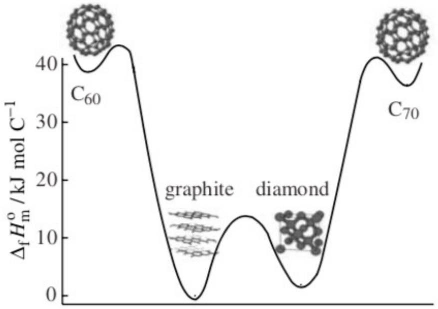
Introduction

Definition of Terms:

Homogeneous Heterogeneous
Ergotic and Non-Ergotic
    (Odyssey way path)
    (Ergotic try all paths => crystal)
    (Non-Ergotic stuck on one path => glass)
Meta-stable
Equilibrium
Extent, extensive: V, Mass
Intensive: Density, Temperature
State Function T, P, ρ, G, H, S,…
First Law, Energy is Conserved
$\Sigma dU = \Sigma dq + \Sigma dw = 0$
Internal Energy, Heat, Work
Adiabatic, Exothermic, Endothermic



For thermodynamics we prefer ergodic, equilibrium states.

Energy Landscape, typically Gibbs Free Energy G = H - TS

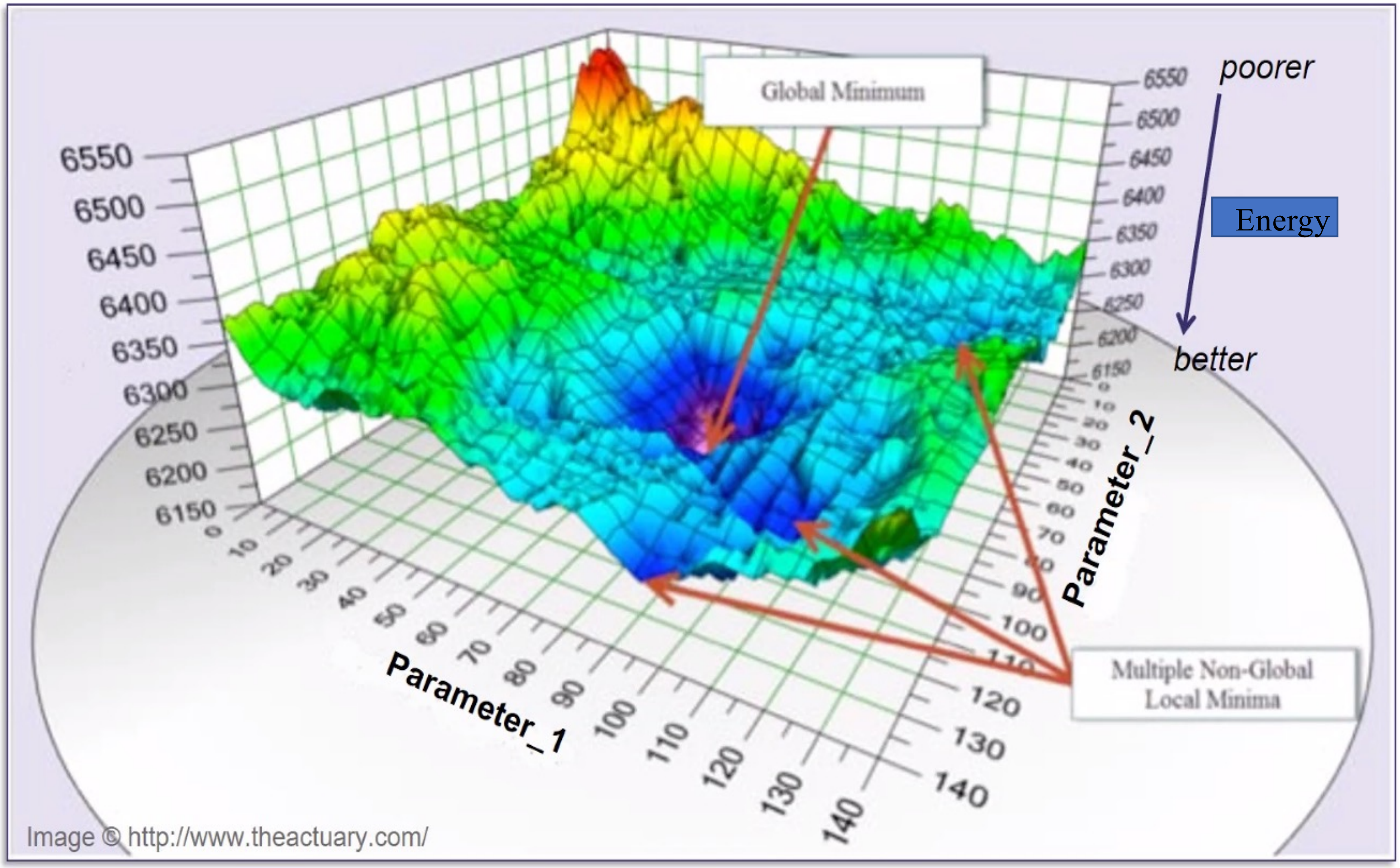


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Table 1.1 Conjugate pairs of variables in work terms for the fundamental equation for the internal energy U. Here f is force of elongation, l is length in the direction of the force, σ is surface tension, A_s is surface area, Φ_i is the electric potential of the phase containing species i, q_i is the contribution of species i to the electric charge of a phase, $\boldsymbol{E}$ is electric field strength, $\boldsymbol{p}$ is the electric dipole moment of the system, $\boldsymbol{B}$ is magnetic field strength (magnetic flux density), and $\boldsymbol{m}$ is the magnetic moment of the system. The dots indicate scalar products of vectors.

Type of work	Intensive variable	Extensive variable	Differential work in dU
Mechanical			
Pressure–volume	$-p$	V	$-p\mathrm{d}V$
Elastic	f	l	$f\mathrm{d}l$
Surface	σ	A_S	$\sigma\mathrm{d}A_S$
Electromagnetic			
Charge transfer	Φ_i	q_i	$\Phi_i\mathrm{d}q_i$
Electric polarization	$\boldsymbol{E}$	$\boldsymbol{p}$	$\boldsymbol{E}\cdot\mathrm{d}\boldsymbol{p}$
Magnetic polarization	$\boldsymbol{B}$	$\boldsymbol{m}$	$\boldsymbol{B}\cdot\mathrm{d}\boldsymbol{m}$

What happens to the energy when I heat a material?
Or How much heat, dq, is required to change the temperature dT? (Heat Capacity, C)

$dq = C\ dT$
$C = dq/dT$

Constant Volume, C_V

$dU = dq + dw$
With only pV work (expansion/contraction), $dw_{ec} = -pdV$
$dU = dq - pdV$
For constant volume
$(dU)_V = dq$, so
$C_V = (dU/dT)_V$, or the energy change with T: $(dU)_V = C_V\ dT$

Constant Volume
Computer **Simulation**
Helmholtz Free Energy, A
$A = U - TS = G - pV$

Constant Pressure, C_p

$dU = dq + dw = dq - pdV$ (only e/c work, i.e. no shaft work)
Invent Entropy $H = U + PV$ so $dH = dU + pdV + Vdp$
$(dH)_p = dU + pdV$ for constant pressure
Rearrange first equation and equate to $(dH)_p$
$dq = dU + pdV = (dH)_p$ and $C = dq/dT$ so
$C_p = (dH/dT)_p$, or the enthalpy change with T: $(dH)_p = C_p\ dT$

Constant Pressure
Atmospheric **Experiments**
Gibbs Free Energy, G
$G = H - TS = A + pV$

State Functions (https://en.wikipedia.org/wiki/State_function)

Parameters that depend only on the current equilibrium state (Pressure, temperature, enthalpy, specific volume, energy) Not on the path taken to reach that state (work and heat). Work is not a conserved value like energy.

