

Oxygen Chemical Potential

According to the Shomate Equation

see the NIST Chemistry Webbook

<https://webbook.nist.gov/cgi/cbook.cgi?ID=C7782447&Units=SI&Type=JANAFG&Table=on#JANAFG>

Define functions for enthalpy and entropy:

VERY IMPORTANT:

- 1) enthalpy is given in kJ/mol
- 2) entropy is given in J/mol - K
- 3) t denotes the reduced temperature T/1000 with T in Kelvin.
- 4) These expressions are valid at atmospheric pressure. We will add pressure effects later via $kT \ln(P/P_{\text{atm}})$

$$\begin{aligned} \text{enthalpy}[t_] &:= AA \cdot t + \frac{1}{2} BB \cdot t^2 + \frac{1}{3} CC \cdot t^3 + \frac{1}{4} DD \cdot t^4 - \frac{EE}{t} + FF - HH + HoRT \\ \text{entropy}[t_] &:= AA \cdot \log[t] + BB \cdot t + \frac{1}{2} CC \cdot t^2 + \frac{1}{3} DD \cdot t^3 - \frac{EE}{2 \cdot t^2} + GG \end{aligned}$$

■ Choose temperature range of interest:

- 1) T = 100 - 700 K :

$\text{In}[3] :=$ AA = 31.32234; BB = -20.23531; CC = 57.86644; DD = -36.50624;
EE = -0.007374; FF = -8.903471; GG = 246.7945; HH = 0; HoRT = 0;

- 2) T = 700 - 2000 K :

$\text{In}[4] :=$ AA = 30.03235; BB = 8.772972; CC = -3.988133; DD = 0.788313;
EE = -0.741599; FF = -11.32468; GG = 236.1663; HH = 0;
HoRT = 0;

- 3) T = 2000 - 6000 K :

AA = 20.91111; BB = 10.72071; CC = -2.020498; DD = 0.146449;
EE = 9.245722;
FF = 5.337651;
GG = 237.6185; HH = 0;
HoRT = 0;

■ Make plots of enthalpy and entropy

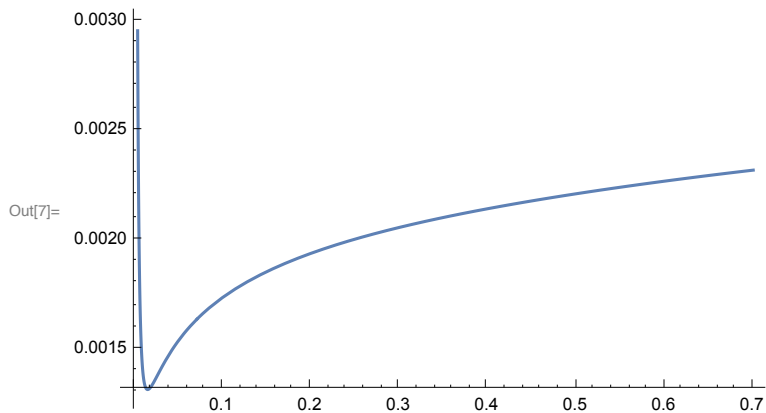
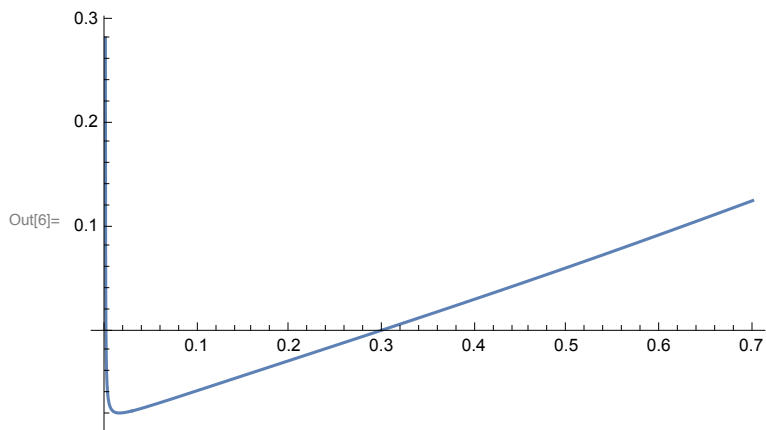
- 1) Notice that the behavior becomes funny as T approaches 0 Kelvin. This is a numerical artifact.
- 2) The prefactor converts from kJ/mol to eV (enthalpy) or from J/mol-K to eV/K (entropy), so the y axes below both are plotting in units of eV.

```
In[4]:= Hprefactor = 0.01
        Sprefactor = 0.00001
```

```
Out[4]= 0.01
```

```
Out[5]= 0.00001
```

```
In[6]:= Plot[Hprefactor enthalpy[t], {t, 0, 0.7}]
        Plot[Sprefactor entropy[t], {t, 0, 0.7}]
```



