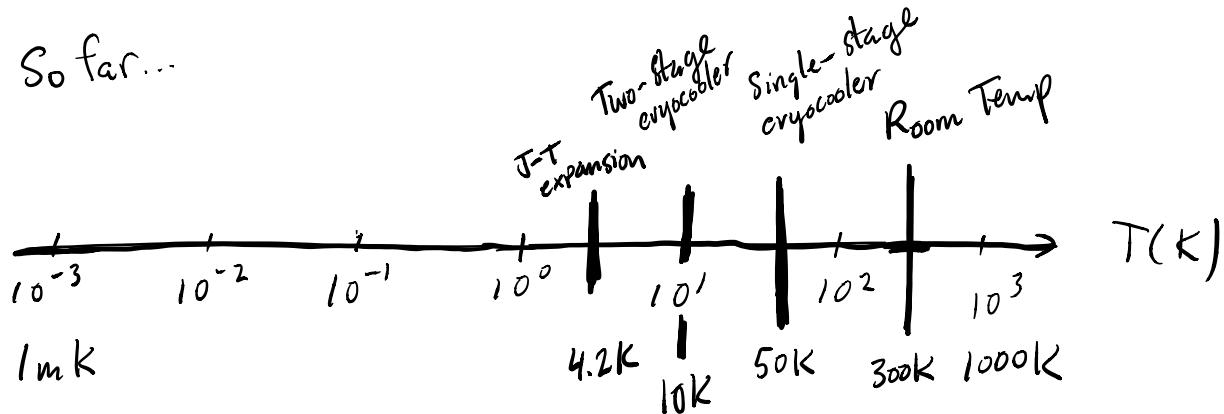


# PHYS 425 - w2l2

So far...



We discussed Stirling cycle in detail.

There are other cryocooler cycles in use.

- Gifford-McMahon (G.M) cryocooler
- Pulse Tube cryocoolers → Two stage pulse-tube cryocooler can reach 2 K.

Goal for today is to see how we can use pressure to manipulate the boiling temp. of a bath of liquid  ${}^4\text{He}$ .

Boiling temps. of other cryogenic liquids at 1 atm

Oxygen : 90 K

Neon : 27.2 K

Argon : 87 K

Hydrogen : 20.3 K

\* Nitrogen: 77.3 K

\*  ${}^4\text{He}$  : 4.21 K

${}^3\text{He}$  : 3.2 K

First, let's try to come up w/ an interpretation of enthalpy:  $H = U + PV$

Know  $dU = dQ - PdV$

$\therefore$  for an isochoric process ( $dV=0$ ) increase in internal energy is equal to heat added.

Likewise  $H = U + PV$

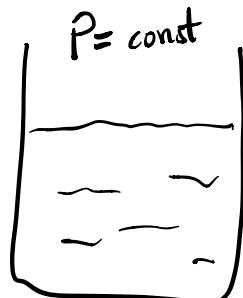
$$dH = dQ - PdV + PdV + VdP$$

$$dH = dQ + VdP$$

$\therefore$  for an isobaric process ( $dP=0$ ) increase in enthalpy of a sys. is equal to the heat added.

Eg. Process in an open beaker

- boil liquid
- chemical reaction



## Latent Heat & Enthalpy

Consider a liquid of volume  $V_1$  at its boiling temp. Now a quantity of heat  $L$  is added which is sufficient to completely vaporize the liquid. After vaporization, the volume of the gas is  $V_2$ . If vapour is expanded against const pressure, then:

