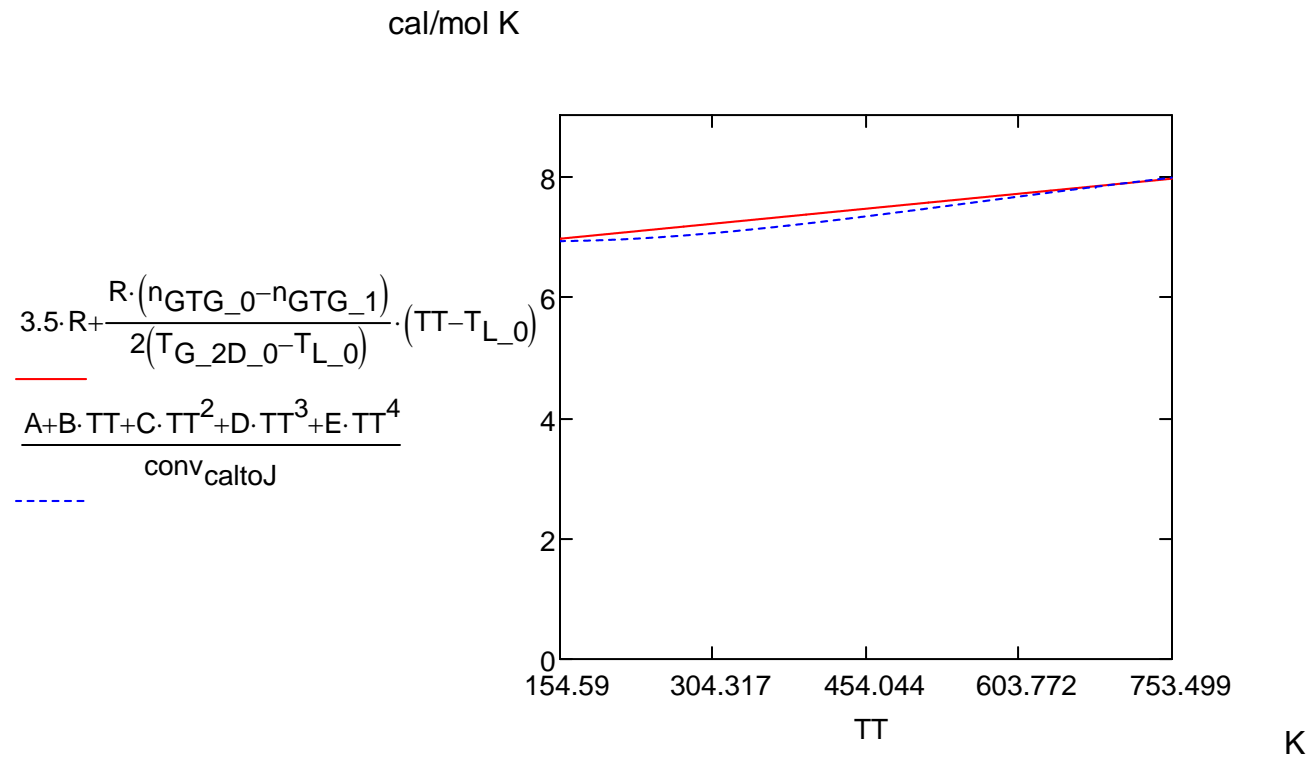


Figure 31. Oxygen Gas Specific Heat

$$T_{\text{diss}} := \frac{7.0 \cdot T_{L_0} - 7.0 \cdot T_{G_2D_0} - 5.0 \cdot T_{L_0} \cdot n_a + 5.0 \cdot T_{G_2D_0} \cdot n_a + T_{L_0} \cdot n_{GTG_0} - 1.0 \cdot T_{L_0} \cdot n_{GTG_1}}{n_{GTG_0} - 1.0 \cdot n_{GTG_1}}$$

$$T_{\text{diss}} = 1951.31667 \quad \text{K}$$

Methane Specific Heat, CH₄**Reciprocal System** (Using T_{G_2D_0} and T_{G_3D_0})

$$n_a := 5 \quad n_{GTG_0} := 2 \quad n_{GTG_1} := 1$$

$$w_{\text{methane}} := 16.414 \quad n_T := 1 \quad T_{c_methane} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{\text{methane}}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{\text{methane}}}{1}}$$

$$T_{c_methane} = 196.4331 \quad T_{c_methane_obs} := 190.56 \quad \text{We'll use this pending clarification.}$$

$$T_{c_methane} := T_{c_methane_obs}$$

$$T_{L_0} := T_{c_methane} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -64.84 \quad K \quad T_{L_0} := T_{c_methane} \quad \text{cannot have anything below 0 K}$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - |T| \cdot T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 717.52889$$

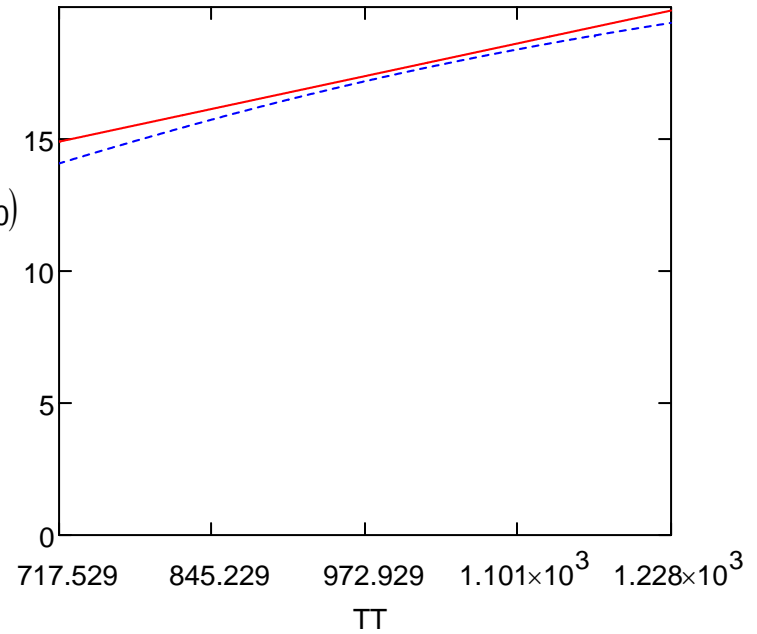
$$T_{G_3D_0} := 3 \cdot T_{SL_u} - |T| \cdot T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1228.32889$$

Yaws Regression (Ref. [8])

$$A := 34.942 \quad B := -3.9957 \cdot 10^{-2} \quad C := 1.9184 \cdot 10^{-4} \quad D := -1.5303 \cdot 10^{-7} \quad E := 3.9321 \cdot 10^{-11}$$

cal/mol K

$$\frac{\frac{5}{2} \cdot R \cdot (n_a - n_{\text{GTG}_0}) + \frac{5 \cdot R \cdot (n_{\text{GTG}_0} - n_{\text{GTG}_1})}{2(T_{\text{G}_3\text{D}_0} - T_{\text{G}_2\text{D}_0})} \cdot (T - T_{\text{G}_2\text{D}_0})}{\frac{A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^4}{\text{conv}_{\text{caltoJ}}}}$$



K

Figure 32. Methane Gas Specific Heat

$$T_{\text{diss}} := -\frac{T_{\text{G}_2\text{D}_0} \cdot n_{\text{GTG}_1} - T_{\text{G}_3\text{D}_0} \cdot n_{\text{GTG}_0}}{n_{\text{GTG}_0} - n_{\text{GTG}_1}}$$

$$T_{\text{diss}} = 1739.12889 \text{ K}$$

Propane Specific Heat, C₃H₈**Reciprocal System** (Using T_{G_2D_0} and T_{G_3D_0})

$$n_a := 11 \quad n_{\text{GTG}_0} := 4 \quad n_{\text{GTG}_1} := 1$$

$$w_{\text{propane}} := 44.096 \quad n_T := 1 \quad T_{\text{c_propane}} := \frac{T_{\text{SL_u}}}{2} \cdot \left[\left(\frac{w_{\text{propane}}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{\text{SL_u}} \cdot \frac{n_T}{\frac{w_{\text{propane}}}{1}}$$

$$T_{\text{c_propane}} = 379.57601 \quad T_{\text{c_propane_obs}} := 369.83$$

We'll use this pending clarification. $T_{\text{c_propane}} := T_{\text{c_propane_obs}}$

$$T_{\text{L}_0} := T_{\text{c_propane}} - \frac{T_{\text{SL_u}}}{2} \quad T_{\text{L}_0} = 114.43 \quad \text{K}$$

$$T_{\text{G}_2\text{D}_0} := 2 \cdot T_{\text{SL_u}} - 1_T \cdot T_{\text{SL_u}} - T_{\text{L}_0} \quad T_{\text{G}_2\text{D}_0} = 793.65889$$

$$T_{\text{G}_3\text{D}_0} := 3 \cdot T_{\text{SL_u}} - 1_T \cdot T_{\text{SL_u}} - T_{\text{L}_0} \quad T_{\text{G}_3\text{D}_0} = 1304.45889$$

Yaws Regression (Ref. [8])

$$A := 28.277 \quad B := 1.1600 \cdot 10^{-1} \quad C := 1.9597 \cdot 10^{-4} \quad D := -2.3271 \cdot 10^{-7} \quad E := 6.8669 \cdot 10^{-11}$$

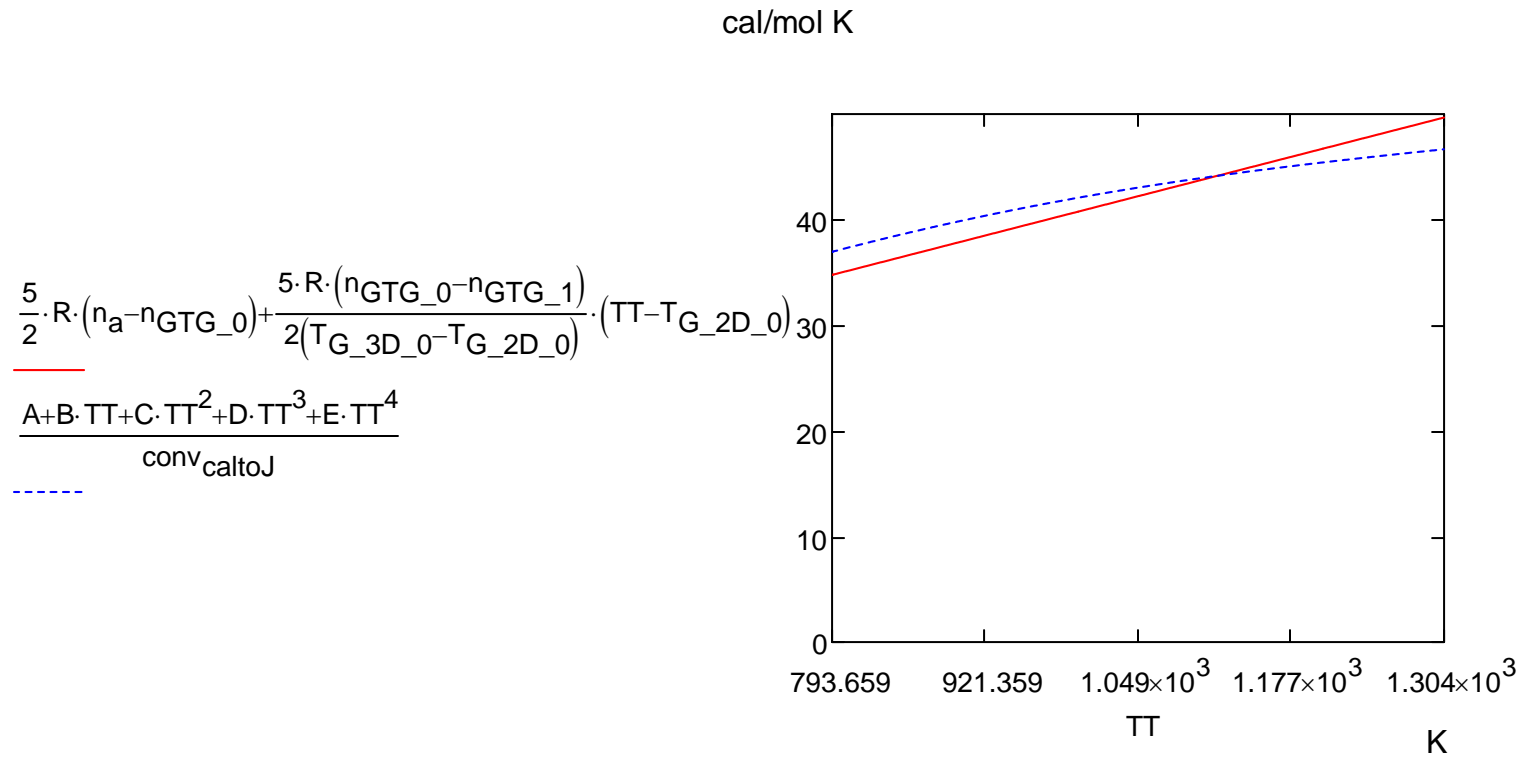


Figure 33. Propane Gas Specific Heat

$$T_{\text{diss}} := -\frac{T_{\text{G}_2\text{D}_0} \cdot n_{\text{GTG}_1} - T_{\text{G}_3\text{D}_0} \cdot n_{\text{GTG}_0}}{n_{\text{GTG}_0} - n_{\text{GTG}_1}} \quad T_{\text{diss}} = 1474.72556 \text{ K}$$

