In-class problem linked to lecture pages 176 – 190

Suppose that you want to predict how energy varies with temperature and pressure during a non-diffusive process. Show that:

$$\left.\frac{\partial E}{\partial p}\right|_T = V\left(p\kappa - T\beta\right)$$

and

$$\left.\frac{\partial E}{\partial T}\right|_p = C_P - pV\beta$$

In-class 176-190

Generally $dE = TdS - pdV + \mu dN$
Here $dN = 0$
Let $dS = dT \left.\frac{\partial S}{\partial T}\right|_p + dp \left.\frac{\partial S}{\partial p}\right|_T$

Let $dV = dT \left.\frac{\partial V}{\partial T}\right|_p + dp \left.\frac{\partial V}{\partial p}\right|_T$

Then

$$dE = T\left.\frac{\partial S}{\partial T}\right|_p dT + T\left.\frac{\partial S}{\partial p}\right|_T dp - p\left.\frac{\partial V}{\partial T}\right|_p dT - p\left.\frac{\partial V}{\partial p}\right|_T dp$$

Eq1. $$= \left[T\left.\frac{\partial S}{\partial T}\right|_p - p\left.\frac{\partial V}{\partial T}\right|_p\right] dT + \left[T\left.\frac{\partial S}{\partial p}\right|_T - p\left.\frac{\partial V}{\partial p}\right|_T\right] dp$$

Note Maxwell Relation M10 (Stowe p. 217):

$$-\left.\frac{\partial S}{\partial p}\right|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{p,N} = V\beta \qquad (\beta = \text{coef of volume exp, Stowe p. 169})$$

If $dQ = TdS$, then $\left.\frac{\partial S}{\partial T}\right|_p = \frac{1}{T}\left.\frac{dQ}{\partial T}\right|_p = \frac{1}{T}C_p$

Isothermal compressibility $K = \frac{-1}{V}\left.\frac{\partial V}{\partial p}\right|_T$,

$$\text{so } \left.\frac{\partial V}{\partial p}\right|_T = -KV$$

Plug into Eq 1 to get:

$$dE = \left[T \cdot \frac{1}{T} C_p - pV\beta\right] dT + \left[T(-V\beta) - p(-KV)\right] dp$$

$$= \left[C_p - pV\beta\right] dT + \left[pKV - T\beta V\right] dp \qquad \text{"physics eq"}$$

Compare this to the "math eq":

$$dE = \left.\frac{\partial E}{\partial T}\right|_p dT + \left.\frac{\partial E}{\partial p}\right|_T dp$$ to conclude:

$$\left.\frac{\partial E}{\partial T}\right|_p = C_p - pV\beta$$

$$\left.\frac{\partial E}{\partial p}\right|_T = (pK - T\beta)V$$