Dimension of the “state space” which is always two for us. PV = nRT so with two state functions we can describe the “state” PV or P/T or P/V or VT describe the state. (see Steam Table)

For the 2-dimensional state space we can trace out a path:

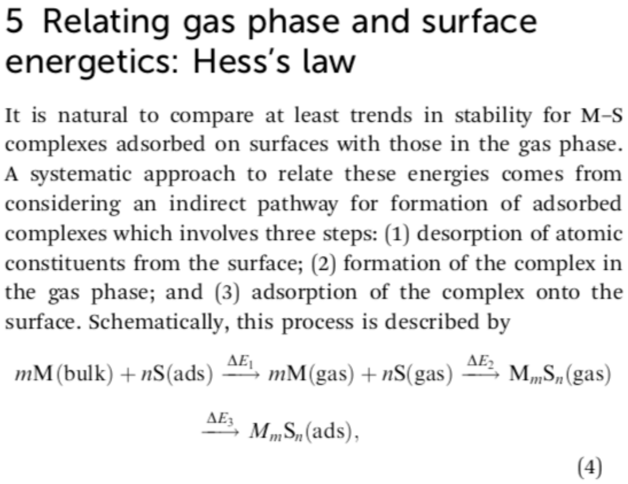
$$W(t_0,t_1) = \int_0^1 P\,dV = \int_{t_0}^{t_1} P(t)\frac{dV(t)}{dt}\,dt$$

The end point is not dependent on the path for equilibrium states. So, you could take a constant pressure path and add a constant volume path to replace a variable pressure and volume path and calculate the state parameters of the end state.

$$\begin{aligned}\Phi(t_0,t_1) &= \int_{t_0}^{t_1} P\frac{dV}{dt}\,dt + \int_{t_0}^{t_1} V\frac{dP}{dt}\,dt \\ &= \int_{t_0}^{t_1} \frac{d(PV)}{dt}\,dt = P(t_1)V(t_1) - P(t_0)V(t_0)\end{aligned}$$

Generally, we don’t know absolute values for H, S, G, A state parameters so we are always using a “reference state”. That is, should we consider the energy of fusion in calculating the energy of water.

Hess' Law
(total enthalpy of a reaction is the sum of the changes regardless of the path; Justification for the use of standard enthalpy of formation)



5 Relating gas phase and surface energetics: Hess's law

It is natural to compare at least trends in stability for M–S complexes adsorbed on surfaces with those in the gas phase. A systematic approach to relate these energies comes from considering an indirect pathway for formation of adsorbed complexes which involves three steps: (1) desorption of atomic constituents from the surface; (2) formation of the complex in the gas phase; and (3) adsorption of the complex onto the surface. Schematically, this process is described by

$$m\mathrm{M}(\text{bulk}) + n\mathrm{S}(\text{ads}) \xrightarrow{\Delta E_1} m\mathrm{M}(\text{gas}) + n\mathrm{S}(\text{gas}) \xrightarrow{\Delta E_2} \mathrm{M}_m\mathrm{S}_n(\text{gas}) \xrightarrow{\Delta E_3} M_m\mathrm{S}_n(\text{ads}), \quad (4)$$

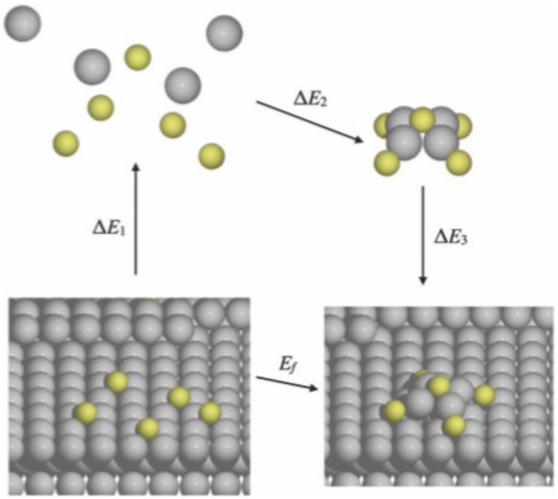
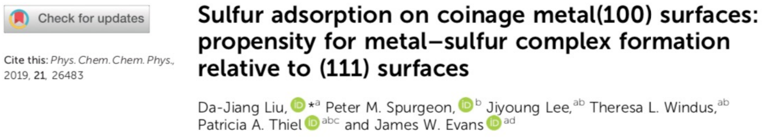


Fig. 3 Schematic for Hess's law specifically illustrating the case of M_4S_5.



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Sulfur adsorption on coinage metal(100) surfaces: propensity for metal–sulfur complex formation relative to (111) surfaces

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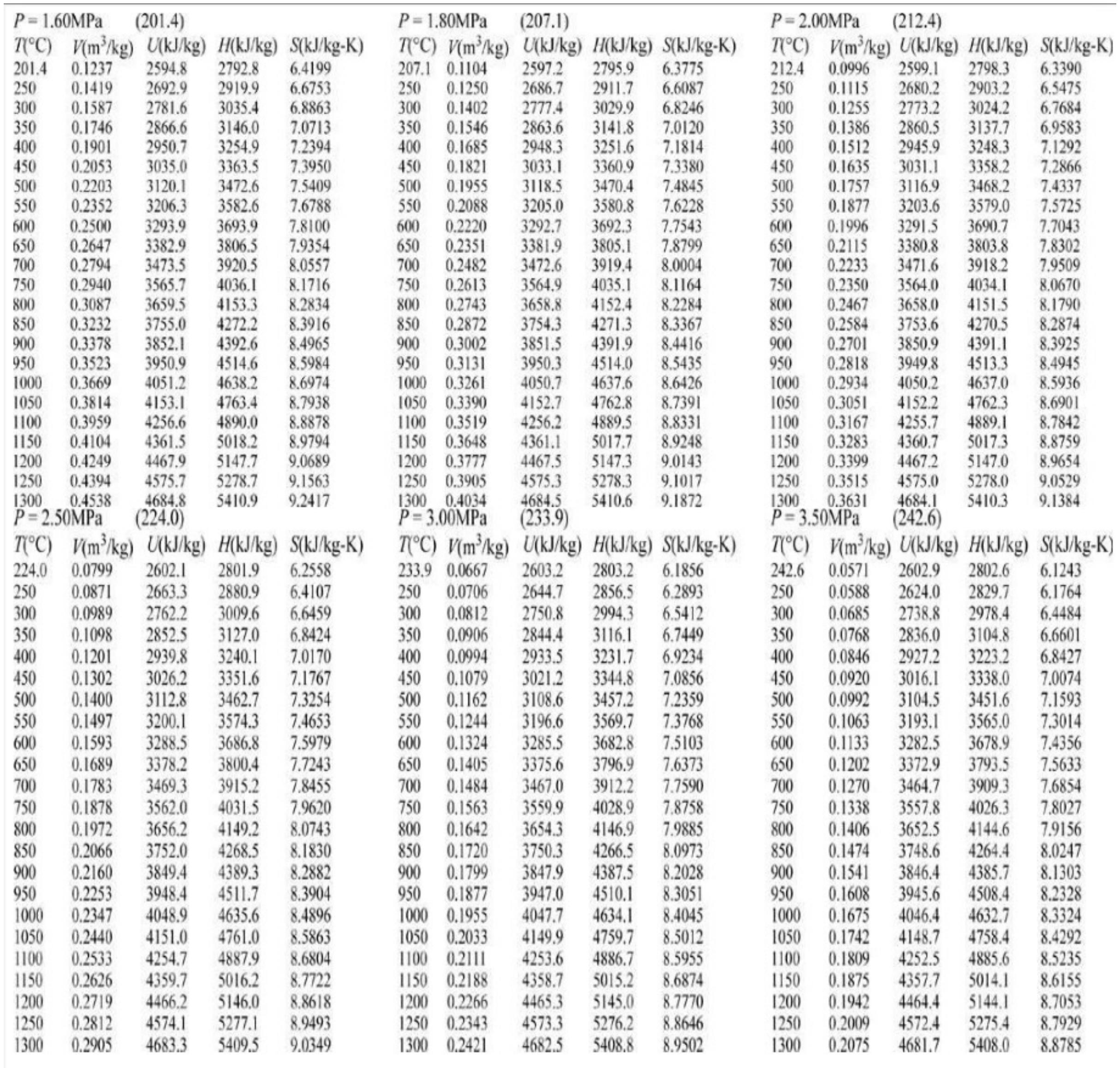
Steam Tables

If I know P and T
I can get V, U, H, S

If I know H and S
I can get P, T, V, U

These tables are generated by the PREOS Equation of State which is a state function like PV=nRT



P = 1.60MPa (201.4)