Octane Specific Heat, C₈H₁₈**Reciprocal System** (Using T_{G_2D_0} and T_{G_3D_0})

$$n_a := 26 \quad n_{\text{GTG}_0} := 10 \quad n_{\text{GTG}_1} := 4$$

$$w_{\text{octane}} := 114.2290 \quad n_T := 1 \quad T_{\text{c_octane}} := \frac{T_{\text{SL_u}}}{2} \cdot \left[\left(\frac{w_{\text{octane}}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{\text{SL_u}} \cdot \frac{n_T}{\frac{w_{\text{octane}}}{1}}$$

$$T_{\text{c_octane}} = 570.61525 \quad T_{\text{c_octane_obs}} := 568.7$$

$$T_{\text{L}_0} := T_{\text{c_octane}} - \frac{T_{\text{SL_u}}}{2} \quad T_{\text{L}_0} = 315.21525 \quad \text{K}$$

$$T_{\text{G}_2\text{D}_0} := 2 \cdot T_{\text{SL_u}} - T_{\text{T}} \cdot T_{\text{SL_u}} - T_{\text{L}_0} \quad T_{\text{G}_2\text{D}_0} = 592.87364$$

$$T_{\text{G}_3\text{D}_0} := 3 \cdot T_{\text{SL_u}} - T_{\text{T}} \cdot T_{\text{SL_u}} - T_{\text{L}_0} \quad T_{\text{G}_3\text{D}_0} = 1103.67364$$

Yaws Regression

$$A := 29.053 \quad B := 5.8016 \cdot 10^{-1} \quad C := -5.7103 \cdot 10^{-5} \quad D := -1.9548 \cdot 10^{-7} \quad E := 7.6614 \cdot 10^{-11}$$

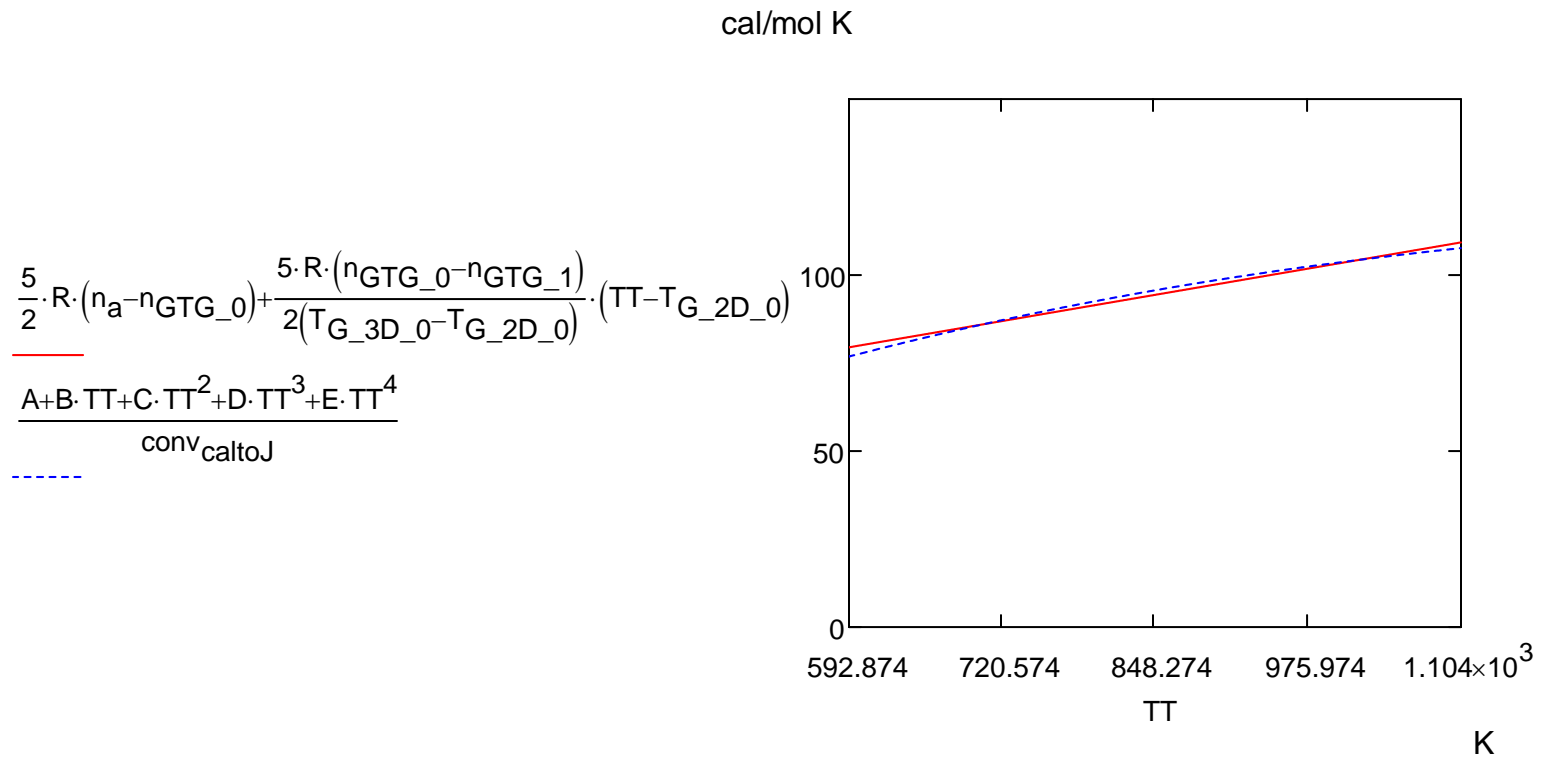


Figure 34. Octane Gas Specific Heat

$$T_{\text{diss}} := -\frac{T_{\text{G}_2\text{D}_0} \cdot n_{\text{GTG}_1} - T_{\text{G}_3\text{D}_0} \cdot n_{\text{GTG}_0}}{n_{\text{GTG}_0} - n_{\text{GTG}_1}}$$

$$T_{\text{diss}} = 1444.20698 \text{ K}$$

Gas Enthalpy

1) using $T_{G_2D_0}$ and $T_{G_3D_0}$

$$h_{G_a}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{G_3D_0}, h_{2D_0}) := h_{2D_0} + \int_{T_{G_2D_0}}^T \left[\frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) + \frac{5 \cdot R \cdot (n_{GTG_1})}{2(T_{G_3D_0})} \right] dT \quad (89a)$$

Carrying out the integration:

$$h_{G_a}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{G_3D_0}, h_{2D_0}) := h_{2D_0} + \frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) \cdot (T - T_{G_2D_0}) + \frac{5 \cdot R \cdot (n_{GTG_1})}{2(T_{G_3D_0})} \cdot (T - T_{G_2D_0}) \quad (89b)$$

h_{2D_0} is the liquid enthalpy at $T_{G_2D_0}$

Water Gas Enthalpy, H₂O**Reciprocal System**

$$T_{L_0} := T_{c_H2O} - \frac{T_{SL_u}}{2} \quad I_T := \frac{2}{9} \quad n_a := 3 \quad n_{GTG_0} := 1.3 \quad (\text{apparently an average of 1 and 1.5})$$

$$T_{L_0} = 391.73 \quad K \quad n_{GTG_1} := 1$$

$$T_{G_3D_0} := 3 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1027.15889 \quad K$$

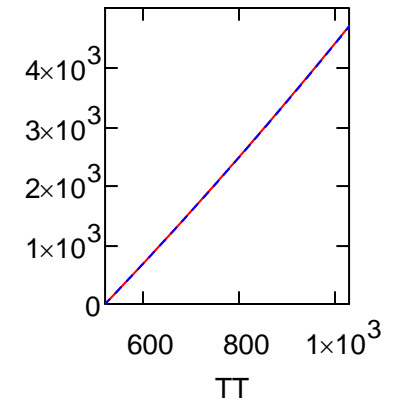
$$T_{G_2D_0} := 2 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 516.35889 \quad K \quad h_{2D_0} := 0 \quad (\text{just to obtain relative enthalpy})$$

Yaws Regression (Ref. [8])

$$A := 33.933 \quad B := -8.4186 \cdot 10^{-3} \quad C := 2.9906 \cdot 10^{-5} \quad D := -1.7825 \cdot 10^{-8} \quad E := 3.6934 \cdot 10^{-12}$$

$$\frac{h_{G_a}(TT, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{G_3D_0}, h_{2D_0})}{\text{conv}_{\text{caltoJ}}} + \frac{A \cdot (TT - T_{G_2D_0}) + \frac{B}{2} \cdot (TT^2 - T_{G_2D_0}^2) + \frac{C}{3} \cdot (TT^3 - T_{G_2D_0}^3) + \frac{D}{4} \cdot (TT^4 - T_{G_2D_0}^4) + \frac{E}{5} \cdot (TT^5 - T_{G_2D_0}^5)}{\text{conv}_{\text{caltoJ}}}$$

cal/mol



K

Figure 35. Water Gas *Relative* Enthalpy

2) using $T_{G_3D_0}$

$$h_{G_b}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_3D_0}, T_{L_0}, h_{L_0}) := h_{L_0} + \int_{T_{L_0}}^T \left(3.5 \cdot R + \frac{R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_3D_0} - T_{L_0})} \right) \cdot (T - T_{L_0}) \, dT \quad (90a)$$

Carrying out the integration:

$$h_{G_b}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_3D_0}, T_{L_0}, h_{L_0}) := h_{L_0} + 3.5 \cdot R \cdot (T - T_{L_0}) + \frac{R \cdot (T - T_{L_0})^2 \cdot (n_{GTG_0} - n_{GTG_1})}{4 \cdot (T_{G_3D_0} - T_{L_0})} \quad (90b)$$

Nitrogen Gas Enthalpy, N_2

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{N2} := 28.0134 \quad n_T := 5.5 \quad T_{c_N2} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{N2}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{N2}}{1}} \quad T_{c_N2} = 131.59826$$

$$T_{c_N2_obs} := 126.21 \quad K \quad (\text{we'll use this value, pending clarification}) \quad T_{c_N2} := T_{c_N2_obs}$$

$$T_{L_0} := T_{c_N2} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -129.19 \quad K \quad T_{L_0} := T_{c_N2} \quad \text{cannot have anything below 0 K}$$

$$T_{G_3D_0} := 3 \cdot T_{SL_u} - T_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1292.67889 \quad K$$

Yaws Regression (Ref. [8])

$$A := 29.342 \quad B := -3.5395 \cdot 10^{-3} \quad C := 1.0076 \cdot 10^{-5} \quad D := -4.3116 \cdot 10^{-9} \quad E := 2.5935 \cdot 10^{-13}$$