Connecting DFT results to real-world temperature and pressure (T,P)

■ Background

The expression that we use is :

$$\mu_{O_2}(T, P) = \frac{1}{2} \left[E_{O_2}^{TOT} + \bar{\mu}_{O_2}(T, P_{atm}) + kT \ln \left(\frac{P}{P_{atm}} \right) \right]$$

1) The first term is

$$E_{O_2}^{TOT} = E_{DFT-PBE} + E_{corr} + ZPE$$

is the value of at $T = 0$ K, $P = 1$ atm. Here the three terms are the DFT-PBE energy of O_2 computed in the ground state spin triplet state, the correction to account for the PBE overbinding of the molecule (see Phys. Rev. Lett 80, 890 (1998)), and the zero point energy (all per O_2 molecule). The first number is what I get in VASP using PBE. All of the units below are in eV per O_2 molecule.

```
In[8]:= Edftpbe = -9.8593;
Ecorr = 0.9193;
ZPE = 0.1220;
```

2) The second term $\bar{\mu}_{O_2}(T, P_{atm})$ represents the shift from the first term ($T = 0$ K, $P = 1$ atm) to non-zero temperature, and is evaluated using the equations above:

$$\bar{\mu}_{O_2}(T, P_{atm}) = \Delta H - T \Delta S + \Delta\mu \quad (\text{Gibbs free energy per molecule of } O_2)$$

where the term $\Delta\mu$ is a shift that is present to account for the fact that the ΔH , ΔS Shomate expressions above are relative to RT rather than $T = 0$. This is tricky to get, but I will extrapolate the offset between $T = 0$ K and room temperature as

at RT ($T = 300$ K or $t = 0.3$), the equations above give $\Delta G = \Delta H - T \Delta S = 0$

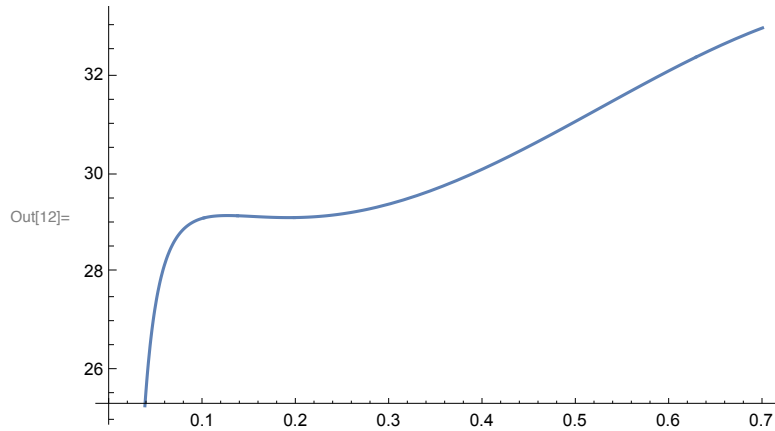
at $T = 0$ K, we have $\Delta G = \Delta H - T \Delta S = \Delta H = -29$ (0.3) kJ/mol = -0.09017 eV per O_2 (see below).

I get this roughly from the slope around $t = 0.2$ ($T = 200$ K), which is 29 kJ/mol.

Therefore the required shift is then $\Delta\mu = \mu(T = 300 \text{ K}) - \mu(T = 0 \text{ K}) = 0.09017$ eV per O_2 .

```
In[11]:= dHdt = D[enthalpy[t], t]
Plot[dHdt, {t, 0, 0.7}]
```

```
Out[11]= 31.3223 -  $\frac{0.007374}{t^2}$  - 20.2353 t + 57.8664 t2 - 36.5062 t3
```



```
In[24]:= Δμ = 0.09017;
```

3) And then finally the last term allows us to shift to a different pressure from atmospheric.