T(°C)	V(m^3/kg)	U(kJ/kg)	H(kJ/kg)	S(kJ/kg-K)
201.4	0.1237	2594.8	2792.8	6.4199
250	0.1419	2692.9	2919.9	6.6753
300	0.1587	2781.6	3035.4	6.8863
350	0.1746	2866.6	3146.0	7.0713
400	0.1901	2950.7	3254.9	7.2394
450	0.2053	3035.0	3363.5	7.3950
500	0.2203	3120.1	3472.6	7.5409
550	0.2352	3206.3	3582.6	7.6788
600	0.2500	3293.9	3693.9	7.8100
650	0.2647	3382.9	3806.5	7.9354
700	0.2794	3473.5	3920.5	8.0557
750	0.2940	3565.7	4036.1	8.1716
800	0.3087	3659.5	4153.3	8.2834
850	0.3232	3755.0	4272.2	8.3916
900	0.3378	3852.1	4392.6	8.4965
950	0.3523	3950.9	4514.6	8.5984
1000	0.3669	4051.2	4638.2	8.6974
1050	0.3814	4153.1	4763.4	8.7938
1100	0.3959	4256.6	4890.0	8.8878
1150	0.4104	4361.5	5018.2	8.9794
1200	0.4249	4467.9	5147.7	9.0689
1250	0.4394	4575.7	5278.7	9.1563
1300	0.4538	4684.8	5410.9	9.2417

P = 1.80MPa (207.1)

T(°C)	V(m^3/kg)	U(kJ/kg)	H(kJ/kg)	S(kJ/kg-K)
207.1	0.1104	2597.2	2795.9	6.3775
250	0.1250	2686.7	2911.7	6.6087
300	0.1402	2777.4	3029.9	6.8246
350	0.1546	2863.6	3141.8	7.0120
400	0.1685	2948.3	3251.6	7.1814
450	0.1821	3033.1	3360.9	7.3380
500	0.1955	3118.5	3470.4	7.4845
550	0.2088	3205.0	3580.8	7.6228
600	0.2220	3292.7	3692.3	7.7543
650	0.2351	3381.9	3805.1	7.8799
700	0.2482	3472.6	3919.4	8.0004
750	0.2613	3564.9	4035.1	8.1164
800	0.2743	3658.8	4152.4	8.2284
850	0.2872	3754.3	4271.3	8.3367
900	0.3002	3851.5	4391.9	8.4416
950	0.3131	3950.3	4514.0	8.5435
1000	0.3261	4050.7	4637.6	8.6426
1050	0.3390	4152.7	4762.8	8.7391
1100	0.3519	4256.2	4889.5	8.8331
1150	0.3648	4361.1	5017.7	8.9248
1200	0.3777	4467.5	5147.3	9.0143
1250	0.3905	4575.3	5278.3	9.1017
1300	0.4034	4684.5	5410.6	9.1872

P = 2.00MPa (212.4)

T(°C)	V(m^3/kg)	U(kJ/kg)	H(kJ/kg)	S(kJ/kg-K)
212.4	0.0996	2599.1	2798.3	6.3390
250	0.1115	2680.2	2903.2	6.5475
300	0.1255	2773.2	3024.2	6.7684
350	0.1386	2860.5	3137.7	6.9583
400	0.1512	2945.9	3248.3	7.1292
450	0.1635	3031.1	3358.2	7.2866
500	0.1757	3116.9	3468.2	7.4337
550	0.1877	3203.6	3579.0	7.5725
600	0.1996	3291.5	3690.7	7.7043
650	0.2115	3380.8	3803.8	7.8302
700	0.2233	3471.6	3918.2	7.9509
750	0.2350	3564.0	4034.1	8.0670
800	0.2467	3658.0	4151.5	8.1790
850	0.2584	3753.6	4270.5	8.2874
900	0.2701	3850.9	4391.1	8.3925
950	0.2818	3949.8	4513.3	8.4945
1000	0.2934	4050.2	4637.0	8.5936
1050	0.3051	4152.2	4762.3	8.6901
1100	0.3167	4255.7	4889.1	8.7842
1150	0.3283	4360.7	5017.3	8.8759
1200	0.3399	4467.2	5147.0	8.9654
1250	0.3515	4575.0	5278.0	9.0529
1300	0.3631	4684.1	5410.3	9.1384

P = 2.50MPa (224.0)

T(°C)	V(m^3/kg)	U(kJ/kg)	H(kJ/kg)	S(kJ/kg-K)
224.0	0.0799	2602.1	2801.9	6.2558
250	0.0871	2663.3	2880.9	6.4107
300	0.0989	2762.2	3009.6	6.6459
350	0.1098	2852.5	3127.0	6.8424
400	0.1201	2939.8	3240.1	7.0170
450	0.1302	3026.2	3351.6	7.1767
500	0.1400	3112.8	3462.7	7.3254
550	0.1497	3200.1	3574.3	7.4653
600	0.1593	3288.5	3686.8	7.5979
650	0.1689	3378.2	3800.4	7.7243
700	0.1783	3469.3	3915.2	7.8455
750	0.1878	3562.0	4031.5	7.9620
800	0.1972	3656.2	4149.2	8.0743
850	0.2066	3752.0	4268.5	8.1830
900	0.2160	3849.4	4389.3	8.2882
950	0.2253	3948.4	4511.7	8.3904
1000	0.2347	4048.9	4635.6	8.4896
1050	0.2440	4151.0	4761.0	8.5863
1100	0.2533	4254.7	4887.9	8.6804
1150	0.2626	4359.7	5016.2	8.7722
1200	0.2719	4466.2	5146.0	8.8618
1250	0.2812	4574.1	5277.1	8.9493
1300	0.2905	4683.3	5409.5	9.0349

P = 3.00MPa (233.9)

T(°C)	V(m^3/kg)	U(kJ/kg)	H(kJ/kg)	S(kJ/kg-K)
233.9	0.0667	2603.2	2803.2	6.1856
250	0.0706	2644.7	2856.5	6.2893
300	0.0812	2750.8	2994.3	6.5412
350	0.0906	2844.4	3116.1	6.7449
400	0.0994	2933.5	3231.7	6.9234
450	0.1079	3021.2	3344.8	7.0856
500	0.1162	3108.6	3457.2	7.2359
550	0.1244	3196.6	3569.7	7.3768
600	0.1324	3285.5	3682.8	7.5103
650	0.1405	3375.6	3796.9	7.6373
700	0.1484	3467.0	3912.2	7.7590
750	0.1563	3559.9	4028.9	7.8758
800	0.1642	3654.3	4146.9	7.9885
850	0.1720	3750.3	4266.5	8.0973
900	0.1799	3847.9	4387.5	8.2028
950	0.1877	3947.0	4510.1	8.3051
1000	0.1955	4047.7	4634.1	8.4045
1050	0.2033	4149.9	4759.7	8.5012
1100	0.2111	4253.6	4886.7	8.5955
1150	0.2188	4358.7	5015.2	8.6874
1200	0.2266	4465.3	5145.0	8.7770
1250	0.2343	4573.3	5276.2	8.8646
1300	0.2421	4682.5	5408.8	8.9502

P = 3.50MPa (242.6)

T(°C)	V(m^3/kg)	U(kJ/kg)	H(kJ/kg)	S(kJ/kg-K)
242.6	0.0571	2602.9	2802.6	6.1243
250	0.0588	2624.0	2829.7	6.1764
300	0.0685	2738.8	2978.4	6.4484
350	0.0768	2836.0	3104.8	6.6601
400	0.0846	2927.2	3223.2	6.8427
450	0.0920	3016.1	3338.0	7.0074
500	0.0992	3104.5	3451.6	7.1593
550	0.1063	3193.1	3565.0	7.3014
600	0.1133	3282.5	3678.9	7.4356
650	0.1202	3372.9	3793.5	7.5633
700	0.1270	3464.7	3909.3	7.6854
750	0.1338	3557.8	4026.3	7.8027
800	0.1406	3652.5	4144.6	7.9156
850	0.1474	3748.6	4264.4	8.0247
900	0.1541	3846.4	4385.7	8.1303
950	0.1608	3945.6	4508.4	8.2328
1000	0.1675	4046.4	4632.7	8.3324
1050	0.1742	4148.7	4758.4	8.4292
1100	0.1809	4252.5	4885.6	8.5235
1150	0.1875	4357.7	5014.1	8.6155
1200	0.1942	4464.4	5144.1	8.7053
1250	0.2009	4572.4	5275.4	8.7929
1300	0.2075	4681.7	5408.0	8.8785