There is no $T_{G_2D_0}$ for N_2 . The specific heat at T_{L_0} is R for the internal motion and $2.5 R$ for the external motion, for a total of $3.5 R$ for the molecule. There is a linear increase to $4 R$ at $T_{G_3D_0}$.

$$h_{L_0} := 0 \quad (\text{for relative enthalpy}) \quad \text{cal/mol}$$

$$\frac{h_{G_b}(TT, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_3D_0}, T_{L_0}, h_{L_0})}{\text{conv}_{\text{caltoJ}}} = \frac{A \cdot (TT - T_{L_0}) + \frac{B}{2} \cdot (TT - T_{L_0})^2 + \frac{C}{3} \cdot (TT - T_{L_0})^3 + \frac{D}{4} \cdot (TT - T_{L_0})^4 + \frac{E}{5} \cdot (TT - T_{L_0})^5}{\text{conv}_{\text{caltoJ}}}$$

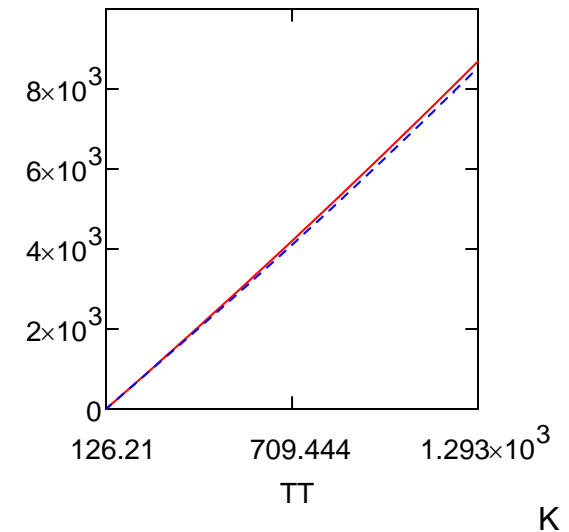


Figure 36. Nitrogen Gas *Relative* Enthalpy

3) using $T_{G_2D_0}$

$$h_{G_c}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{L_0}, h_{L_0}) := h_{L_0} + \int_{T_{L_0}}^T \left(3.5 \cdot R + \frac{R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_2D_0} - T_{L_0})} \cdot (T - T_{L_0}) \right) dT$$

Carrying out the integration:

(91a)

$$h_{G_c}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{L_0}, h_{L_0}) := h_{L_0} + 3.5 \cdot R \cdot (T - T_{L_0}) + \frac{R \cdot (T - T_{L_0})^2 \cdot (n_{GTG_0} - n_{GTG_1})}{4 \cdot (T_{G_2D_0} - T_{L_0})}$$

(91b)

O₂

Reciprocal System

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{O2} := 31.9988 \quad n_T := 6 \quad T_{c_O2} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{O2}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{O2}}{1}} \quad T_{c_O2} = 160.48412$$

$$T_{c_O2_obs} := 154.59 \quad \text{we'll use this pending clarification } T_{c_O2} := T_{c_O2_obs}$$

$$T_{L_0} := T_{c_O2} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -100.81 \quad K \quad T_{L_0} := T_{c_O2} \quad \text{cannot have anything below 0 K}$$

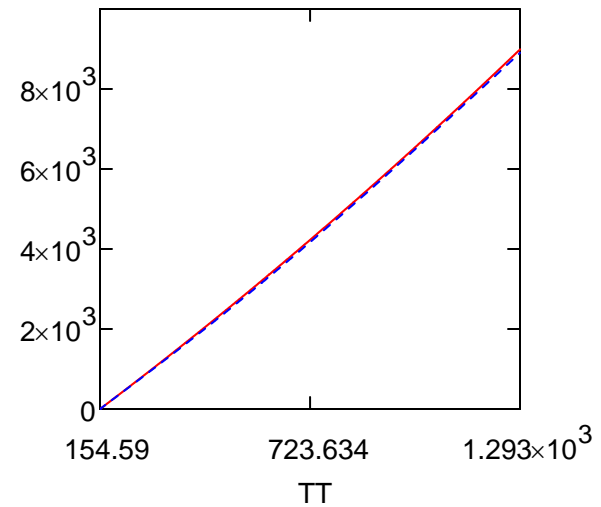
$$T_{G_2D_0} := 2 \cdot T_{SL_u} - T_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 753.49889 \quad h_{L_0} := 0 \quad (\text{for relative enthalpy})$$

Yaws Regression (Ref. [8])

$$A := 29.526 \quad B := -8.8999 \cdot 10^{-3} \quad C := 3.8083 \cdot 10^{-5} \quad D := -3.2629 \cdot 10^{-8} \quad E := 8.8607 \cdot 10^{-12}$$

$$\frac{h_{G_c}(TT, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{L_0}, h_{L_0})}{\text{conv}_{\text{caltoJ}}} = A \cdot (TT - T_{L_0}) + \frac{B}{2} \cdot (TT - T_{L_0})^2 + \frac{C}{3} \cdot (TT - T_{L_0})^3 + \frac{D}{4} \cdot (TT - T_{L_0})^4 + \frac{E}{5} \cdot (TT - T_{L_0})^5$$

cal/mol



K

Figure 37. Oxygen Gas *Relative Enthalpy*

4) using $T_{G_2.5D_0}$

$$h_{G_d}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2.5D_0}, T_{L_0}, h_{L_0}) := h_{L_0} + \int_{T_{L_0}}^T \left(3.5 \cdot R + \frac{R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_2.5D_0} - T_{L_0})} \right) \cdot (T - T_{L_0}) dT \quad (92a)$$

Carrying out the integration:

$$h_{G_d}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2.5D_0}, T_{L_0}, h_{L_0}) := h_{L_0} + 3.5 \cdot R \cdot (T - T_{L_0}) + \frac{R \cdot (T - T_{L_0})^2 \cdot (n_{GTG_0} - n_{GTG_1})}{4 \cdot (T_{G_2.5D_0} - T_{L_0})} \quad (92b)$$

CO

Reciprocal System

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$w_{CO} := 28.01 \quad n_T := 5.5 \quad T_{c_CO} := \frac{T_{SL_u}}{2} \cdot \left[\left(\frac{w_{CO}}{1} \right)^{\frac{1}{4}} - 1 \right] - 2 \cdot T_{SL_u} \cdot \frac{n_T}{\frac{w_{CO}}{1}} \quad T_{c_CO} = 131.55609$$

$$T_{c_CO_obs} := 132.86 \quad \text{we'll use this pending clarification } T_{c_CO} := T_{c_CO_obs}$$

$$T_{L_0} := T_{c_CO} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -122.54 \quad K \quad T_{L_0} := T_{c_CO} \quad \text{cannot have anything below 0 K}$$

$$T_{G_2.5D_0} := 2.5 \cdot T_{SL_u} - 1T \cdot T_{SL_u} - T_{L_0} \quad T_{G_2.5D_0} = 1030.62889 \quad h_{L_0} := 0 \quad (\text{for relative enthalpy})$$

Yaws Regression (Ref. [8])

$$A := 29.556 \quad B := -6.5807 \cdot 10^{-3} \quad C := 2.0130 \cdot 10^{-5} \quad D := -1.2227 \cdot 10^{-8} \quad E := 2.2617 \cdot 10^{-12}$$

$$\frac{h_{G_d}(TT, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2.5D_0}, T_{L_0}, h_{L_0})}{\text{conv}_{\text{caltoJ}}}$$

$$A \cdot (TT - T_{L_0}) + \frac{B}{2} \cdot (TT - T_{L_0})^2 + \frac{C}{3} \cdot (TT - T_{L_0})^3 + \frac{D}{4} \cdot (TT - T_{L_0})^4 + \frac{E}{5} \cdot (TT - T_{L_0})^5$$

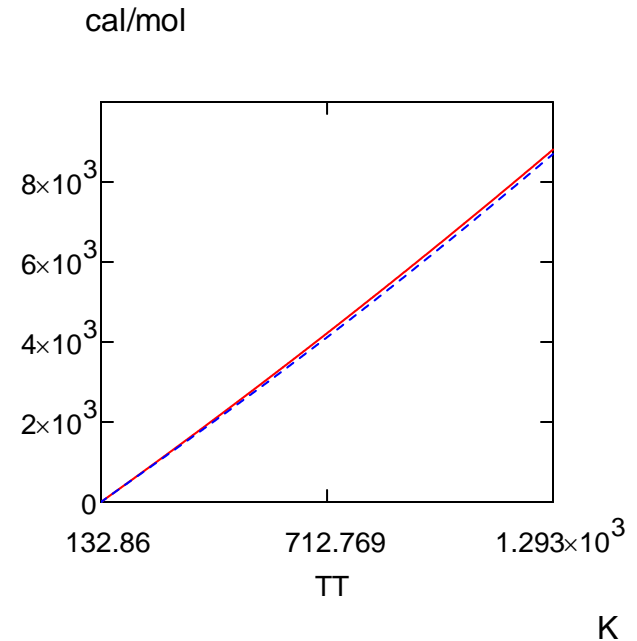


Figure 38. Carbon Monoxide Gas *Relative* Enthalpy

The Reciprocal System Database will be able to calculate both absolute and relative enthalpy for any gas.

Gas Entropy

By definition: $s := s_i + \int_{T_i}^{T_f} \frac{c_p(T)}{T} dT$ (93a)

We can apply this equation to the same conditions as for enthalpy.

1) using $T_{G_2D_0}$ and $T_{G_3D_0}$

$$s_{G_a}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{G_3D_0}, h_{2D_0}) := s_{2D_0} + \int_{T_{G_2D_0}}^T \frac{\frac{5}{2} \cdot R \cdot (n_a - n_{GTG_0}) + \frac{5 \cdot R \cdot (n_{GTG_0})}{2(T_{G_3D_0} - T)}}{T} dT$$

s_{2D_0} is the liquid entropy at $T_{G_2D_0}$

(93b)

Carrying out the integration:

$$s_{G_a}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{G_3D_0}, s_{2D_0}) := s_{2D_0} + \left[\frac{5 \cdot R \cdot (T \cdot n_{GTG_0} - T \cdot n_{GTG_1} - T_{G_2D_0} \cdot n_G)}{T} \right]$$

(93c)

Yaws Regression (Ref. [8])

$$\int_{T_{\text{init}}}^{TT} \frac{\frac{AA}{TT} + BB + CC \cdot TT + DD \cdot TT^2 + EE \cdot TT^3}{\text{conv}_{\text{caltoJx}}} dTT \rightarrow \left| \begin{array}{l} \frac{12 \cdot AA \cdot \ln(TT) - 12 \cdot AA \cdot \ln(T_{\text{init}}) + 12 \cdot BB \cdot TT - 12 \cdot BB \cdot T_{\text{init}} + 6 \cdot CC \cdot T}{12 \cdot \text{cor}} \\ \frac{12 \cdot AA \cdot \ln(TT) - 12 \cdot AA \cdot \ln(T_{\text{init}}) + 12 \cdot BB \cdot TT - 12 \cdot BB \cdot T_{\text{init}} + 6 \cdot CC \cdot T}{1} \end{array} \right.$$

$$sG_{\text{Yaws}}(T_{\text{init}}, T, A, B, C, D, E) := \frac{12 \cdot A \cdot \ln(T) - 12 \cdot A \cdot \ln(T_{\text{init}}) + 12 \cdot B \cdot T - 12 \cdot B \cdot T_{\text{init}} + 6 \cdot C \cdot T^2 - 6 \cdot C \cdot T_{\text{init}}^2 + 4 \cdot D \cdot T^3 - 4 \cdot D \cdot T_{\text{init}}^3}{12 \cdot \text{conv}_{\text{caltoJ}}}$$

