Foundations of Physics 2B/3C   2019-2020
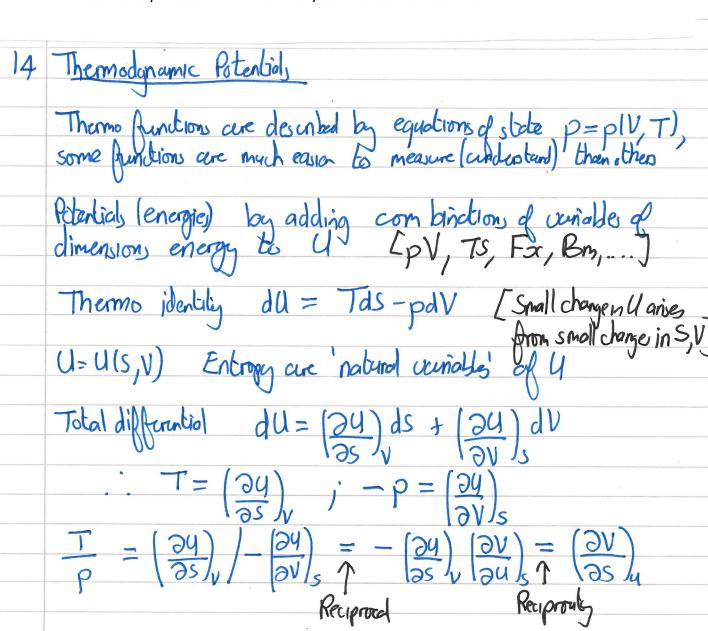
Thermodynamics – Lecture 7 Recap

- Finished looking at entropy, including entropy change in various processes and saw how entropy relates to the arrow of time.
- Looked at temperature-entropy diagrams and their uses.
- Considered the thermodynamic identity:

$$\boxed{dU = TdS - pdV.}$$

Thermodynamics – Lecture 8 Aims

- To be introduced to the thermodynamic potentials.
- To be introduced to the Maxwell Relations
- To see the TdS and Energy equations.
- To see how problems in thermodynamics can be solved.

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14 Thermodynamic Potentials

Thermo functions are described by equations of state $p = p(V, T)$, some functions are much easier to measure (understand) then others

Potentials (energies) by adding combinations of variables of dimensions energy to U $\quad [pV, TS, Fx, Bm, \ldots]$

Thermo identity $\quad dU = TdS - pdV \quad$ [Small change in U arises from small change in S, V]

$U = U(S, V) \quad$ Entropy are 'natural variables' of U

Total differential $\quad dU = \left(\dfrac{\partial U}{\partial S}\right)_V dS + \left(\dfrac{\partial U}{\partial V}\right)_S dV$

$\therefore \quad T = \left(\dfrac{\partial U}{\partial S}\right)_V \quad ; \quad -p = \left(\dfrac{\partial U}{\partial V}\right)_S$

$\dfrac{T}{p} = \left(\dfrac{\partial U}{\partial S}\right)_V \Big/ -\left(\dfrac{\partial U}{\partial V}\right)_S = -\left(\dfrac{\partial U}{\partial S}\right)_V \left(\dfrac{\partial V}{\partial U}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_U$

$\qquad\qquad\qquad\qquad\qquad\qquad \uparrow \qquad\qquad\qquad\qquad\qquad\qquad \uparrow$

$\qquad\qquad\qquad\qquad\quad$ Reciprocal $\qquad\qquad\qquad\qquad$ Reciprocity

Enthalpy $\quad H = U + pV \quad$ [Constant pressure processes]

$$dH = d(U + \boxed{pV}) \overset{\text{Chain rule}}{=} dU + pdV + Vdp$$

Sub in $dU = TdS - pdV$; $\quad dH = TdS - pdV + pdV + Vdp$

$$= TdS + Vdp$$

Enthalpy natural variables are $\quad H = H(S, p)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \qquad T = \left(\frac{\partial H}{\partial S}\right)_p ; \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

At constant pressure $dp = 0$; $\quad \therefore \quad dH = TdS = \delta Q_{rev}$

$$= C_p dT$$

$$\Delta H = \int_A^B dH = H_B - H_A = \int_A^B \delta Q_{rev} = \int_A^B C_p dT$$

$\uparrow$

Heat absorbed / rejected at constant pressure.
$\quad \Delta H > 0$, endothermic, $\quad \Delta H < 0$, exothermic.
$dp = 0 \quad$ Lot processes are open to the atmosphere

U and H both depend on entropy change — difficult to measure...

Potentials ~~don't~~ depend on entropy. free energies don't
$\qquad$ Helmholtz $\qquad F = F(V, T)$
$\qquad$ Gibbs $\qquad G = G(p, T)$

Example 14.1 $\qquad F = U - TS$

$$dF = dU - TdS - SdT = \cancel{TdS} - pdV - \cancel{TdS} - SdT$$

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

Isothermal $dT=0$ so $dF = -pdV = \delta W$

Helmholtz is reversible work done on surroundings

If $dF > 0$ $F_{final} > F_{initial} \implies \delta W > 0$
Must provide work to the process.

