

Thermodynamic Potential: Energy Cons, Volume
Rev S

$$dE = dQ + dW$$

$$\star dE = T dS - p dV \quad dQ_{rev} = T dS$$

① The "natural variables" to describe E are S and V , $E(S, V)$

We have:

$$dE = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV$$

\star Comparing to \star we have

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

↑ we had this
as

$$\left(\frac{dS}{dE} \right)_V = \frac{1}{T}$$

$$p = - \left(\frac{\partial U}{\partial V} \right)_S$$

② For constant volume processes

$$dE = T dS = dQ_{rev}$$

i.e. the energy increases due to the heat inflow.
Then if volume is constant

$$dQ_v^{\text{rev}} = C_v dT$$

So

$$\underline{du}_v = C_v dT \Rightarrow \boxed{\left(\frac{\partial u}{\partial T}\right)_v = C_v}$$

And

$$\Delta E = \int_{T_1}^{T_2} C_v(T) dT \quad (\text{constant volume})$$

Thermodynamic Potential: Enthalpy S, P

Many processes occur at const pressure (and entropy). Then the enthalpy is useful and defined as

$$H \equiv E + PV$$

$$dH = \underbrace{(T dS - \cancel{p dV})}_{du} + (\cancel{p dV} + V dp)$$

$$\star dH = T dS + V dp$$

① The "natural" variables of H are S and P

Since

$$dH = \left(\frac{\partial H}{\partial S} \right)_P dS + \left(\frac{\partial H}{\partial P} \right)_S dP$$

We have by comparison to Δ

$$T = \left(\frac{\partial H}{\partial S} \right)_P \quad \left(\frac{\partial H}{\partial P} \right)_S = V$$

② The enthalpy is particularly useful for describing the energetics of processes at constant pressure

$$dH = T dS + \cancel{V dP}^0 \quad (P_{\text{const}})$$

So since $T dS = dQ^{\text{rev}}$, we have:

$$dH = T dS = dQ^{\text{rev}} = C_p dT$$

↖ pressure const

So

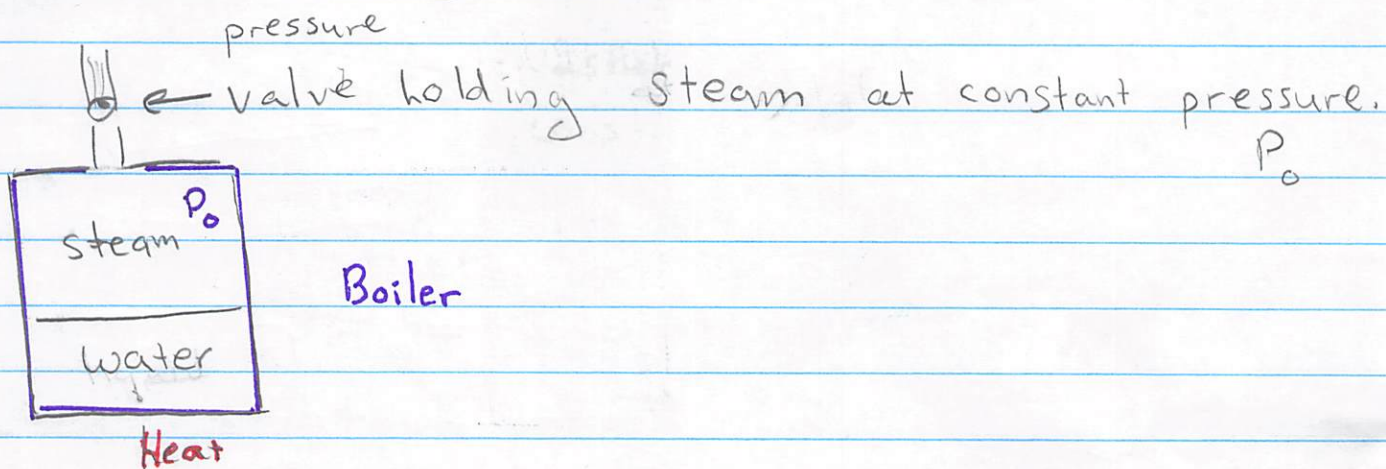
$$C_p \Rightarrow \left(\frac{\partial H}{\partial T} \right)_P$$

or

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

(constant pressure)