Thermodynamic Square

$-S$	U	V
H		A
$-p$	G	T

$$H = U + PV$$

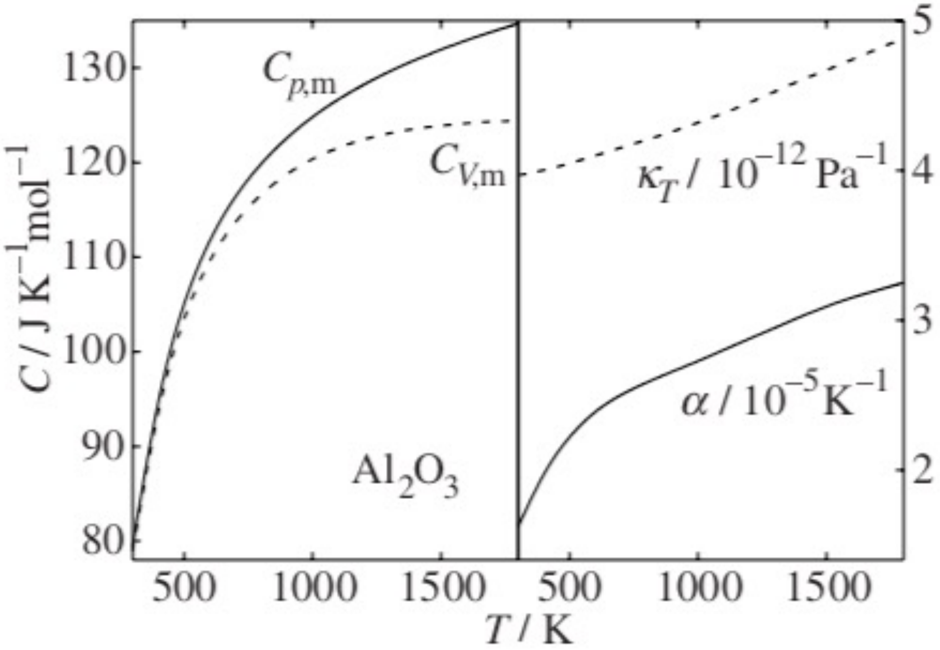
$$A = U - TS = G - pV$$

$$G = H - TS = A + pV$$

$C_p - C_v = \alpha^2 VT/\kappa_T$

$\alpha = (1/V)\,(dV/dT)_p$
$\kappa_T = (1/V)\,(dV/dP)_T$

We will obtain this later



Slope is C_p, this is not defined at first order transitions
(melting and vaporization, crystalline phase change, order/disorder transition)

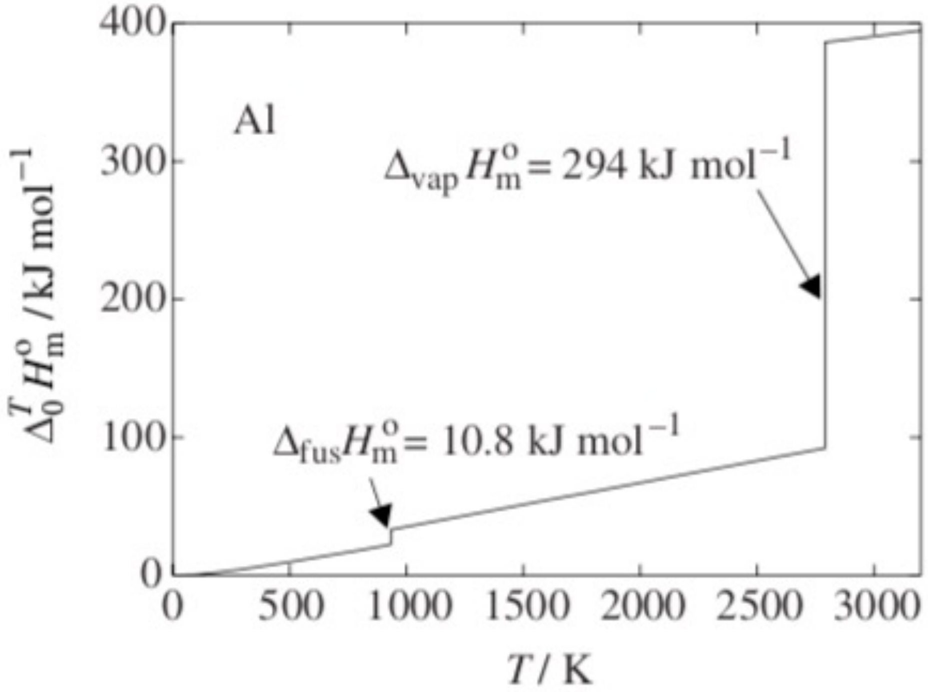


Figure 1.3 Standard enthalpy of aluminium relative to 0 K. The standard enthalpy of fusion ($\Delta_{fus}H_m^o$) is significantly smaller than the standard enthalpy of vaporization ($\Delta_{vap}H_m^o$).

Size dependent enthalpy of melting
(Gibbs-Thompson Equation)

For bulk materials, $r = \infty$, at the melting point $\Delta G = \Delta H - T_\infty \Delta S = 0$
So, $T_\infty = \Delta H/\Delta S$ Larger bonding enthalpy leads to higher T_∞ , Greater randomness gain on melting leads to lower T_∞.

For nanoparticles there is also a surface term,
$(\Delta G)\ V = (\Delta H - T_r\Delta S)V + \sigma A = 0$, where T_r is the melting point for size r nanoparticle
If $V = r^3$ and $A = r^2$ and using $\Delta S = \Delta H/T_\infty$ this becomes,
$\Delta S\ r = \sigma/(\Delta H(1- T_r/T_\infty))$ or $T_r = T_\infty\ (1 - \sigma/(r\ \Delta H)$
Smaller particles have a lower melting point, and the dependence suggests a plot of T_r/T_∞ against 1/r with negative slope $-\sigma/\Delta H$

Second Law: Reversibility

For an adiabatic reversible system $\Delta S = 0$
In a process this is often used by engineers in calculations

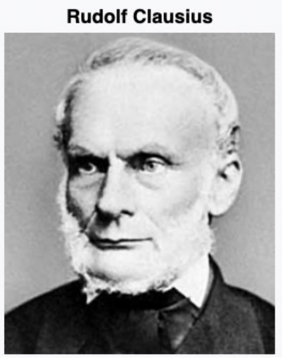
1) Assume $\Delta S = 0$, calculate ΔH for the process
2) Use an efficiency, η, to modify ΔH to a larger value
3) Calculate the actual $\Delta S > 0$ for the process

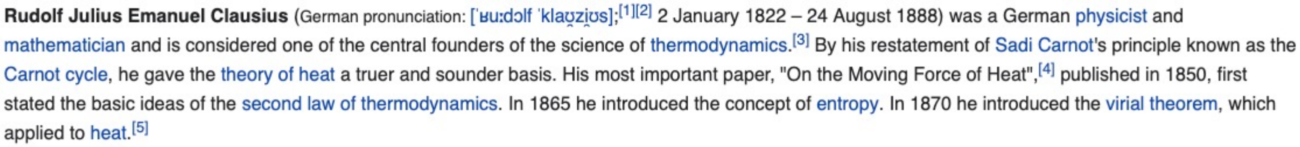
The change in entropy is tied to the concept of efficiency
100% efficient process has $\Delta S = 0$

Calusius Theorem is that entropy increases or stays the same but can not spontaneously decrease

For a reversible process $dS_{rev} = (dq/T)_{rev}$

For any process $dS \geq (dq/T)$





Rudolf Julius Emanuel Clausius (German pronunciation: [ˈʁuːdɔlf ˈklaʊ̯zi̯ʊs];[1][2] 2 January 1822 – 24 August 1888) was a German physicist and mathematician and is considered one of the central founders of the science of thermodynamics.[3] By his restatement of Sadi Carnot's principle known as the Carnot cycle, he gave the theory of heat a truer and sounder basis. His most important paper, "On the Moving Force of Heat",[4] published in 1850, first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of entropy. In 1870 he introduced the virial theorem, which applied to heat.[5]

Equilibrium

For any process $dS \geq (dq/T)$ (Calusius Theorem)

Or $dq - TdS <= 0$

$dq - TdS$ we can call the “Change in Free Energy”
(This is the free energy available to do work.)
For a reversible process at ***thermodynamic equilibrium,*** it is equal to 0
This is a quantitative definition for equilibrium

At **constant volume** (Simulations) $dq = dU$
The Helmholtz Free Energy is defined: $A = U - TS$ so $dA = dU - TdS - SdT$
$dA = dU - TdS$ (at constant temperature)
$dA = 0$ at equilibrium for constant V and T

At **constant pressure** (Experiments) $dq = dH$
The Gibbs Free Energy is defined: $G = H - TS$ so $dG = dH - TdS - SdT$
$dG = dH - TdS$ (at constant temperature)
$dG = 0$ at equilibrium for constant p and T

-S	U	V
H		A
-p	G	T

Third Law

$S = k_B \ln\Omega$
Ω is the number of states
For an infinite perfect crystal there is only one state
$\Omega = 1$ and $\ln\Omega = 0$ so $S = 0$
This could only occur at $T = 0$ for an ergodic system where there is no thermal motion. (without thermal motion the system can't be ergodic, so it is not possible to reach this hypothetical state)

Legendre transformation to obtain Maxwell Relationship

These are relationships that are useful to relate differential thermodynamic properties
Like heat capacities, thermal expansion coefficient etc.

