Last time we arrived at 3 fundamental functions for a system with fixed V & N

entropy: $S(U,V,N)$ - U is controlled, this is maximized

energy: $U(S,V,N)$ - S is controlled, this is minimized

Helmholtz FE: $F(T,V,N)$ - T is controlled, this is minimized

(something else is always held fixed, or controlled, and the state function of interest is maximized or minimized at equilibrium)

We need to define 2 more functions for more realistic lab conditions

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Enthalpy

$$H(S,P,N) = U + PV$$

$$dH = dU + P\,dV + V\,dP$$

dU: we know this because $U(S,V,N)$

$$dU = T\,dS - p\,dV + \mu\,dN$$

$$\therefore \quad dH = T\,dS - p\,dV + \mu\,dN + p\,dV + V\,dP$$

$$dH = T\,dS + V\,dP + \mu\,dN$$

This exact differential tells us a few things:

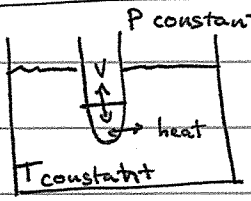
$H = H(S,P,N)$: S is controlled at boundaries, H is minimized

Also:

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \qquad V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

In general S is difficult to control, so we need:

Gibbs Free Energy



← Pressure & Temperature are held constant, and Volume & Heat can change.

$$G \equiv H - TS \quad \text{or} \quad F + pV$$

$$dG = dH - TdS - SdT$$

$$\uparrow$$

$$dH = TdS + VdP + \mu dN$$

$$dG = \cancel{TdS} + VdP + \mu dN - \cancel{TdS} - SdT$$

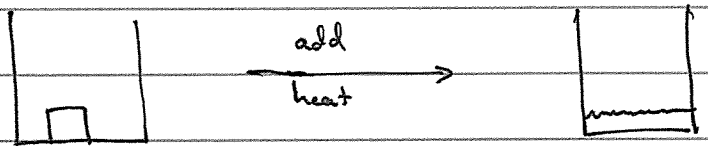
$$\therefore \quad dG = -SdT + VdP + \mu dN$$

What we know ← natural variables are how we usually carry out experiments!

$$G = G(T, P, N)$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

Consider Melting ice:



T = negligibly below 0°c
G is at a minimum
$= G_{solid}$

T = negligibly above 0°c
G is at a minimum
$= G_{liquid}$

What is $\Delta G = G_{liquid} - G_{solid}$

$dP = 0$
$dN = 0$ (ignore evaporation for now)
$dT = 0$

$\therefore dG = 0$ for the phase transition!

If $\Delta G = 0$ then $\Delta H = T_0 \Delta S$ (T_0: phase transition temperature)

The increase in entropy is balanced by an increase in enthalpy (weakened interactions)

Are these state functions: $U(T,V,N)$, $S(T,V,N)$, $H(T,P,N)$, $S(T,P,N)$ useful?

Unnatural variables for S

Consider:

$$F(T,V,N) = U(T,V,N) - TS(T,V,N)$$

minimizing $U(T,V,N)$ or maximizing $S(T,V,N)$ individually does not predict the state of equilibrium, but combining them to form F identified an equilibrium if the constraints are T,V,N

We can measure $C_V(T)$ using a constant volume calorimeter

$$\Delta U = \int C_V(T)\, dT \quad \text{and} \quad \Delta S = \int \frac{C_V(T)}{T} dT$$

Combine them to get:

$$F(T) = U(T) - TS(T)$$

Alternatively, under constant N,T,P conditions, $G(T,P)$ identifies the equilibrium state.

$$dH = d(U+PV) = dU + pdV + Vdp$$
$$= \delta q + \delta w + PdV + Vdp$$

$$dH = \delta q + \underbrace{\delta w + P dV}_{\text{0 for a quasistatic process}} + \cancel{V dP}^{\,0 \text{ at constant } P}$$

$dH = \delta q$ at constant P

$$C_p = \left(\frac{\delta q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

So: $$\Delta H(T,P) = \int_{T_A}^{T_B} C_p(T)\, dT$$

$$\Delta S(T,P) = \int_{T_A}^{T_B} \frac{C_p(T)}{T}\, dT$$

So, from a constant pressure calorimeter, we can get

$$G(T,P) = A(T,P) - TS(T,P)$$

The 3rd law of thermodynamics:

$$S(T) = \int_0^T \frac{C_v}{T'}\, dT' + S(0)$$

What is $S(0)$? The 3rd law defines $S(0) = 0$ for a pure perfectly crystalline substance @ $T = 0K$.

Let's do a few simple examples:

Equilibrium temperatures of objects in thermal contact:

object A	object B
C_A, T_A	C_B, T_B

We know that at equilibrium they'll both have the same T.

$\Delta H = \Delta H_A + \Delta H_B = 0$ (because we'll postulate that the objects are isolated from their surroundings)

$$\Delta H_A = \int_{T_A}^{T} C_A \, dT' = C_A (T - T_A)$$

← whatever final T we get

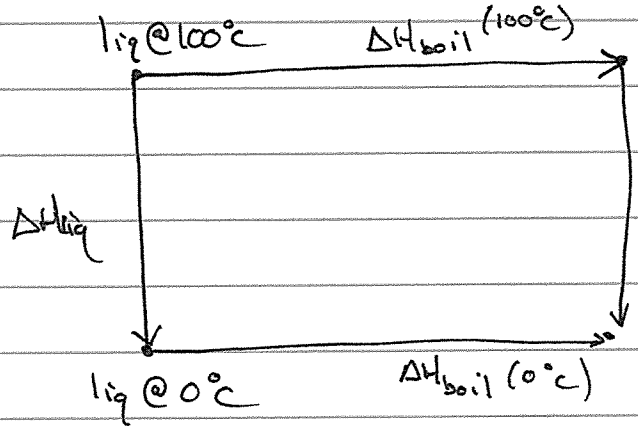
Likewise

$$\Delta H_B = C_B (T - T_B)$$

$$C_A (T - T_A) + C_B (T - T_B) = 0$$

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B} \qquad \text{if } C_A = C_B \Rightarrow T = \frac{T_A + T_B}{2}$$

Another example: Use Thermodynamic cycles to determine hard to measure quantities.



$\Delta H_{boil}^{(100°C)} = 540 \frac{cal}{g}$

$C_{p,l} = 1.00 \frac{cal}{kg}$

$C_{p,steam} = 0.448 \frac{cal}{kg}$

$$\Delta H_{liq} = \int_{100}^{0} C_{p,liq} \, dT = -100 \text{ cal g}^{-1}$$

$$\Delta H_{steam} = \int_{100}^{0} C_{p,steam} \, dT = -44.8 \text{ cal g}^{-1}$$

$$\Delta H_{boil}(0°C) = \Delta H_{boil}(100°C) - \Delta H_{liq} + \Delta H_{steam}$$

$$= (540 + 100 - 44.8)\ cal\ g^{-1} =$$

$$= 595.2\ \frac{cal}{g}$$