Example where Enthalpy is relevant



The heat that is added changes the energy for the substance ΔE , but as the substance expands from the volume of water to the volume of steam the gas does work $P_0 \Delta V$. So the heat required to evaporate the water is $\Delta H = Q$

$$Q = \Delta H = \Delta E + P \Delta V.$$

↖ this is larger ^{than ΔE} since the substance does work as it changes phase

Thermodynamic Potential

The Helmholtz Free Energy (T, V)

- Often processes happen at constant temperature but not constant volume

Defines

$$F \equiv E - TS$$

$$dF = (\cancel{T} dS - p dV) - (\cancel{T} dS + S dT)$$

$$\star = -S dT - p dV$$

- ① The natural variables here are T and V
So, $F(T, V)$

$$dF = \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right) dV$$

So

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

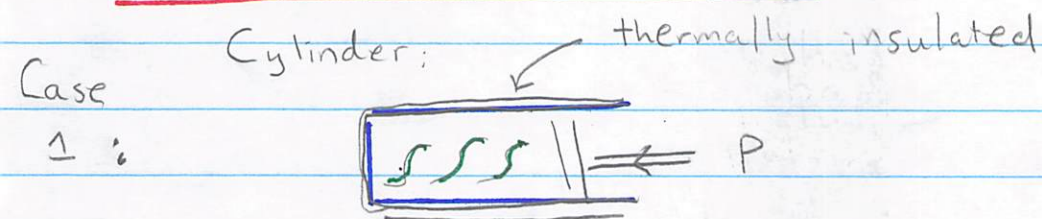
$$p = - \left(\frac{\partial F}{\partial V} \right)_T$$

- ② If the temperature is constant:

$$dF = -p dV$$

$$\Delta F = - \int_{V_1}^{V_2} p dV$$

Compare these two cases:



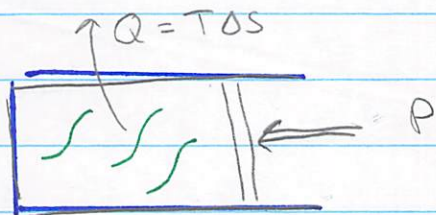
Gas is compressed.

① If no heat is allowed to flow out of the cylinder. Then the work done by me equals the change in energy of the system

$$\Delta E = W$$

② But if the heat flows out of the cylinder and is absorbed by the environment at temperature T . Then the work by me is the change in energy of the system minus the heat expelled, $Q = T\Delta S$

$$\Delta F = \Delta E - T\Delta S = W$$



Reservoir at constant temperature

Thermodynamic Potential

The Gibbs Free Energy $G(T, P)$

- Finally many processes occur at const temperature and pressure. For instance most chemical reactions occur at const temperature and pressure

$$G = E + PV - TS$$

$$dG = (\cancel{T}ds - \cancel{P}dV) + (\cancel{P}dV + VdP) - (\cancel{T}ds + SdT)$$

$$dG = -SdT + VdP$$

So since

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

Leading to

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

- An example where G is important is during a phase transition. Here the two phases (water and ice) are at the same temperature and pressure (phase coexistence). As we go from all water to ice G on both sides remains fixed, i.e. $G_{\text{water}} = G_{\text{ice}}$. More about this later.

Definitions of Thermodynamic Potentials

Function of state		Differential	Natural variables	First derivatives	
Internal energy	U	$dU = TdS - pdV$	$U = U(S, V)$	$T = \left(\frac{\partial U}{\partial S}\right)_V,$	$p = -\left(\frac{\partial U}{\partial V}\right)_S$
Enthalpy	$H = U + pV$	$dH = TdS + Vdp$	$H = H(S, p)$	$T = \left(\frac{\partial H}{\partial S}\right)_p,$	$V = \left(\frac{\partial H}{\partial p}\right)_S$
Helmholtz function	$F = U - TS$	$dF = -SdT - pdV$	$F = F(T, V)$	$S = -\left(\frac{\partial F}{\partial T}\right)_V,$	$p = -\left(\frac{\partial F}{\partial V}\right)_T$
Gibbs function	$G = H - TS$	$dG = -SdT + Vdp$	$G = G(T, p)$	$S = -\left(\frac{\partial G}{\partial T}\right)_p,$	$V = \left(\frac{\partial G}{\partial p}\right)_T$