$dU = dq + dw$

1) For only ec work

$$dU = dq - pdV$$

2) $dq = TdS$ for a reversible process

$$dU = TdS - pdV$$

So U is naturally broken into functions of S and V

$\mathbf{(dU/dS)_V = T}$ ***Use below***

$\mathbf{(dU/dV)_S = -p}$ ***Use below***

$dU = (dU/dS)_V\ dS + (dU/dV)_S\ dV$

$dU = (dU/dS)_V\ dS + (dU/dV)_S\ dV$

Take the second derivative

$d^2U/(dSdV) = (d\ (dU/dV)_S\ /dS)_V = (d\ (dU/dS)_V\ /dV)_S = d^2U/(dVdS)$

Using the above expressions and the middle two terms

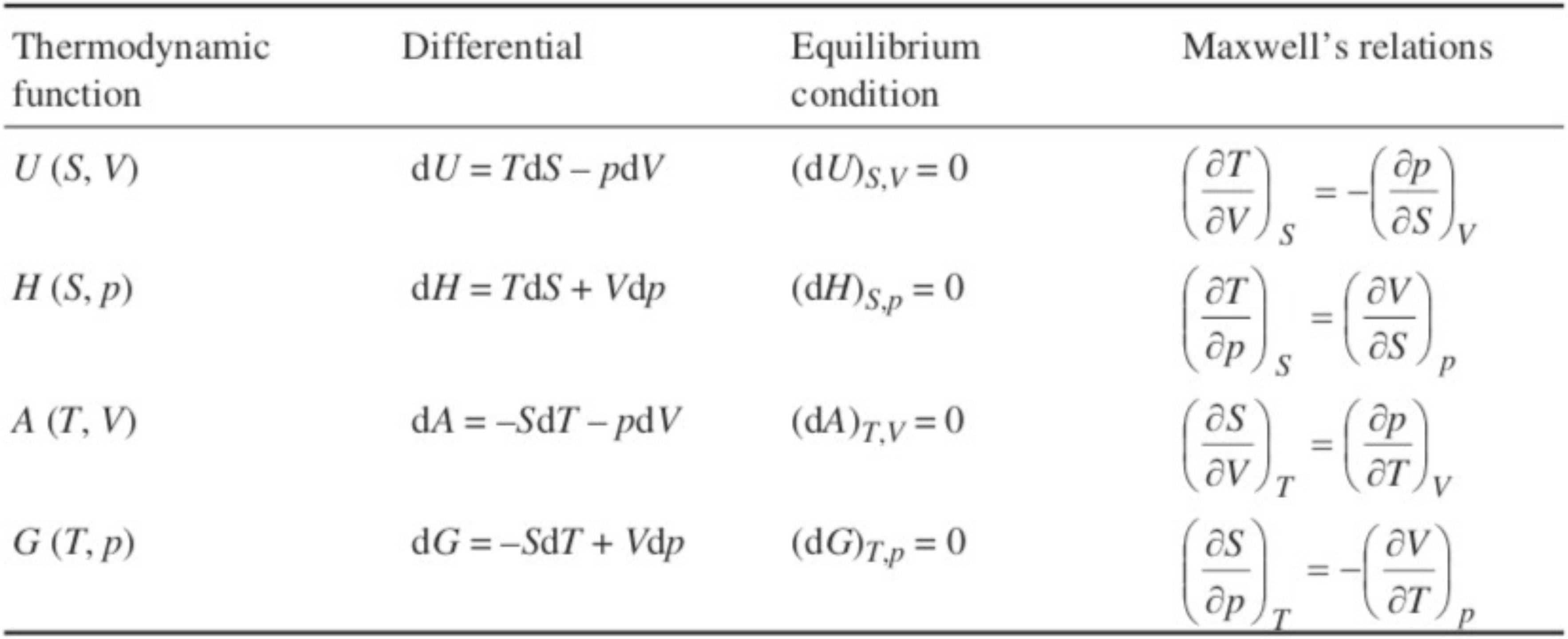
$-(dp/dS)_V = (dT/dV)_S$

This is a Maxwell Relationship, and the process is called a Legendre transformation

This can be done for all four fundamental equations, U; H; G; A

-S	U	V
H		A
-p	G	T

Table 1.6 The Maxwell relations.



Thermodynamic function	Differential	Equilibrium condition	Maxwell's relations
$U\ (S, V)$	$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$	$(\mathrm{d}U)_{S,V} = 0$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$H\ (S, p)$	$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$	$(\mathrm{d}H)_{S,p} = 0$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$A\ (T, V)$	$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$	$(\mathrm{d}A)_{T,V} = 0$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
$G\ (T, p)$	$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$	$(\mathrm{d}G)_{T,p} = 0$	$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

Thermodynamic Square

-S	U	V
H		A
-p	G	T

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Thermodynamic Square

-S	U	V
H		A
-p	G	T

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

$$\mathrm{d}A = -S\mathrm{d}T - p\mathrm{d}V$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

Definition of G = H – TS

$dG = dH - T\,dS - S\,dT$

Definition of H = U + PV

$dH = dU + PdV + V\,dP$

Definition of dU = dw + dq

No shaft work and reversible (2’d law)

$dU = -PdV + TdS$

So, $dH = -PdV + TdS + PdV + VdP = TdS + VdP$

$dG = TdS + VdP - TdS - SdT$

$= VdP - SdT$

Useful Rules for thermodynamic differentials

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \qquad 6.11$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_x = 0 \quad \text{and} \quad \left(\frac{\partial x}{\partial y}\right)_y = \infty} \qquad 6.12$$

$$\boxed{\left(\frac{\partial x}{\partial x}\right)_y = 1} \qquad 6.13$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_F = \left(\frac{\partial x}{\partial z}\right)_F\left(\frac{\partial z}{\partial y}\right)_F} \qquad 6.16$$

Chain rule interposing a variable.

$$\boxed{\left(\frac{\partial F}{\partial w}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y\left(\frac{\partial x}{\partial w}\right)_z + \left(\frac{\partial F}{\partial y}\right)_x\left(\frac{\partial y}{\partial w}\right)_z} \qquad 6.17$$

The expansion rule.

Triple Product Rule

Suppose $F = F(x,y)$, then

$$dF = (\partial F/\partial x)_y\, dx + (\partial F/\partial y)_x\, dy \qquad 6.14$$

Consider what happens when $dF = 0$ (i.e., at constant F). Then,

$$0 = \left(\frac{\partial F}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_F + \left(\frac{\partial F}{\partial y}\right)_x \Rightarrow \left(\frac{\partial x}{\partial y}\right)_F = \frac{-\left(\frac{\partial F}{\partial y}\right)_x}{\left(\frac{\partial F}{\partial x}\right)_y} = \frac{-\left(\frac{\partial x}{\partial F}\right)_y}{\left(\frac{\partial y}{\partial F}\right)_x} \text{ or}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_F\left(\frac{\partial y}{\partial F}\right)_x\left(\frac{\partial F}{\partial x}\right)_y = -1} \qquad 6.15$$

Triple product rule.