■ Put everything together

Choose temperature range of interest:

1) $T = 100 - 700 \text{ K}$:

```
In[25]:= AA = 31.32234; BB = -20.23531; CC = 57.86644; DD = -36.50624;
EE = -0.007374; FF = -8.903471; GG = 246.7945; HH = 0; HoRT = 0;
```

2) $T = 700 - 2000 \text{ K}$:

```
In[27]:= AA = 30.03235; BB = 8.772972; CC = -3.988133; DD = 0.788313;
EE = -0.741599; FF = -11.32468; GG = 236.1663; HH = 0;
HoRT = 0;
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3) $T = 2000 - 6000 \text{ K}$:

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AA = 20.91111; BB = 10.72071; CC = -2.020498; DD = 0.146449;
EE = 9.245722;
FF = 5.337651;
GG = 237.6185; HH = 0;
HoRT = 0;
```

Assemble Pieces

In[18]:= $E_{O2} = E_{dftpb} + E_{corr} + ZPE;$

$\bar{\mu}_{O_2}[T_] := H_{prefactor} \text{enthalpy}[T / 1000] - T \text{Sprefactor entropy}[T / 1000] + \Delta\mu$

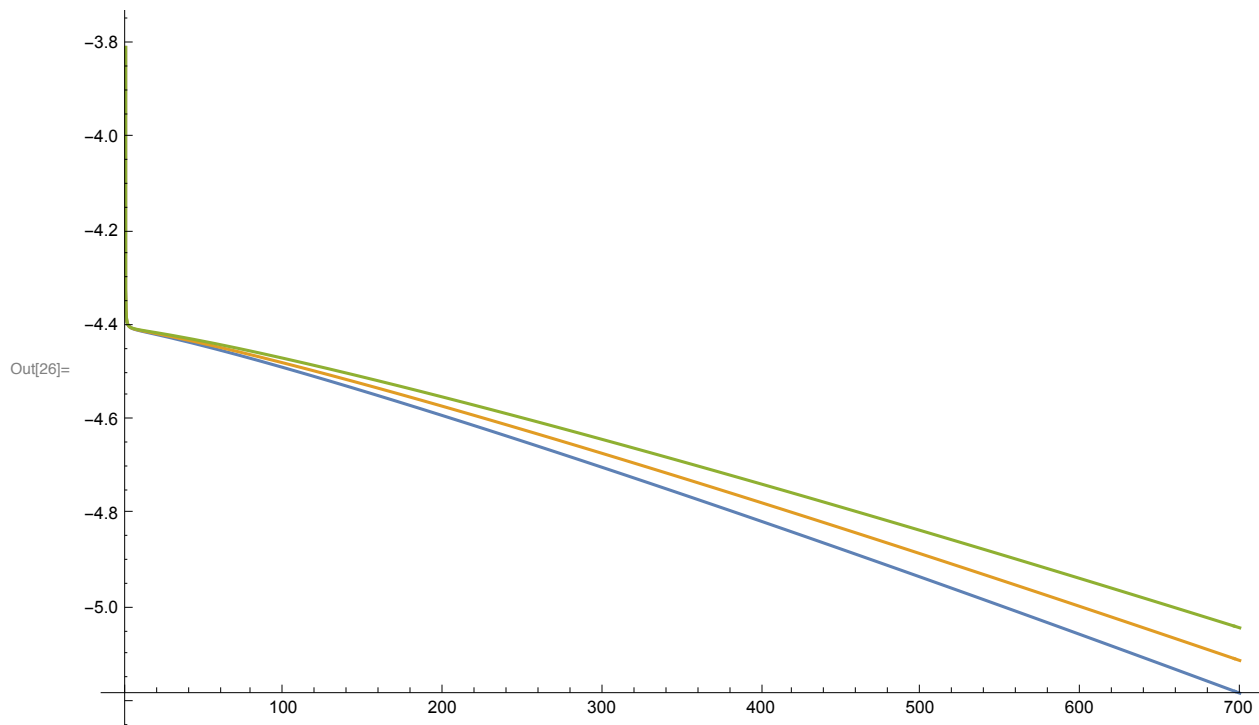
$k_B = 8.617333 \times 10^{-5};$

$\mu_o[T_ , P_] := \frac{1}{2} \left(E_{O2} + \bar{\mu}_{O_2}[T] + k_B T \text{Log}\left[\frac{P}{1}\right] \right)$

The plot below then shows μ_o at $P = 0.1$ atm, $P = 1$ atm, and $P = 10$ atm as a function of temperature from $T = 0$ K to $T = 700$ K. Note that if we want to go to higher ranges of T , we need to choose the right set of parameters in the Shomate equation up at the top.

Plot Chemical Potentials

In[26]:= $\text{Plot}[\{\mu_o[T, 0.1], \mu_o[T, 1], \mu_o[T, 10]\}, \{T, 0, 700\}]$



Here it is, re - evaluated in the higher temperature range:

```
In[28]:= Plot[{ $\mu_o[T, 0.1]$ ,  $\mu_o[T, 1]$ ,  $\mu_o[T, 10]$ }, {T, 700, 2000}]  
Plot[{ $\mu_o[1000, P]$ }, {P, 0.01, 100}, PlotRange -> All]
```

