Entropy and the Second Law

- **Entropy defined as** $dS = \frac{\delta q_{rev}}{T}$ **is a state function. In an adiabatic system dS≥0.**

- **The entropy of the universe cannot decrease.**
- **etc.**

Combined statements of 1st and 2nd Law

$$dU = TdS - PdV + \delta w'$$

Define $\boxed{G = H - TS}$

thus

$$\boxed{dG = VdP - SdT + \delta w'}$$

At constant P and T, G is minimum!

Recall that extra terms can appear…

$$dG = VdP - SdT + \delta w'$$

$$G' = f(P, T, n_1, \ldots, n_c)$$

$$dG' = V'dP - S'dT + \sum_{i=1}^{c} \left(\frac{\partial G'}{\partial n_i} \right)_{P,T,n_{j \neq i}} dn_i$$

can we calculate the chemical potentials in TC? How?

But thermodynamic variables are not "independent"

$$H = \int c_p dT$$

$$S = \int \frac{c_p}{T} dT$$

$$G = H - TS = \int c_p dT - T \int \frac{c_p}{T} dT$$

Following the polynomial proposed by Kubaschewski at $T > \Theta_D$

Cp=			m_3	$+m_4\,T$	$+m_5\,/T^2$	$+m_6\,T^2$
H=	m_1		$+m_3\,T$	$+m_4\,T^2/2$	$+m_5\,/T$	$+m_6\,T^3/3$
S=		m_2	$+m_3\,\ln T$	$+m_4\,T$	$-m_5\,/(2T^2)$	$+\,m_6\,T^2/2$
G=	$m_1 - m_2$	T	$+\,m_3 T(1-\ln T)$	$-m_4\,T^2/2$	$-m_5\,/(2T)$	$-m_6\,T^3/6$

uff

A CALPHAD decision

- **Based on previous discussion,**
  Knowing one of the functions (H,S c_p or G) is enough.

Common option is G!

Elements

$$G_A^{\varphi} = H_A^{\phi,298.15,1atm} + A + BT + CT(1 - LogT) + DT^2 + \frac{E}{T} + FT^3$$

$$G_A^{\varphi} - H_A^{\phi,298.15,1atm} = A + BT + CT(1 - LogT) + DT^2 + \frac{E}{T} + FT^3$$

Dinsdale, A.T., *SGTE data for Pure Elements.* CALPHAD, 1991. **15**(4): p. 317-425.

The elements in Thermocalc (using GHSER) example..

ELEMENT	STABLE ELEMENT REFERENCE	MASS	H298-H0	S298
0 VA	VACUUM	0.0000E+00	0.0000E+00	0.0000E+00
1 MO	BCC_A2	9.5940E+01	4.5890E+03	2.8560E+01
2 SI	DIAMOND_FCC_A4	2.8086E+01	3.2175E+03	1.8820E+01

```
GHSERMO   20000000
     298.13<T< 2896.00: -7746.302+131.9197*T-23.56414*T*LN(T)
   -.003443396*T**2+5.66283E-07*T**3-1.309265E-10*T**4+65812.39*T**(-1)
    2896.00<T< 4000.00: -30556.41+283.559746*T-42.63829*T*LN(T)
   -4.84931E+33*T**(-9)
 GHSERSI   20000000
     298.13<T< 1687.00: -8162.609+137.236859*T-22.8317533*T*LN(T)
   -.001912904*T**2-3.552E-09*T**3+176667*T**(-1)
    1687.00<T< 3600.00: -9457.642+167.281367*T-27.196*T*LN(T)
   -4.2037E+30*T**(-9)
 GSIBCC    20000000
     298.13<T< 3600.00: +47000-22.5*T+GHSERSI
```

“Road map”

- **At constant P and T, G’ of a system is minimum at equilibrium.**

  – How can we know G’of a system as a function of P, T and composition?

    - Use assessments of experimental data and fit to models in a process called OPTIMIZATION. This results in a DATABASE

  – How can we find the minimum of G’?

    - Use a MINIMIZER. In TC, that is POLY-3