Derive the expression for $C_p – C_V$

-S	U	V
H		A
-p	G	T

$C_p - C_v = \alpha^2 VT/\kappa_T$
$\alpha = (1/V)\ (dV/dT)_p$
$\kappa_T = (1/V)\ (dV/dP)_T$

$C_V = (dU/dT)_V$
From the Thermodynamic Square
$dU = TdS – pdV$ so $C_V = (dU/dT)_V = T\ (dS/dT)_V - p\ (dV/dT)_V$
Second term is 0 dV at constant V is 0
$(dS/dT)_V = C_V/T$
Similarly
$C_p = (dH/dT)_p$
From the Thermodynamic Square
$dH = TdS + Vdp$ so $C_p = (dH/dT)_p = T\ (dS/dT)_p - V\ (dp/dT)_p$
Second term is 0 dp at constant p is 0
$(dS/dT)_p = C_p/T$

Write a differential expression for dS as a function of T and V
$dS = (dS/dT)_V dT + (dS/dV)_T dV$ using expression for C_V above and Maxwell for $(dS/dV)_T$
$dS = C_V/T\ dT + (dp/dT)_V dV$ use chain rule: $(dp/dT)_V = -(dV/dT)_p\ (dP/dV)_T = V\alpha\ /\ (V\kappa_T)$
Take the derivative for C_p: $C_p/T = (dS/dT)_p = C_V/T\ (dT/dT)_p + (\alpha/\kappa_T)(dV/dT)_p = C_V/T + (V\alpha^2/\kappa_T)$
$C_p - C_v = \alpha^2 VT/\kappa_T$

-S U V
H A
-p G T

$$dG = VdP - SdT$$

Lowest Gibbs Free Energy is the stable phase

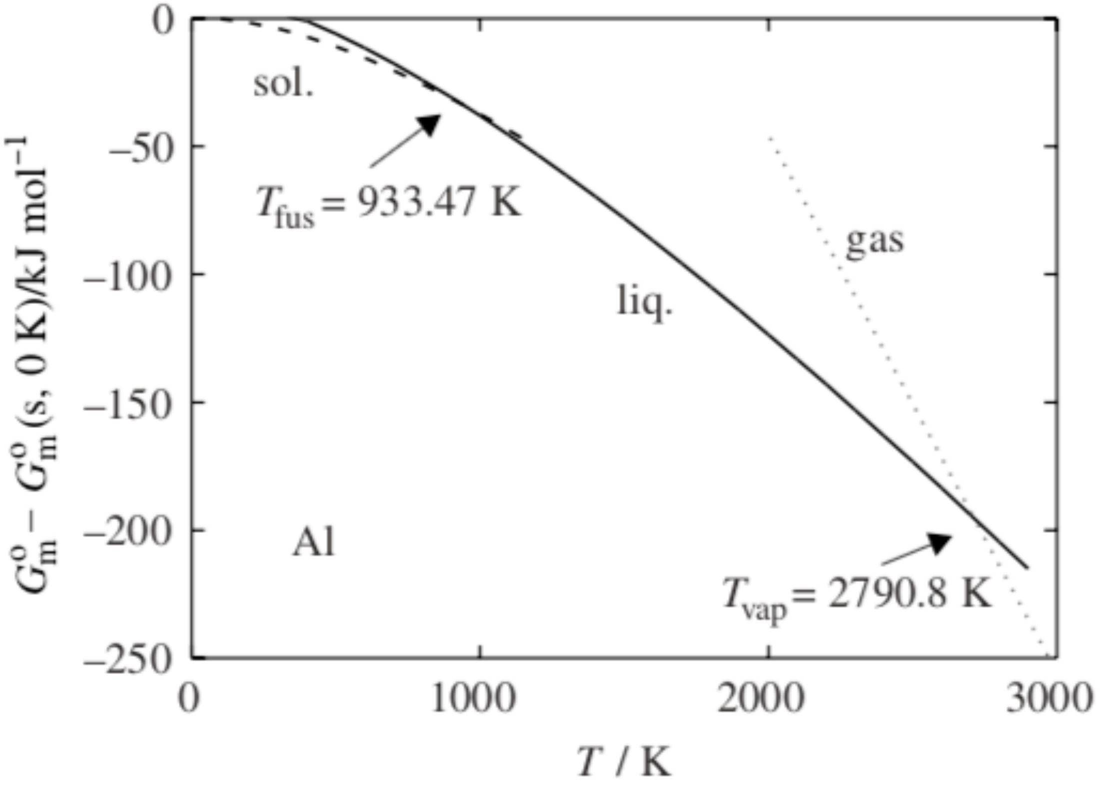


Figure 1.8 Standard Gibbs energy of solid, liquid and gaseous aluminium relative to the standard Gibbs energy of solid aluminium at $T = 0$ K as a function of temperature (at $p = 1$ bar).

Why does G decrease with T?

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

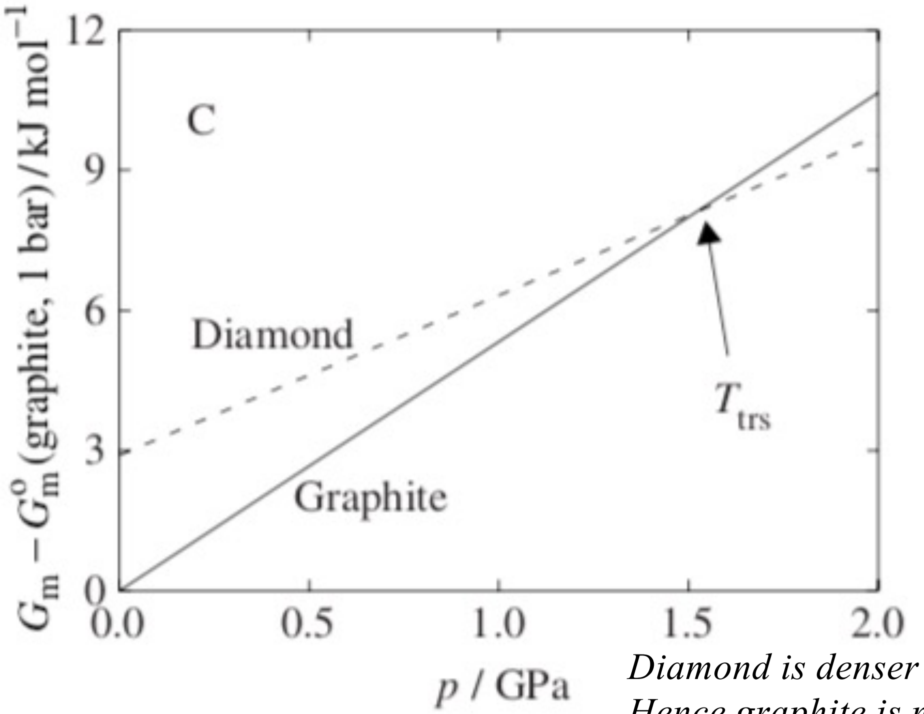
$$G(T_f) = G(T_i) - \int_{T_i}^{T_f} S\,dT$$

S generally increases
With temperature

-S U V
H   A
-p G T

$dG = VdP - SdT$

Lowest Gibbs Free Energy is the stable phase



Diamond is denser than graphite so weaker slope
Hence graphite is more stable at low pressure

Figure 1.9 Standard Gibbs energy of graphite and diamond at T = 298 K relative to the standard Gibbs energy of graphite at 1 bar as a function of pressure.

Why does G increase with p?

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V \mathrm{d}p$$

Volume is positive
So G increases with pressure

Phases at Equilibrium, Chemical Potential or partial molar Gibbs free energy
(For multiple phases and/or components)

Consider water and water vapor at equilibrium. A molecule of water can leave liquid water and join the water vapor due to thermal energy. At equilibrium it can just as likely leave water vapor to join liquid water. We are not considering the interfacial energy.
The total number of moles in the container (system), n_{total}, is fixed. But the number in liquid water can change by $dn_{liquid} = -dn_{vapor}$. This change would change the Gibbs free energy (we are doing an experiment at constant atmospheric pressure).
$\mu_{liq} = (dG_{liq}/dn_{liq}) = (dG_{vap}/dn_{vap}) = \mu_{vap}$ at equilibrium
so that the change for liquid = -the change for vapor;
$dn_{liq} = -dn_{vap}$ for conservation of mass.
$dn_{liq}\ \mu_{liq} = dn_{vap}\ \mu_{vap}$
μ_{vap} is called the chemical potential of water in the vapor phase.
Chemical potential ***always*** has two qualifiers, of ***what component*** in ***what phase***.