Water Entropy, H₂O**Reciprocal System**

$$T_{L_0} := T_{c_H2O} - \frac{T_{SL_u}}{2} \quad I_T := \frac{2}{9} \quad n_a := 3 \quad n_{GTG_0} := 1.3 \quad (\text{apparently an average of 1 and 1.5})$$

$$T_{L_0} = 391.73 \quad K \quad n_{GTG_1} := 1$$

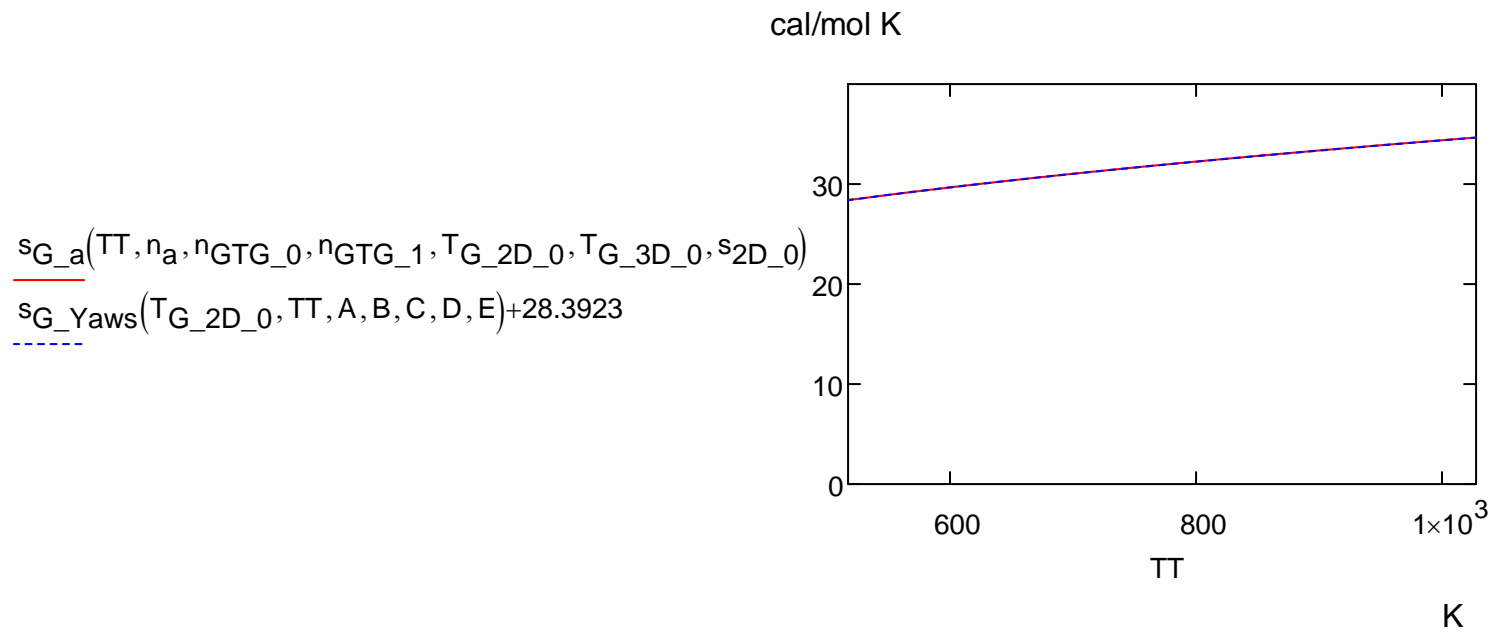
$$T_{G_3D_0} := 3 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1027.15889 \quad K$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - I_T \cdot T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 516.35889 \quad K \quad s_{2D_0} := 28.3923 \quad \text{cal/mol K}$$

(from RS Database to obtain
absolute entropy)

Yaws Regression (Ref. [8])

$$A := 33.933 \quad B := -8.4186 \cdot 10^{-3} \quad C := 2.9906 \cdot 10^{-5} \quad D := -1.7825 \cdot 10^{-8} \quad E := 3.6934 \cdot 10^{-12}$$

Figure 39. Water Gas *Absolute* Entropy

2) using $T_{G_3D_0}$

$$s_{G_b}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_3D_0}, T_{L_0}, s_{L_0}) := s_{L_0} + \int_{T_{L_0}}^T \left(\frac{3.5 \cdot R}{T} + \frac{R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_3D_0} - T_{L_0})} \cdot \frac{(T - T_{L_0})}{T} \right) dT \quad (94)$$

Carrying out the integration gives a rather messy result, so we'll just use the functional form above.

Nitrogen Gas Entropy, N_2 **Reciprocal System**

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$T_{L_0} := T_{c_N2} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -129.19 \text{ K} \quad T_{L_0} := T_{c_N2} \quad \text{cannot have anything below 0 K}$$

$$T_{G_3D_0} := 3 \cdot T_{SL_u} - T_{L_0} \quad T_{G_3D_0} = 1292.67889 \text{ K} \quad s_{L_0} := 0 \quad (\text{for relative entropy})$$

Yaws Regression (Ref. [8])

$$A := 29.342 \quad B := -3.5395 \cdot 10^{-3} \quad C := 1.0076 \cdot 10^{-5} \quad D := -4.3116 \cdot 10^{-9} \quad E := 2.5935 \cdot 10^{-13}$$

There is no $T_{G_2D_0}$ for N_2 . The specific heat at T_{L_0} is R for the internal motion and $2.5 R$ for the external motion, for a total of $3.5 R$ for the molecule. There is a linear increase to $4 R$ at $T_{G_3D_0}$.

$s_{L_0} := 0$ (for *relative* enthalpy) cal/mol

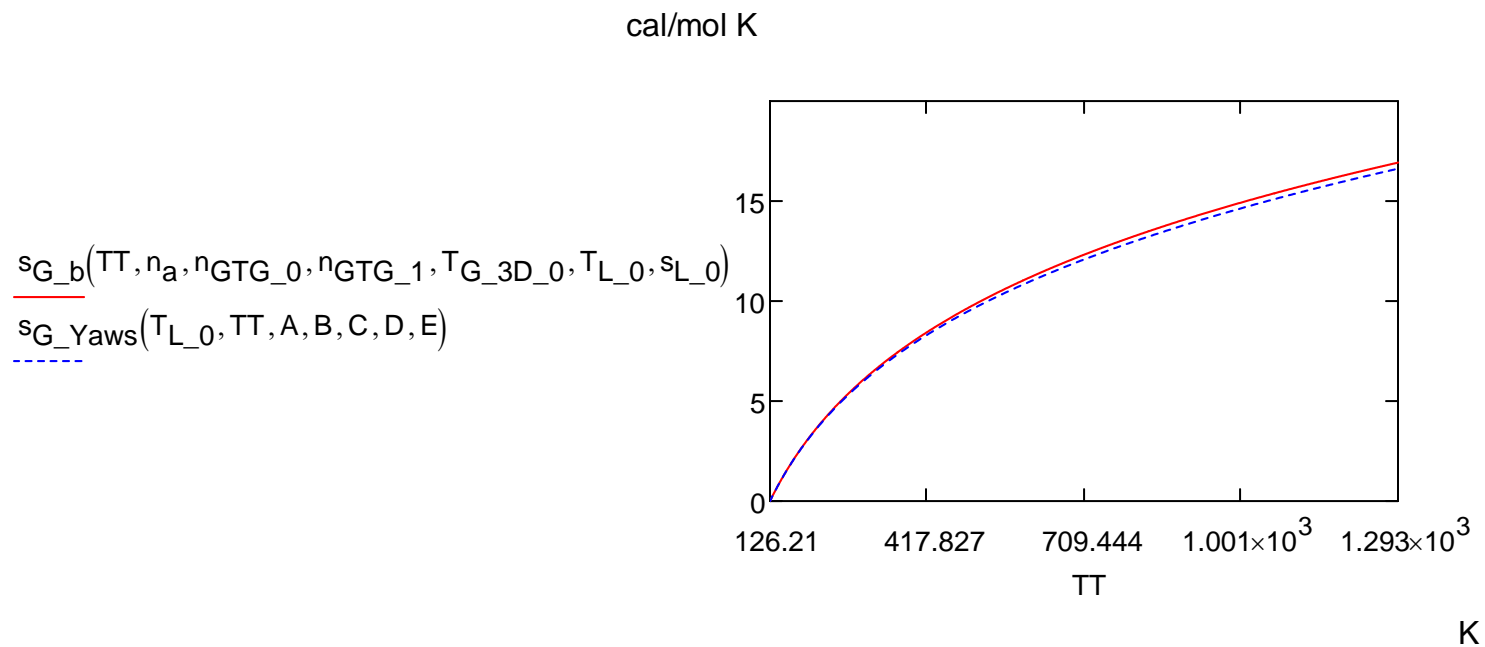


Figure 40. Nitrogen Gas *Relative* Entropy

3) using $T_{G_2D_0}$

$$s_{G_c}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2D_0}, T_{L_0}, s_{L_0}) := s_{L_0} + \int_{T_{L_0}}^T \frac{3.5 \cdot R}{T} + \frac{R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_2D_0} - T_{L_0})} \cdot \frac{(T - T_{L_0})}{T} dT \quad (95)$$

Carrying out the integration gives a rather messy result, so we'll just the functional form above.

O₂

Reciprocal System

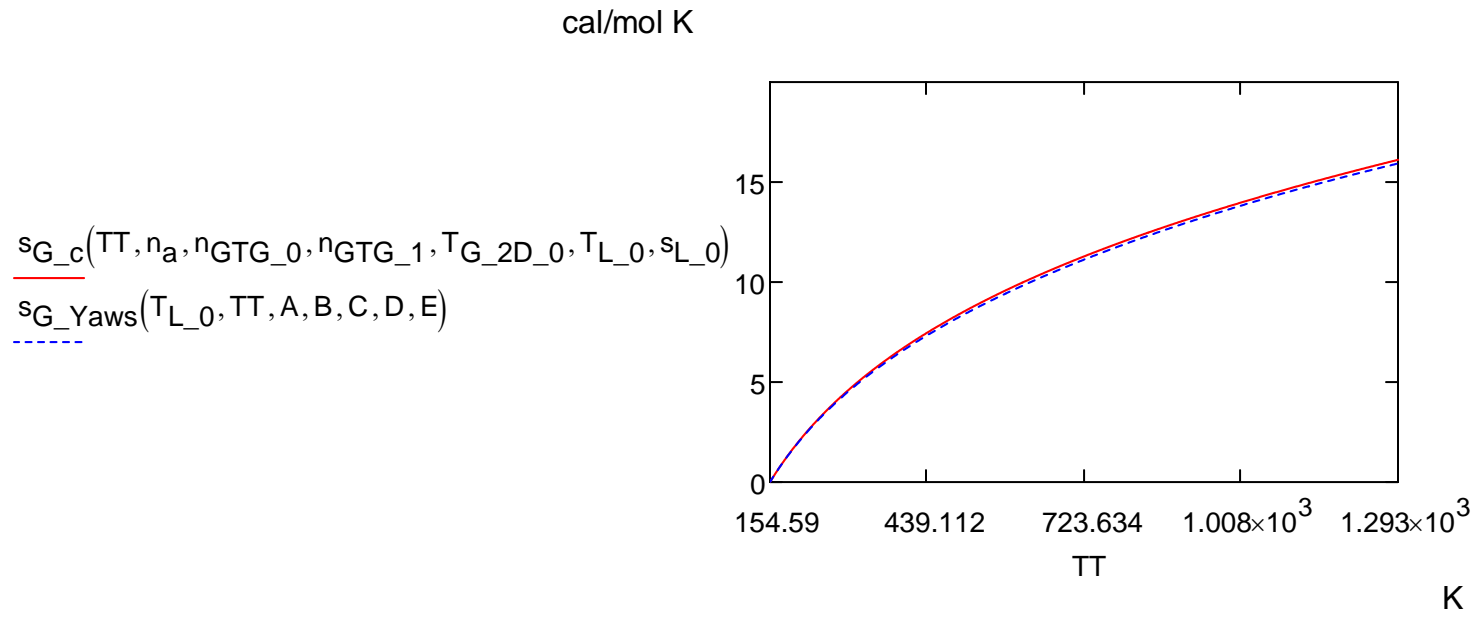
$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$T_{L_0} := T_{c_O2} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -100.81 \text{ K} \quad T_{L_0} := T_{c_O2} \quad \text{cannot have anything below 0 K}$$

$$T_{G_2D_0} := 2 \cdot T_{SL_u} - T_{SL_u} - T_{L_0} \quad T_{G_2D_0} = 753.49889 \quad s_{L_0} := 0 \quad (\text{for relative entropy})$$

Yaws Regression (Ref. [8])

$$A := 29.526 \quad B := -8.8999 \cdot 10^{-3} \quad C := 3.8083 \cdot 10^{-5} \quad D := -3.2629 \cdot 10^{-8} \quad E := 8.8607 \cdot 10^{-12}$$

Figure 40. Oxygen Gas *Relative* Entropy

4) using $T_{G_2.5D_0}$

$$s_{G_d}(T, n_a, n_{GTG_0}, n_{GTG_1}, T_{G_2.5D_0}, T_{L_0}, s_{L_0}) := s_{L_0} + \int_{T_{L_0}}^T \left(\frac{3.5 \cdot R}{T} + \frac{R \cdot (n_{GTG_0} - n_{GTG_1})}{2(T_{G_2.5D_0} - T_{L_0})} \cdot \frac{(T - T_{L_0})}{T} \right) dT \quad (96)$$

Carrying out the integration gives a rather messy result so we'll just use the functional form above.