Minimise F $F_f < F_I$; $dF < 0$, $\delta W < 0$
Maximum work out of a process.

<u>Gibbs Function</u> $G = U + pV - TS$ (add anything else
                                     here....)

$$= H - TS$$
$$= F + pV$$

Please show $dG = Vdp - SdT$ $G = G(p,T)$

Pressure + temperature are easiest variables to vary in the lab.
But isothermal $(dT=0)$ and isobaric $(dp = 0)$
have $dG = 0$. Gibbs function is conserved at a phase change.

$\Delta G = G_f - G_I$ Max non-expansion work a process
                       can do.
                         [Energy stored in an orderly way and
                         free it to do work]

<u>Maxwell Relations</u>

Some functions of state are related to derivatives
$$T = \left(\frac{\partial H}{\partial S}\right)_p > \left(\frac{\partial U}{\partial S}\right)_V , \ldots$$

All potentials are functions of state (exact differentials)
so order of 2nd derivatives doesn't matter $\left(\frac{\partial^2 Z}{\partial x \partial y}\right) = \left(\frac{\partial^2 Z}{\partial y \partial x}\right)$

Use this to relate changes hard to measure to 'nice' ones.

Proof 14.1 U $dU = TdS - pdV$

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

Total differentials are equal $T = \left(\frac{\partial U}{\partial S}\right)_V \; ; \; -p = \left(\frac{\partial U}{\partial V}\right)_S$

U is a function of state $\oint dU = 0$

$$\left(\frac{\partial^2 U}{\partial V \partial S}\right) = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V} = \left(\frac{\partial^2 U}{\partial S \partial V}\right)$$

Generalised Quantities : Some partial derivatives correspond to real physical quantities

Heat Capacity $\frac{\Delta Q}{\Delta T} = C$ or $C_\alpha = \left(\frac{\partial Q}{\partial T}\right)_\alpha$

α is a constant thermo property

But $dS = \frac{\delta Q_{rev}}{T}$ or $\delta Q_{rev} = TdS$

$$C = \frac{\Delta Q}{\Delta T} = \frac{T\Delta S}{\Delta T} \underset{\Delta T \to 0}{\Longrightarrow} C_\alpha = T\left(\frac{\partial S}{\partial T}\right)_\alpha$$

Volume expansivity : Fractional volume change with temperature

[coefficient of thermal expansion, α]

$$\beta = \frac{\Delta V}{V} \times \frac{1}{\Delta T} \qquad \beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \; ; \; \beta_s = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

$\beta_p > 0$ for most materials, but not ice $\to$ water.

Compressibility : Fractional volume change with pressure

$$K = -\frac{\Delta V}{V} \times \frac{1}{\Delta p} \; ; \; K_T = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \; ; \; K_S = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

+ve
coefficient

'Normal' materials, increasing p ($\Delta p > 0$) decreases V ($\Delta V < 0$)

TdS equations — help us examine material behaviour

$$TdS = \delta Q_{rev} \quad \text{heat transfer}$$

Proof 14.2   Consider $S = S(V, T)$

Total differential $T\,dS = T\left(\dfrac{\partial S}{\partial V}\right)_T dV + T\left(\dfrac{\partial S}{\partial T}\right)_V dT$

Multiply by T

Heat Capacity $C_V = \boxed{T\left(\dfrac{\partial S}{\partial T}\right)_V}$

Maxwell Relation (Helmholtz) $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V$

$$T\,dS = T\left(\dfrac{\partial p}{\partial T}\right)_V dV + C_V\,dT$$

Two more $S = S(p, T)$ or $S = S(p, V)$

Example 14.3   A thermally isolated process $\delta Q = 0 = TdS$

$$-C_V\,dT = T\left(\dfrac{\partial p}{\partial T}\right)_V dV$$

From our equation of state $= R/V$ [Ideal]

Separate variables + integrate

$$-C_V\,dT = T\dfrac{R}{V}\,dV$$

$$-\dfrac{C_V}{R}\int \dfrac{dT}{T} = \int \dfrac{dV}{V} \quad , \quad -\dfrac{C_V}{R}\ln T = \ln V + C$$

$$TV^{\gamma-1} = \text{Const}$$

For isothermal $dT = 0$

$$T_0\,dS = T_0\left(\dfrac{\partial p}{\partial T}\right)_V dV \implies dS = \left(\dfrac{\partial p}{\partial T}\right)_V dV$$

$$= \dfrac{R}{V}\,dV$$

Energy Equation: 1st law to write the change in U in terms of things we can measure

2nd energy

$$dU = TdS - pdV \qquad [1st\ Law]$$

Divide by dp when the temperature is constant

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

Maxwell relation from Gibbs $\quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

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