μ_{vap} is the partial molar Gibbs Free Energy of water in the vapor phase.
H, S, V can also have partial molar values in the same way usually signified by a bar.

Gibbs-Duhem Equation

(For multiple phases and/or components)

-S	U	V
H		A
-p	G	T

$$G = \sum_i n_i \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_{j \neq i}} = \sum_i n_i \bar{G}_i = \sum_i n_i \mu_i$$

Consider a binary system A + B makes a solution

$$G = n_A \mu_A + n_B \mu_B$$

$$dG = n_A d\mu_A + dn_A \mu_A + n_B d\mu_B + dn_B \mu_B$$

Fundamental equation with chemical potential:

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

At constant T and p:

$$dG = \mu_A dn_A + \mu_B dn_B$$

So, at constant T and p:

$$n_A d\mu_A + n_B d\mu_B = 0 \quad \text{i.e.} \quad \sum_i n_i d\mu_i = 0$$

Reintroducing the T and p dependences:

$$SdT - Vdp + \sum_i n_i d\mu_i = 0$$

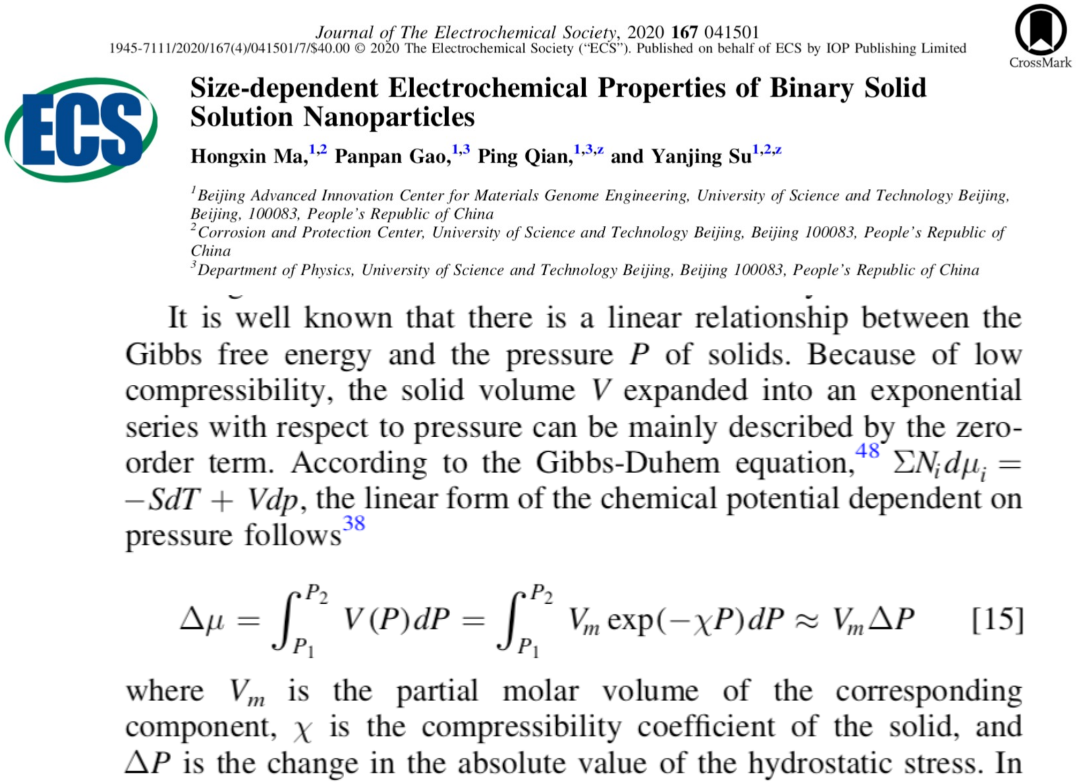
Gibbs-Duhem Equation

Changes in the chemical potential of the phases are related to the temperature and pressure through the entropy and specific volume

(Often used under isothermal and isobaric conditions)

Corrosion in nanoparticles can be higher or lower

Gibbs-Duhem Equation



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Size-dependent Electrochemical Properties of Binary Solid Solution Nanoparticles

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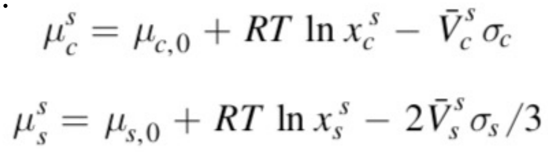
It is well known that there is a linear relationship between the Gibbs free energy and the pressure P of solids. Because of low compressibility, the solid volume V expanded into an exponential series with respect to pressure can be mainly described by the zero-order term. According to the Gibbs-Duhem equation,[48] $\Sigma N_i d\mu_i = -SdT + Vdp$, the linear form of the chemical potential dependent on pressure follows[38]

$$\Delta\mu = \int_{P_1}^{P_2} V(P)dP = \int_{P_1}^{P_2} V_m \exp(-\chi P)dP \approx V_m\Delta P \qquad [15]$$

where V_m is the partial molar volume of the corresponding component, χ is the compressibility coefficient of the solid, and ΔP is the change in the absolute value of the hydrostatic stress. In

σ = the stress (ΔP) so the contribution to chemical potential from stress is proportional to σ V depending on geometry

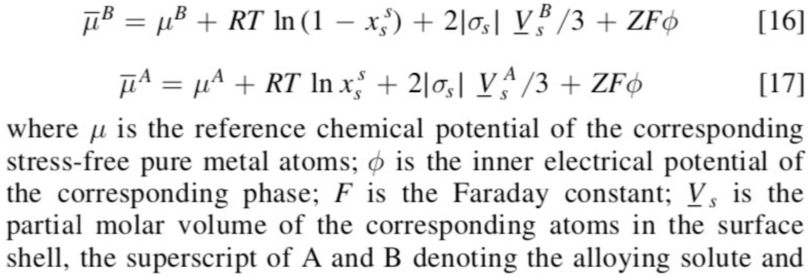
Consider a binary solution in a nanoparticle. There is significant stress on the surface, s, compared to the core, c. Break particle into core and surface regions with different stress, σ_c, σ_s, molar composition of the solute in core, x_c, and surface, x_s. Assume equilibrium, $\mu_c = \mu_s$. "ln" term is gaseous mixing entropy, 0 terms are for infinite dilution.



$$\mu_c^s = \mu_{c,0} + RT\ln x_c^s - \bar{V}_c^s\sigma_c$$

$$\mu_s^s = \mu_{s,0} + RT\ln x_s^s - 2\bar{V}_s^s\sigma_s/3$$

For the two components with an electric potential the equilibrium corrosion potential can be calculated for each component which changes with particle size.



$$\bar{\mu}^B = \mu^B + RT\ln(1 - x_s^s) + 2|\sigma_s|\,\underline{V}_s^B/3 + ZF\phi \qquad [16]$$

$$\bar{\mu}^A = \mu^A + RT\ln x_s^s + 2|\sigma_s|\,\underline{V}_s^A/3 + ZF\phi \qquad [17]$$

where μ is the reference chemical potential of the corresponding stress-free pure metal atoms; ϕ is the inner electrical potential of the corresponding phase; F is the Faraday constant; $\underline{V}_s$ is the partial molar volume of the corresponding atoms in the surface shell, the superscript of A and B denoting the alloying solute and

In the equilibrium state, the total Gibbs free energy change in Eq. 14 $\Delta G = 0$.[34,35] Consequently, the corresponding equilibrium potential[34,35,38] of these electrode reactions developed on the surface of binary solid solution can be written as

$$\overset{\leftrightarrow}{\phi}{}_e^B = \phi_M - \phi_{sol} = \phi_e^B - \frac{RT\ \ln(1 - x_s^s) + 2|\sigma_s|\ \underline{V}_s^B/3}{ZF} \qquad [18]$$

$$\overset{\leftrightarrow}{\phi}{}_e^A = \phi_M - \phi_{sol} = \phi_e^A - \frac{RT\ \ln x_s^s + 2|\sigma_s|\ \underline{V}_s^A/3}{ZF} \qquad [19]$$

where $\phi_e = (\mu_{M^{Z+}} + Z\mu_{e^-} - \mu_M)/(ZF)$ is the equilibrium potential of the corresponding pure bulk materials neglecting their surface stress. Then, the difference in the equilibrium potential between the solvent and solute atoms in the surface shell of binary solid solution can be expressed as

$$\Delta\overset{\leftrightarrow}{\phi}{}_e^{AB} = (\phi_e^B - \phi_e^A) + \frac{1}{ZF}\left(RT\ \ln\frac{x_s^s}{1 - x_s^s} + \frac{2|\sigma_s|(\underline{V}_s^A - \underline{V}_s^B)}{3}\right) \qquad [20]$$