CO

Reciprocal System

$$n_a := 2 \quad n_{GTG_0} := 1 \quad n_{GTG_1} := 0$$

$$T_{L_0} := T_{c_CO} - \frac{T_{SL_u}}{2} \quad T_{L_0} = -122.54 \text{ K} \quad T_{L_0} := T_{c_CO} \quad \text{cannot have anything below 0 K}$$

$$T_{G_2.5D_0} := 2.5 \cdot T_{SL_u} - T_{L_0} \quad T_{G_2.5D_0} = 1030.62889 \quad s_{L_0} := 0 \quad (\text{for relative entropy})$$

Yaws Regression (Ref. [8])

$$A := 29.556 \quad B := -6.5807 \cdot 10^{-3} \quad C := 2.0130 \cdot 10^{-5} \quad D := -1.2227 \cdot 10^{-8} \quad E := 2.2617 \cdot 10^{-12}$$

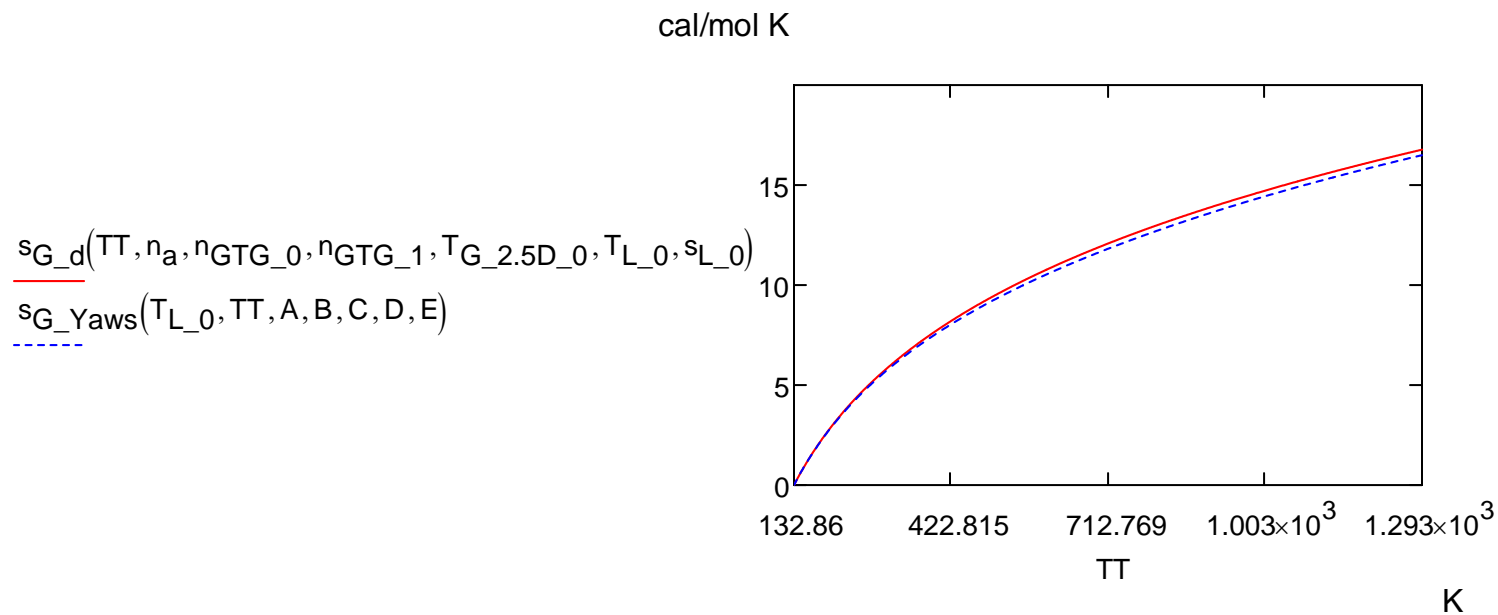


Figure 41. Carbon Monoxide Gas *Relative Entropy*

The Reciprocal System Database will allow calculation of both absolute and relative enthalpy and entropy for any gas.

Conclusion

No previous *theory* has been able to calculate all of the properties of liquids, vapors, and gases; engineers have had to resort to using *empirical regression equations*, such as those given in Ref. [7] and Ref. [8]. But now, with the Reciprocal System, we can calculate, for all liquids, vapors, and gases, the specific volume and density, the specific heat, the enthalpy, and the entropy. We can also calculate the surface tension, viscosity, and thermal conductivity of liquids, from theory alone. Example calculations are given in the paper; the Reciprocal System Database serves to verify the theoretical equations for the elements and thousands of compounds. A few of the equations, such as those for critical temperature and thermal conductivity and enthalpy of vaporization, are still somewhat tentative and subject to change. Most of the theoretical parameters are fully explainable; a few are not at this stage of development of the theory. Reciprocal System equations are usually *linear* in the variables and thus make *physical understanding* possible; this, of course, contrasts with the empirical regression equations, which do not and cannot provide any such physical understanding.

Acknowledgements

Funding for this work came from Transpower Corporation, not the government! Of course, great thanks go to Dewey B. Larson, who served as my theoretical physics mentor from 1965 until his death in 1990. He was, by far, the most intelligent and most logical of any individual I've ever known. Also, thanks go to Prof. Carl Yaws, Ref. [8], for his remarkable collection of empirical regression equations. With these as proxies for the empirical data, it was easy to compare the Reciprocal System theoretical equations with observations and experiments.

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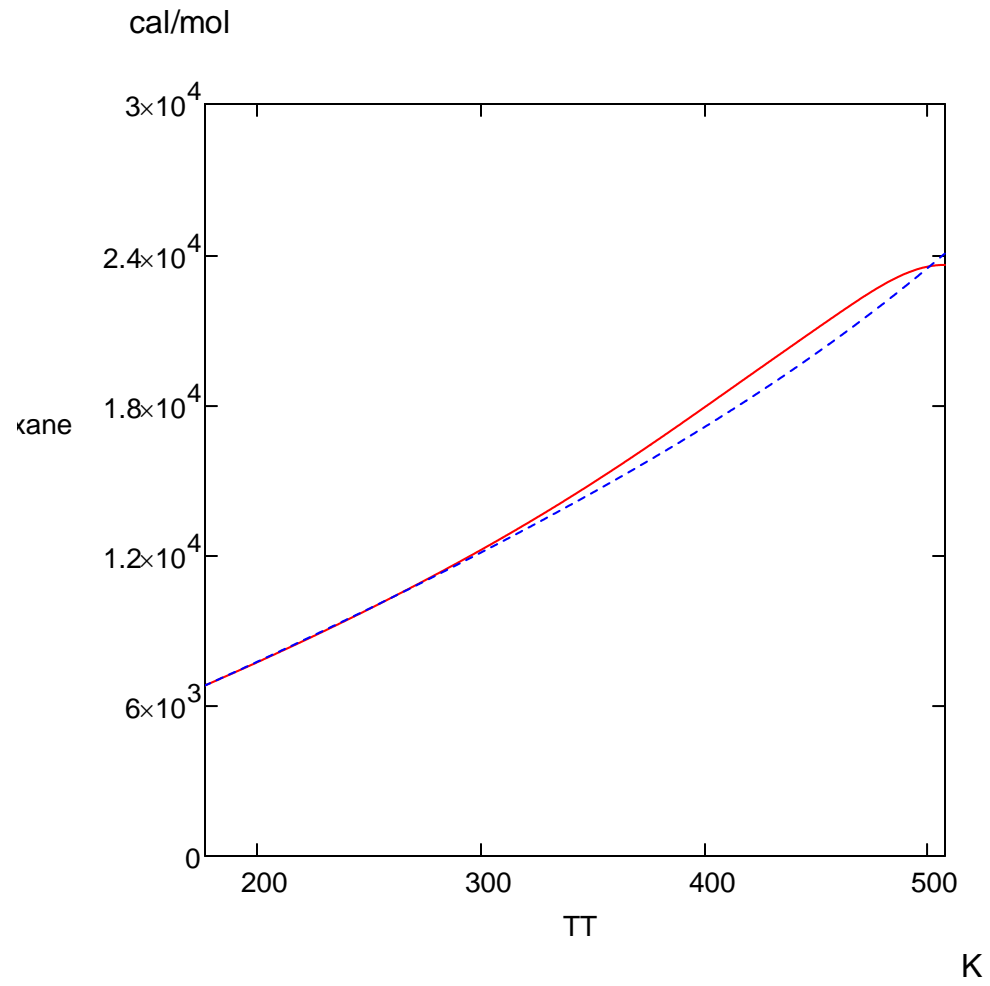
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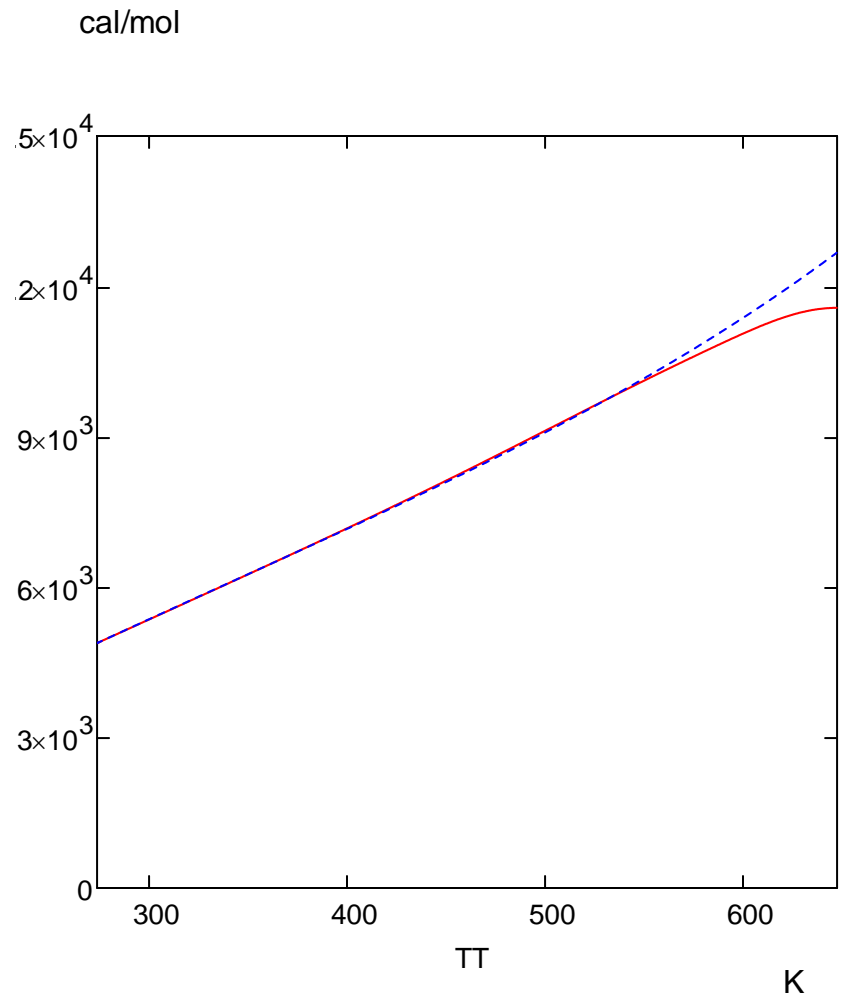
last updated: 07/24/2013

original publishing date: 11/18/2012

$$V_3(n_V, w, T_C, T, 1)$$

$$\frac{T \cdot c_{p_avg_StrG} \cdot n_{initial} \dots}{\Delta T_{StrG} \cdot n_{StrG}}$$



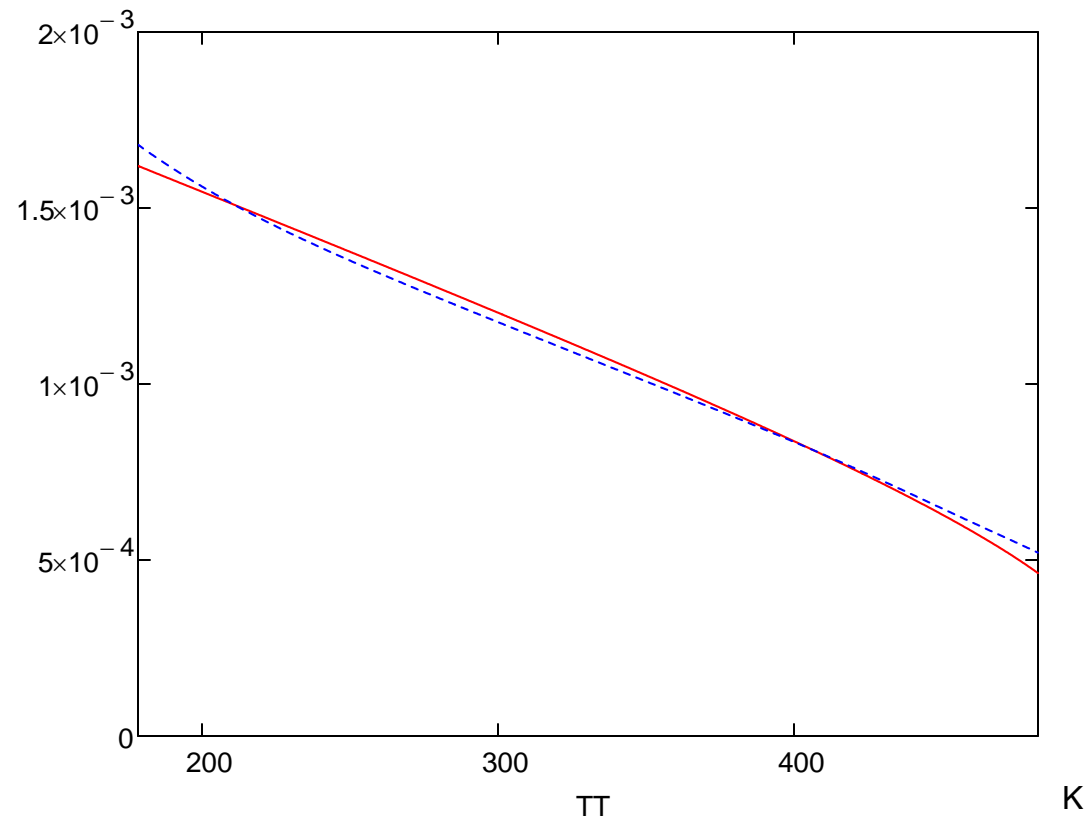


$$\frac{v_{g_StrG} \cdot n_{initial} + 3 \cdot R \cdot T_{SL_u} \cdot n_{LTG} \cdot \ln(T_f) - 3 \cdot R \cdot T_{SL_u} \cdot n_{LTG} \cdot \ln(T_i) + T_{SL_u} \cdot c_{p_avg_StrG} \cdot n_{StrG} \cdot \ln(T_f) - T_{SL_u} \cdot c_{p_avg_StrG} \cdot n_{StrG}}{T_{SL_u}}$$

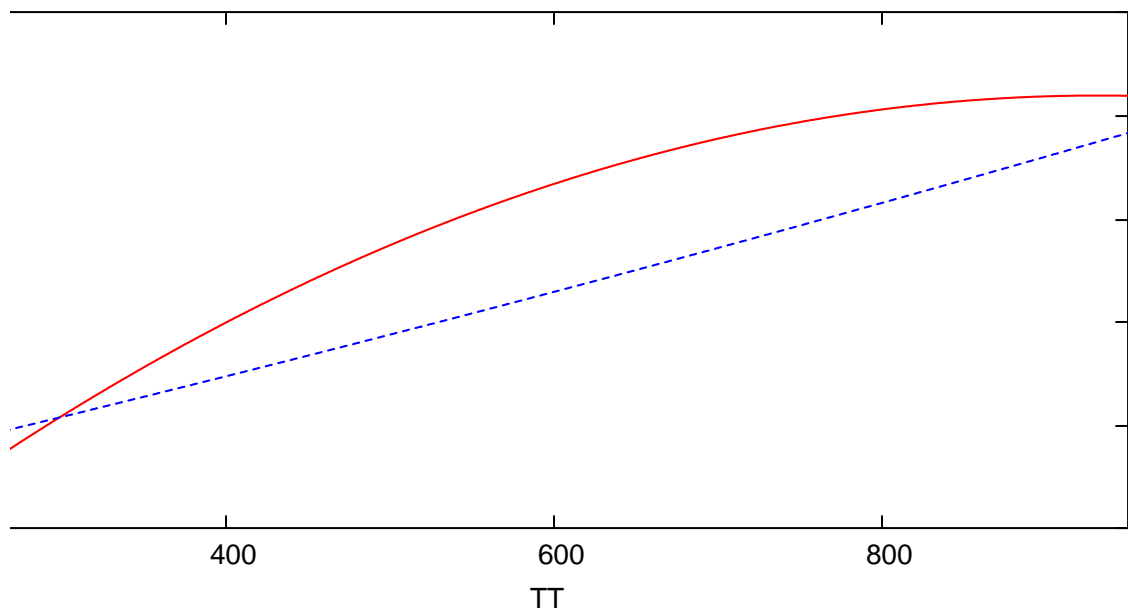
$$\underline{L \cdot T_f^3 - 2 \cdot D_L \cdot T_i^3}$$

$$\left[\frac{Z_H \cdot w_H \cdot (T+1)}{d_{\text{atom}_H}} \cdot \frac{1}{\left[\frac{t_{e_H}}{(t_{p_H}^2 \cdot t_{s_H})^{\frac{1}{3}}} \right]^2} + \frac{m_C}{m_C} \cdot \frac{1}{\left[\frac{t_{e_C}}{(t_{p_C}^2 \cdot t_{s_C})^{\frac{1}{3}}} \right]^2} \right] \cdot 10^{-6}$$

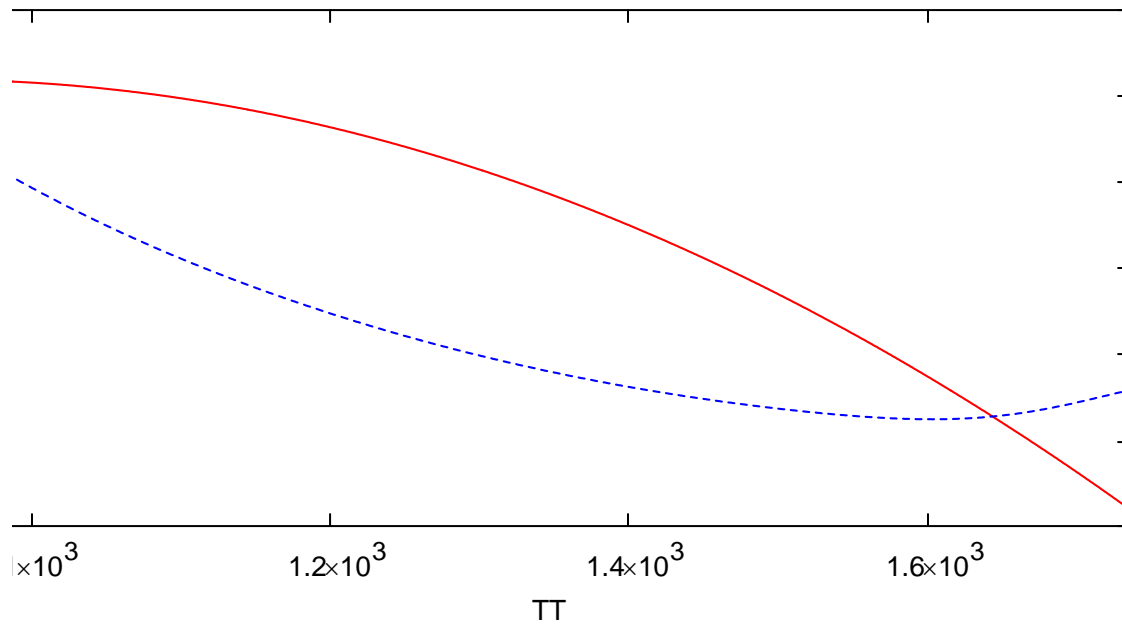
watt / cm K



$$\frac{1 \cdot w_H \cdot (T+1)}{d_{\text{atom}_H}} \cdot \frac{1}{\left[\frac{t_{e_H}}{(t_{p_H}^2 \cdot t_{s_H})^{\frac{1}{3}}} \right]^2} \cdot 10^{-6}$$

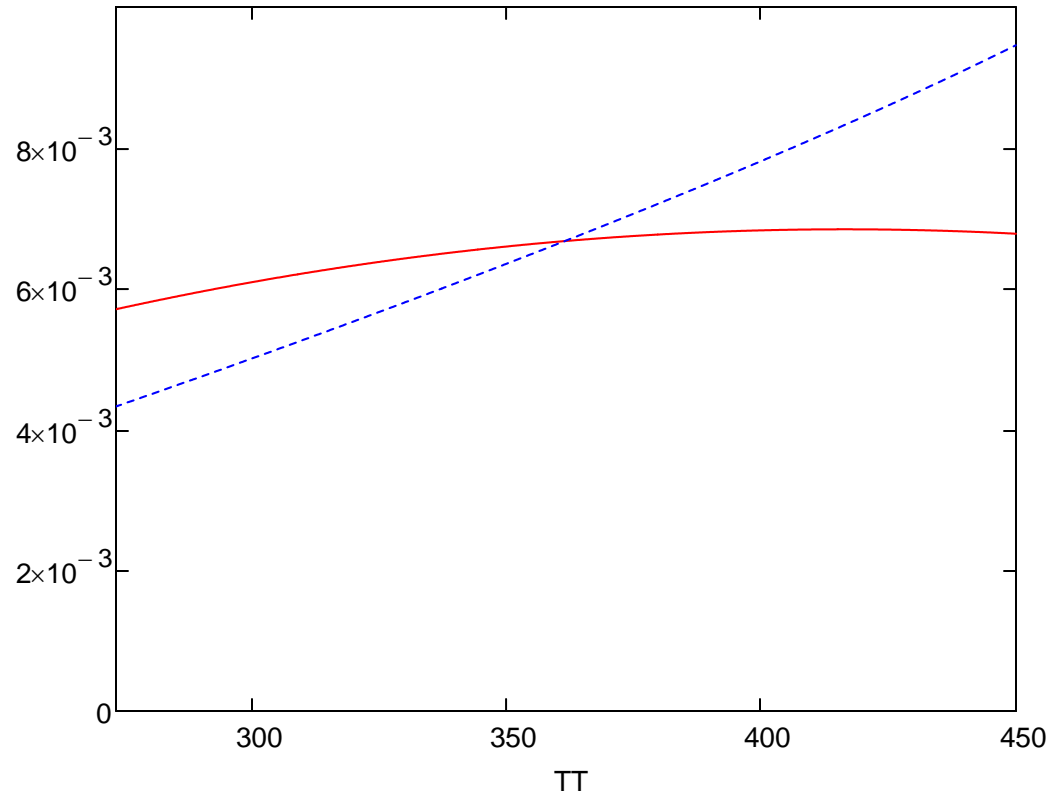


$$(A_{Hg} + B_{Hg} \cdot TT + C_{Hg} \cdot TT^2) \cdot 0.01$$



watt / cm K

$$\frac{T+1}{H} \cdot \frac{1}{\left[\frac{t_{e_H}}{(t_{p_H}^2 \cdot t_{s_H})^{\frac{1}{3}}}]^2 \right]} \cdot 10^{-6}$$