As all we know, if $\Delta\overset{\leftrightarrow}{\phi}{}_e^{AB} \neq 0$, anodic polarization will occur in the lower potential atom phase and cathodic polarization will occur in the higher potential atom phase. That implies that the anodic corrosion in the lower potential atom phase occurs more quickly, while the corrosion in the higher potential atom phase is inhibited, resulting in selective corrosion or galvanic corrosion. Many

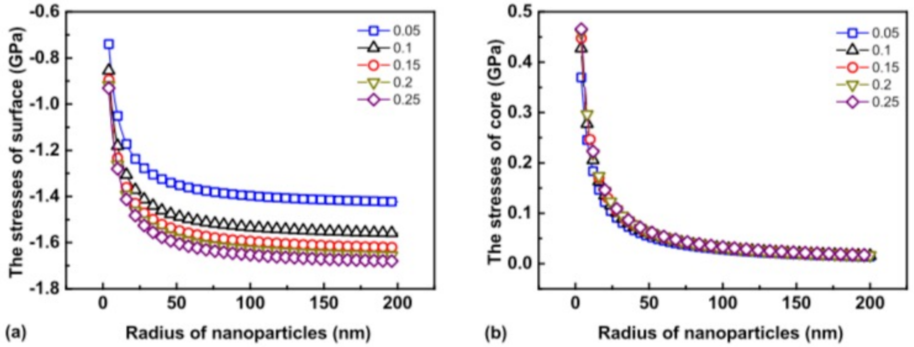


Figure 1. Variations in the stresses in the surface shell (a) and the stresses in the core (b) as a function of the CuZn binary solid solution nanoparticle radius and the apparent Zn concentration.

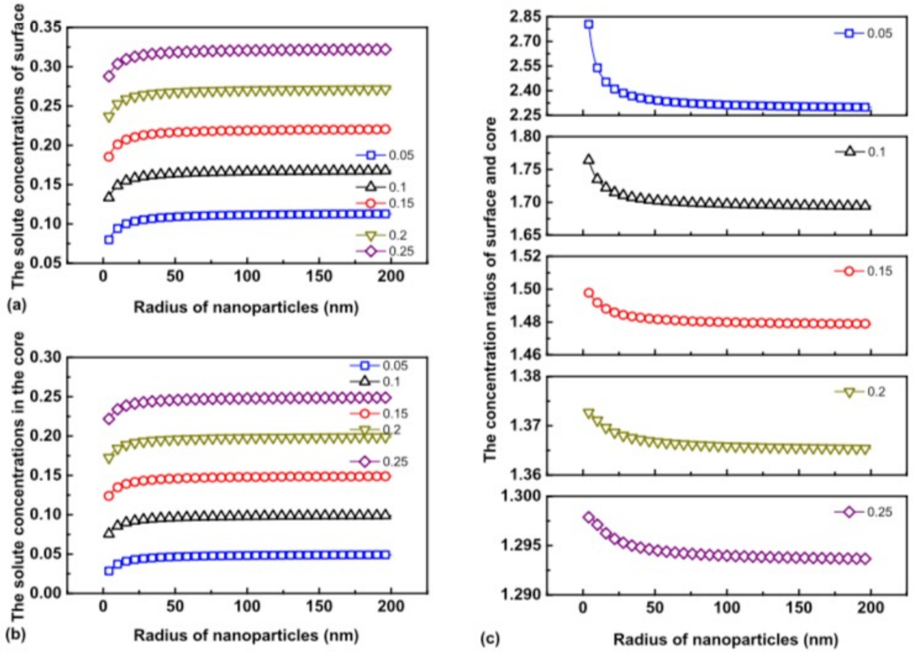


Figure 2. Variations in the Zn concentrations in the surface shell $x_s{}^s$ (a), the Zn concentrations in the core $x_c{}^s$ (b) and the Zn concentration ratios between surface shell and core (x_s^s/x_c^s) (c) as a function of the CuZn binary solid solution nanoparticle radius and the apparent Zn concentration.

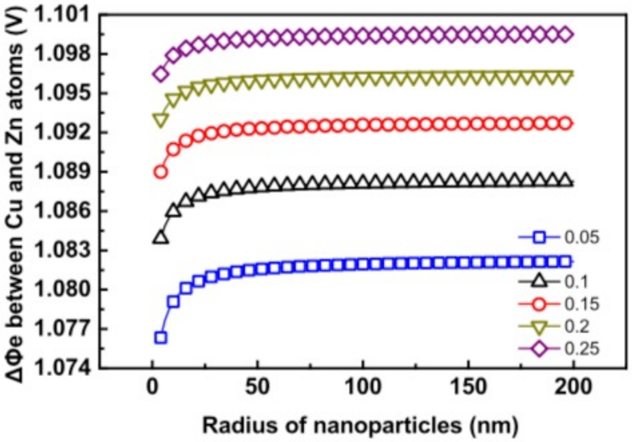


Figure 3. Variations in the equilibrium potential difference between the Cu and Zn atoms in the surface shell of CuZn binary solid solution nanoparticle as a function of the nanoparticle radius and the apparent Zn concentration.

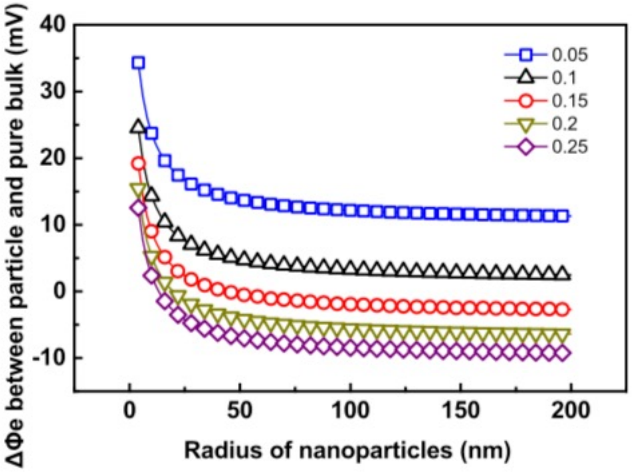


Figure 4. Variations in the equilibrium potential difference between the dissolved Zn atoms in the CuZn nanoparticles and the pure bulk Zn as a function of the nanoparticle radius and the apparent Zn concentration.

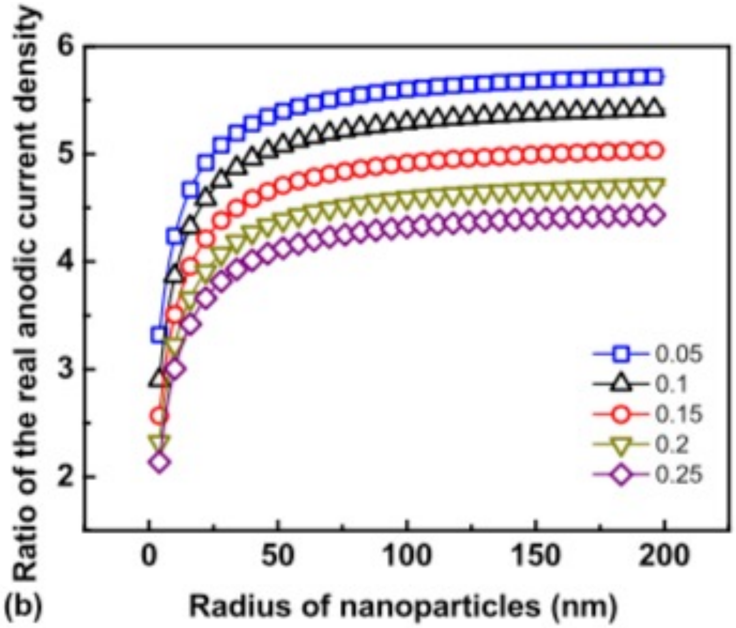


Figure 5. Variations in the ratio of the anodic current density (a) and the ratio of the real anodic current density (b) between the dissolved Zn atoms in the CuZn nanoparticles and the pure bulk Zn as a function of the nanoparticle radius and the apparent Zn concentration.