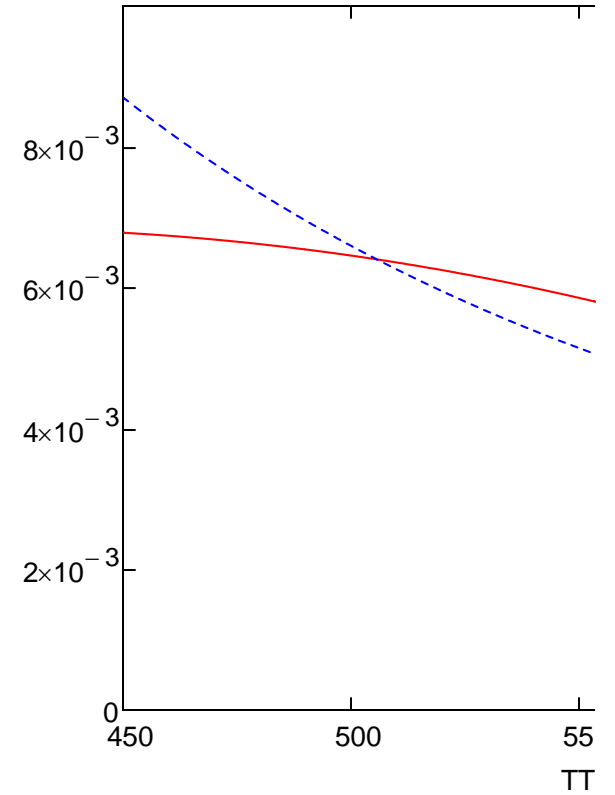


ivity--to midpoint (tentative)

K

watt / cm K

$$\frac{n_{\text{int}}, n_{\text{initial}}, TT \cdot \left(\frac{\text{conv}_{\text{caltoev}}}{n_{\text{e_H2O}} \cdot Av} \cdot .5 \right)^2 \cdot (T_{\text{c_H2O}} - TT + T_{\text{offset}}) \cdot n_T \cdot \frac{T_{\text{c_H2O}}}{TT}}{\left[\frac{\text{H2O} \cdot \text{conv}_{\text{utog}}}{T_u} \cdot R \cdot \left[\frac{Z_O \cdot w_O \cdot (TT+1)}{d_{\text{atom_O}}} \cdot \frac{1}{\left[\frac{t_{\text{e_O}}}{(t_{\text{p_O}}^2 \cdot t_{\text{s_O}})^{\frac{1}{3}}} \right]^2} \right] + \frac{Z_H \cdot w_H \cdot (TT+1)}{d_{\text{atom_H}}} \cdot \frac{1}{\left[\frac{t_{\text{e_H}}}{(t_{\text{p_H}}^2 \cdot t_{\text{s_H}})^{\frac{1}{3}}} \right]^2} \right]} \cdot 10^{-6}}$$



tentative)

$$\frac{6 \cdot C_V \cdot T_i^2 + 4 \cdot D_V \cdot T_f^3 - 4 \cdot D_V \cdot T_i^3 + 3 \cdot E_V \cdot T_f^4 - 3 \cdot E_V \cdot T_i^4}{\text{J}}$$

J

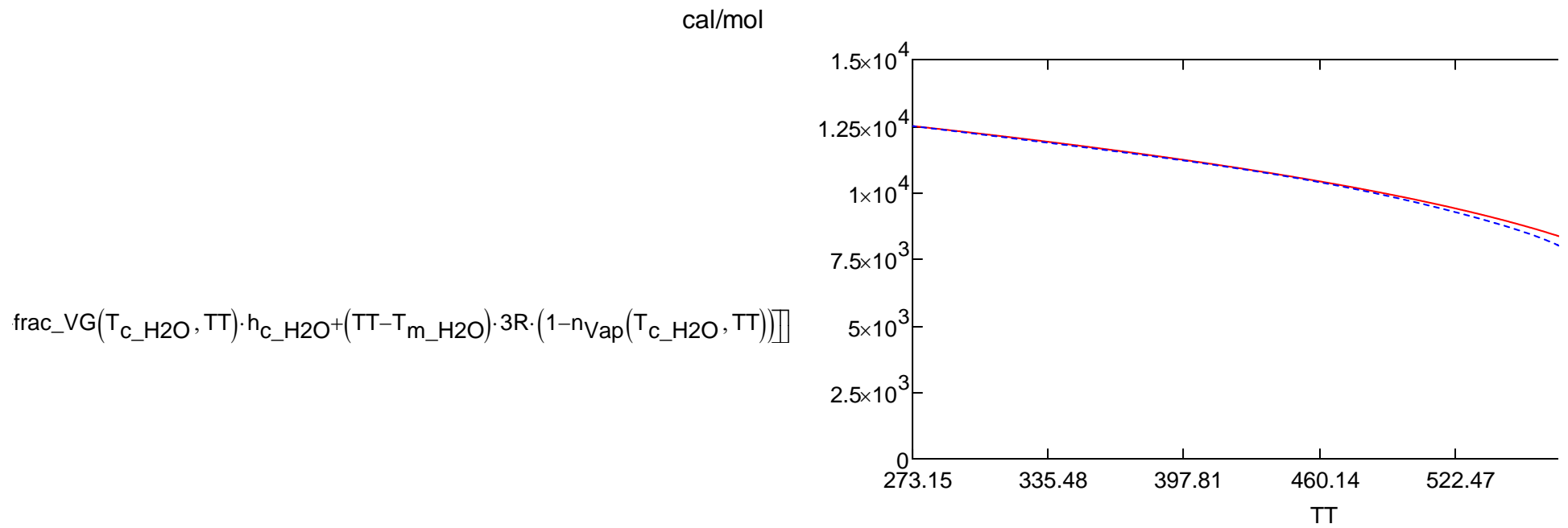


Figure 12. Water Enthalpy of Vaporization

$$\text{initial}, n_{\text{StrG}})) \cdot (1 - \text{frac_VG}(T_{c_H2O}, T_{c_H2O})) + \text{frac_VG}(T_{c_H2O}, T_{c_H2O}) \cdot h_{c_H2O} + (T_{c_H2O} - T_{m_H2O}) \cdot 3R \cdot (1 - n_{\text{vap}}(T_{c_H2O}, T_{c_H2O}))$$

K

$$\cdot V_{C_{LV}} \dots$$
$$- \Phi_u(T_c, T, y)) + (1 - \Phi_{3T}(T_c, T))] \cdot (1 - \text{frac}_S(T, T_m)) \Big]$$

!O,T,T_{m_H2O},y,P_{c_H2O},V_{c_LV_H2O}))

$$H2O(T) - V_{V_sat_H2O}(T_c_H2O, T, T_m_H2O, y, P_c_H2O, V_c_LV_H2O))$$

$$T) - V_{V_SH_aggr_P_sat_H2O}(T))$$

$$\left[\frac{1}{3)^2} + \frac{C_6}{P \cdot 1013} + \frac{C_7}{(T - 273.15)^{C_8}} + C_{11} \cdot \frac{(T - 273.15)}{P \cdot 1013} \right]$$

·T_{SL_u}

SL_u

iL_u

$c, P))$

$$\frac{1}{c_L, V_{c_G}} \cdot (\text{Dev}_V(T, T_c, P, x_V, V_{c_L}) - \text{Dev}_G(T, T_c, P, x_G, V_{c_L}))$$

$$\frac{V_{c_V}}{c_L, T_c, T_c, V_{c_L}, V_{c_V}} \cdot (\text{Dev}_{LV}(T, T_c, P, x_{LV}, V_{c_L}) - \text{Dev}_V(T, T_c, P, x_V, V_{c_L}))$$

$$\frac{1}{c_{LV}} \cdot (\text{Dev}_L(T, T_c, P, x_L, V_{c_L}) - \text{Dev}_{LV}(T, T_c, P, x_{LV}, V_{c_L}))$$

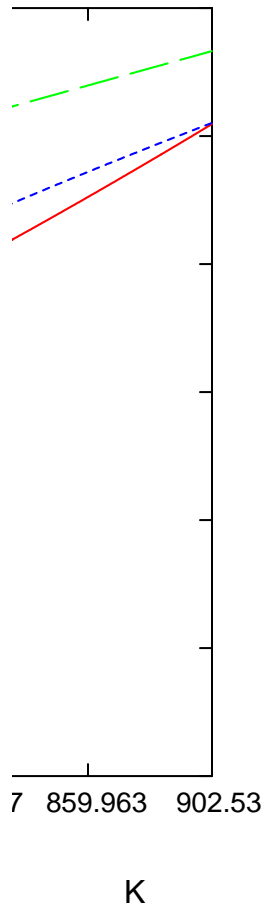
$G, T_c, T_c, V_{c_L}, V_{c_G})$

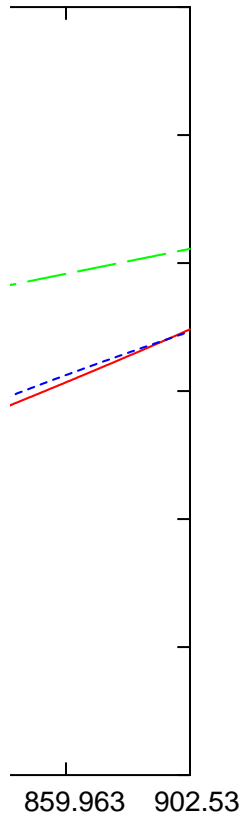
$P \leq P_V(x_V, T_c, T_c, V_{c_L}, V_{c_V})$

$V))$ if $P \leq P_{LV}(x_{LV}, T_c, T_c, V_{c_L}, V_{c_{LV}})$

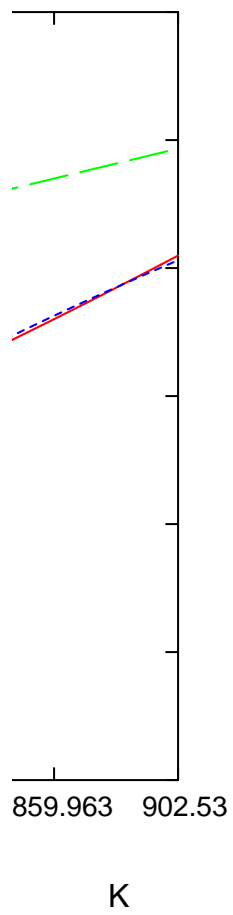
$\leq P_L(x_L, T_c, T_c, V_{c_L})$

$$-\frac{B^3 \cdot u^2}{18} - \frac{B^3 \cdot u^3}{27} + \frac{B \cdot u}{18} + \sqrt{\frac{A^3}{27} - \frac{A^2 \cdot B^2 \cdot u^2}{108} + \frac{2 \cdot A^2 \cdot B^2 \cdot u}{27} + \frac{A^2 \cdot B^2 \cdot w}{9} + \frac{2 \cdot A^2 \cdot B^2}{27} - \frac{5 \cdot A^2 \cdot B \cdot u}{54} - \frac{5 \cdot A^2 \cdot B}{27} - \frac{A^2}{108} - \frac{A \cdot B^4 \cdot u^3}{54} - \frac{A \cdot B^4 \cdot u^2 \cdot w}{54}}$$





K



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$$\frac{1 - n_{\text{GTG}_1}}{T_{\text{G}_2\text{D}_0}} \cdot (T - T_{\text{G}_2\text{D}_0}) \, dT \quad \blacksquare$$

$$\frac{1 - T_{\text{G}_2\text{D}_0}^2 \cdot (n_{\text{GTG}_0} - n_{\text{GTG}_1})}{4 \cdot (T_{\text{G}_3\text{D}_0} - T_{\text{G}_2\text{D}_0})}$$

|

1)

■

T

-1)

$$\frac{-n_{GTG_1}}{T_{G_2D_0}} \cdot (T - T_{G_2D_0}) \quad \blacksquare$$

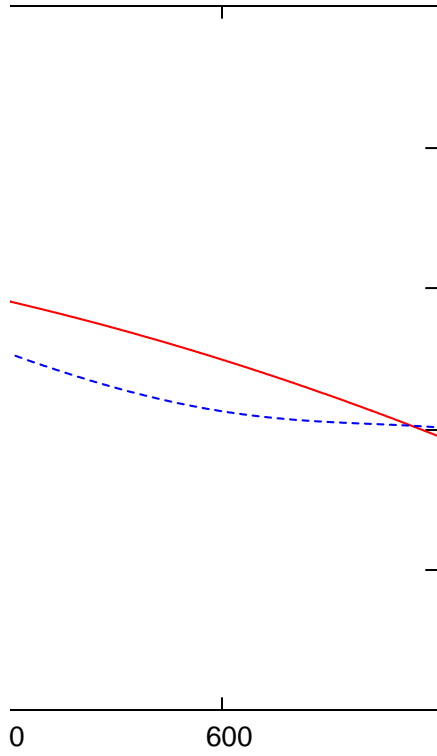
$$\frac{\Gamma_{G_0} + T_{G_2D_0} \cdot n_{GTG_1} - T_{G_2D_0} \cdot n_a \cdot \ln(T) + T_{G_3D_0} \cdot n_a \cdot \ln(T) + T_{G_2D_0} \cdot n_{GTG_1} \cdot \ln(T) - T_{G_3D_0} \cdot n_{GTG_0} \cdot \ln(T) + T_{G_2D_0}}{2 \cdot (T_{G_2D_0} - T_{G_3D_0})}$$

$$\frac{T^2 - 6 \cdot CC \cdot T_{\text{init}}^2 + 4 \cdot DD \cdot TT^3 - 4 \cdot DD \cdot T_{\text{init}}^3 + 3 \cdot EE \cdot TT^4 - 3 \cdot EE \cdot T_{\text{init}}^4}{V_{\text{caltoJx}}} \quad \text{if } 0 > TT \vee T_{\text{init}} > 0$$

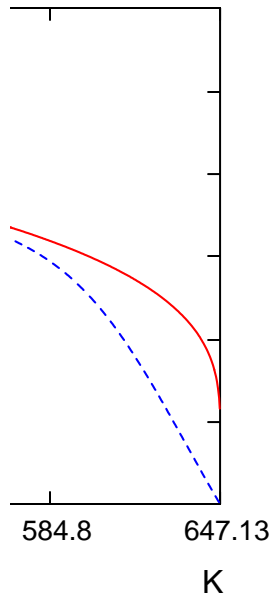
$$\frac{T^2 - 6 \cdot CC \cdot T_{\text{init}}^2 + 4 \cdot DD \cdot TT^3 - 4 \cdot DD \cdot T_{\text{init}}^3 + 3 \cdot EE \cdot TT^4 - 3 \cdot EE \cdot T_{\text{init}}^4 + 12i \cdot \pi \cdot AA}{2 \cdot \text{conv}_{\text{caltoJx}}} \quad \text{if } T_{\text{init}} \leq 0 \leq TT$$

$$\frac{D \cdot T_{\text{init}}^3 + 3 \cdot E \cdot T^4 - 3 \cdot E \cdot T_{\text{init}}^4}{}$$

$$\underline{\cdot \ln(\tau_i)}$$



K



$$z_{\text{O}, T_{\text{c_H2O}}})] = 0.19841$$

$$+ \frac{A \cdot B^4 \cdot u^2}{54} + \frac{4 \cdot A \cdot B^4 \cdot u \cdot w}{27} + \frac{2 \cdot A \cdot B^4 \cdot u}{27} + \frac{A \cdot B^4 \cdot w^2}{9} + \frac{4 \cdot A \cdot B^4 \cdot w}{27} + \frac{A \cdot B^4}{27} + \frac{A \cdot B^3 \cdot u^3}{54} + \frac{5 \cdot A \cdot B^3 \cdot u^2}{54} - \frac{A \cdot B^3 \cdot u \cdot w}{54} + \frac{A \cdot B^3 \cdot u}{6} - \frac{A \cdot B^3 \cdot w}{27} + \frac{A \cdot B}{9}$$

$$\left[\frac{T_{G_2D_0} \cdot n_a \cdot \ln(T_{G_2D_0}) - T_{G_3D_0} \cdot n_a \cdot \ln(T_{G_2D_0}) - T_{G_2D_0} \cdot n_{GTG_1} \cdot \ln(T_{G_2D_0}) + T_{G_3D_0} \cdot n_{GTG_0} \cdot \ln(T_{G_2D_0})}{1} \right]$$

$$\frac{2 \cdot B}{9} - \frac{A}{3} + \frac{B^2 \cdot u}{9} - \frac{B^2 \cdot w}{3} + \frac{B^2}{9} + \frac{B^2 \cdot u^2}{9} + \frac{B \cdot u}{9} + \frac{1}{9}$$

$$- + \frac{2 \cdot A \cdot B^2 \cdot u^2}{27} + \frac{A \cdot B^2 \cdot u}{9} - \frac{5 \cdot A \cdot B^2 \cdot w}{27} + \frac{A \cdot B^2}{9} + \frac{A \cdot B \cdot u}{54} + \frac{A \cdot B}{27} - \frac{B^6 \cdot u^4}{108} - \frac{B^6 \cdot u^3 \cdot w}{54} - \frac{B^6 \cdot u^3}{54} - \frac{B^6 \cdot u^2 \cdot w^2}{108} + \frac{B^6 \cdot u^2 \cdot w}{54} - \frac{B^6 \cdot u^2}{108} + \frac{2 \cdot B^6 \cdot u \cdot w}{27}$$

$$\begin{aligned}
 & - + \frac{2 \cdot B^6 \cdot u \cdot w}{27} + \frac{B^6 \cdot w^3}{27} + \frac{2 \cdot B^6 \cdot w^2}{27} + \frac{B^6 \cdot w}{27} - \frac{B^5 \cdot u^4}{54} - \frac{B^5 \cdot u^3 \cdot w}{54} - \frac{B^5 \cdot u^3}{18} + \frac{B^5 \cdot u^2 \cdot w}{27} - \frac{B^5 \cdot u^2}{27} + \frac{2 \cdot B^5 \cdot u \cdot w^2}{27} + \frac{2 \cdot B^5 \cdot u \cdot w}{9} + \frac{4 \cdot B^5 \cdot w^2}{27} + \frac{4 \cdot B^5 \cdot w}{27} ;
 \end{aligned}$$

$$\frac{3^5 \cdot w}{27} - \frac{B^4 \cdot u^4}{108} - \frac{B^4 \cdot u^3}{18} + \frac{B^4 \cdot u^2 \cdot w}{54} - \frac{B^4 \cdot u^2}{18} + \frac{2 \cdot B^4 \cdot u \cdot w}{9} + \frac{2 \cdot B^4 \cdot w^2}{27} + \frac{2 \cdot B^4 \cdot w}{9} - \frac{B^3 \cdot u^3}{54} - \frac{B^3 \cdot u^2}{27} + \frac{2 \cdot B^3 \cdot u \cdot w}{27} + \frac{4 \cdot B^3 \cdot w}{27} - \frac{B^2 \cdot u^2}{108} + \frac{B^2 \cdot w}{27}.$$

$$\frac{1}{3} + \left(\frac{B}{9} - \frac{A}{6} + \frac{B^2 \cdot u}{9} + \frac{B^3 \cdot u}{18} + \frac{B^2 \cdot w}{3} + \frac{B^3 \cdot w}{3} + \frac{B^2}{9} + \frac{B^3}{27} + \frac{A \cdot B}{3} - \frac{B^2 \cdot u^2}{18} - \frac{B^3 \cdot u^2}{18} - \frac{B^3 \cdot u^3}{27} + \frac{B \cdot u}{18} + \sqrt{\frac{A^3}{27} - \frac{A^2 \cdot B}{18}} \right. \\ \left. + \frac{B^3 \cdot u \cdot w}{6} + \frac{A \cdot B \cdot u}{6} + \frac{1}{27} \right)^{\frac{1}{3}}$$

$$\frac{A^2 \cdot u^2}{108} + \frac{2 \cdot A^2 \cdot B^2 \cdot u}{27} + \frac{A^2 \cdot B^2 \cdot w}{9} + \frac{2 \cdot A^2 \cdot B^2}{27} - \frac{5 \cdot A^2 \cdot B \cdot u}{54} - \frac{5 \cdot A^2 \cdot B}{27} - \frac{A^2}{108} - \frac{A \cdot B^4 \cdot u^3}{54} - \frac{A \cdot B^4 \cdot u^2 \cdot w}{54} + \frac{A \cdot B^4 \cdot u^2}{54} + \frac{4 \cdot A \cdot B^4 \cdot u \cdot w}{27} + \frac{2 \cdot A \cdot B^4 \cdot u}{27} +$$

$$-\frac{A \cdot B^4 \cdot w^2}{9} + \frac{4 \cdot A \cdot B^4 \cdot w}{27} + \frac{A \cdot B^4}{27} + \frac{A \cdot B^3 \cdot u^3}{54} + \frac{5 \cdot A \cdot B^3 \cdot u^2}{54} - \frac{A \cdot B^3 \cdot u \cdot w}{54} + \frac{A \cdot B^3 \cdot u}{6} - \frac{A \cdot B^3 \cdot w}{27} + \frac{A \cdot B^3}{9} + \frac{2 \cdot A \cdot B^2 \cdot u^2}{27} + \frac{A \cdot B^2 \cdot u}{9} - \frac{5 \cdot A \cdot B^2 \cdot w}{27} +$$

$$\frac{A \cdot B^2}{9} + \frac{A \cdot B \cdot u}{54} + \frac{A \cdot B}{27} - \frac{B^6 \cdot u^4}{108} - \frac{B^6 \cdot u^3 \cdot w}{54} - \frac{B^6 \cdot u^3}{54} - \frac{B^6 \cdot u^2 \cdot w^2}{108} + \frac{B^6 \cdot u^2 \cdot w}{54} - \frac{B^6 \cdot u^2}{108} + \frac{2 \cdot B^6 \cdot u \cdot w^2}{27} + \frac{2 \cdot B^6 \cdot u \cdot w}{27} + \frac{B^6 \cdot w^3}{27} + \frac{2 \cdot B^6 \cdot w^2}{27} + \frac{B^6}{27}$$

$$\frac{B^5 \cdot w}{27} - \frac{B^5 \cdot u^4}{54} - \frac{B^5 \cdot u^3 \cdot w}{54} - \frac{B^5 \cdot u^3}{18} + \frac{B^5 \cdot u^2 \cdot w}{27} - \frac{B^5 \cdot u^2}{27} + \frac{2 \cdot B^5 \cdot u \cdot w^2}{27} + \frac{2 \cdot B^5 \cdot u \cdot w}{9} + \frac{4 \cdot B^5 \cdot w^2}{27} + \frac{4 \cdot B^5 \cdot w}{27} - \frac{B^4 \cdot u^4}{108} - \frac{B^4 \cdot u^3}{18} + \frac{B^4 \cdot u^2 \cdot w}{54} - \frac{B^4}{1}$$

$$\left. \frac{\cdot u^2}{8} + \frac{2 \cdot B^4 \cdot u \cdot w}{9} + \frac{2 \cdot B^4 \cdot w^2}{27} + \frac{2 \cdot B^4 \cdot w}{9} - \frac{B^3 \cdot u^3}{54} - \frac{B^3 \cdot u^2}{27} + \frac{2 \cdot B^3 \cdot u \cdot w}{27} + \frac{4 \cdot B^3 \cdot w}{27} - \frac{B^2 \cdot u^2}{108} + \frac{B^2 \cdot w}{27} + \frac{B^3 \cdot u \cdot w}{6} + \frac{A \cdot B \cdot u}{6} + \frac{1}{27} \right)^{\frac{1}{3}} + \frac{1}{3}$$