$$dU = dQ - PdV$$

$$U_2 - U_1 = L - P(V_2 - V_1)$$

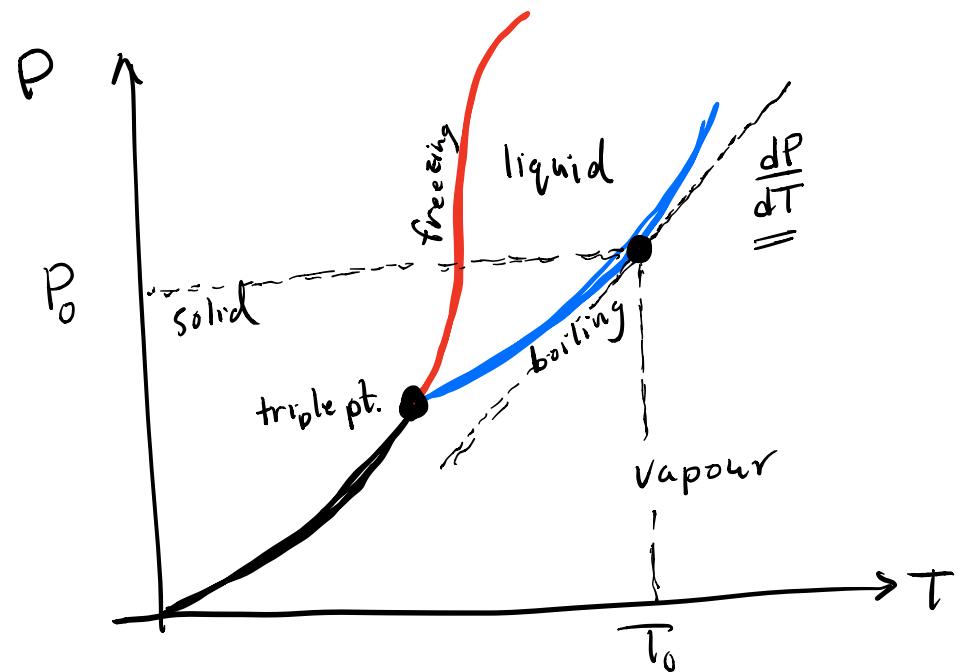
$$L = \underbrace{(U_2 + PV_2)}_{H_2} - \underbrace{(U_1 + PV_1)}_{H_1}$$

$$L = H_2 - H_1$$

∴ during change of state at const. pressure, the latent heat of transformation is equal to the change in enthalpy.

## Clausius-Clapeyron Eq'n

Phase Diagram



Lines separating two phases are called coexistence curves. The so-called Clausius-Clapeyron eq'n gives slope of tangents to coexistence curves.

$$\text{We will show that } \frac{dP}{dT} = \frac{L}{T\Delta V}$$

Start with entropy expressed in terms of  $V \& T$

$$S = S(V, T)$$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

During a phase change at const  $P$ , must have  
 $T = \text{const.}$

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV \quad \textcircled{P}$$

---

Aside : Develop a Maxwell relation:

Start w/ Helmholtz free energy

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$= dQ - PdV - TdS - SdT$$

$$= \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$\therefore dF = \underline{-PdV} - \underline{SdT}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$\downarrow \qquad \qquad \downarrow$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_V \quad \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right)_T$$

$\brace{ \quad } = \brace{ \quad }$

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

Maxwell Relation.

$\therefore$  Returning to ④, we have

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore dS = \left(\frac{\partial P}{\partial T}\right)_V dV \quad \leftarrow$$

Now assume that we're boiling an open pot of liquid. The pressure above the liquid surface remains const.

$\therefore$  From the coexistence curve on the phase diagram,  $T = \text{const.}$   $\{$  the slope of a tangent line  $\frac{dP}{dT} = \text{const.}$

$$\int dS = \int \left( \frac{dP}{dT} \right) dV = \frac{dP}{dT} \int dV$$

$$\therefore \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

Enthalpy  $H = U + PV$

$$dH = dU + PdV + VdP$$

$$= dQ - PdV + PdV + VdP$$

$$\therefore dH = TdS + VdP$$

For a phase transition @ const  $P \{ T$

$$dH = TdS$$

$$\Rightarrow \Delta H = T \Delta S$$

$$\therefore \Delta S = \frac{\Delta H}{T} = \frac{L}{T}$$

∴ we finally have the desired Clausius-Clapeyron eq'n

$$\boxed{\frac{dP}{dT} = \frac{L}{T\Delta V}}$$

For a liquid-to-gas phase change

$$\Delta V = V_{\text{gas}} - V_{\text{liquid}} \approx V_{\text{gas}}$$

$$\frac{dP}{dT} \approx \frac{L}{TV_{\text{gas}}}$$

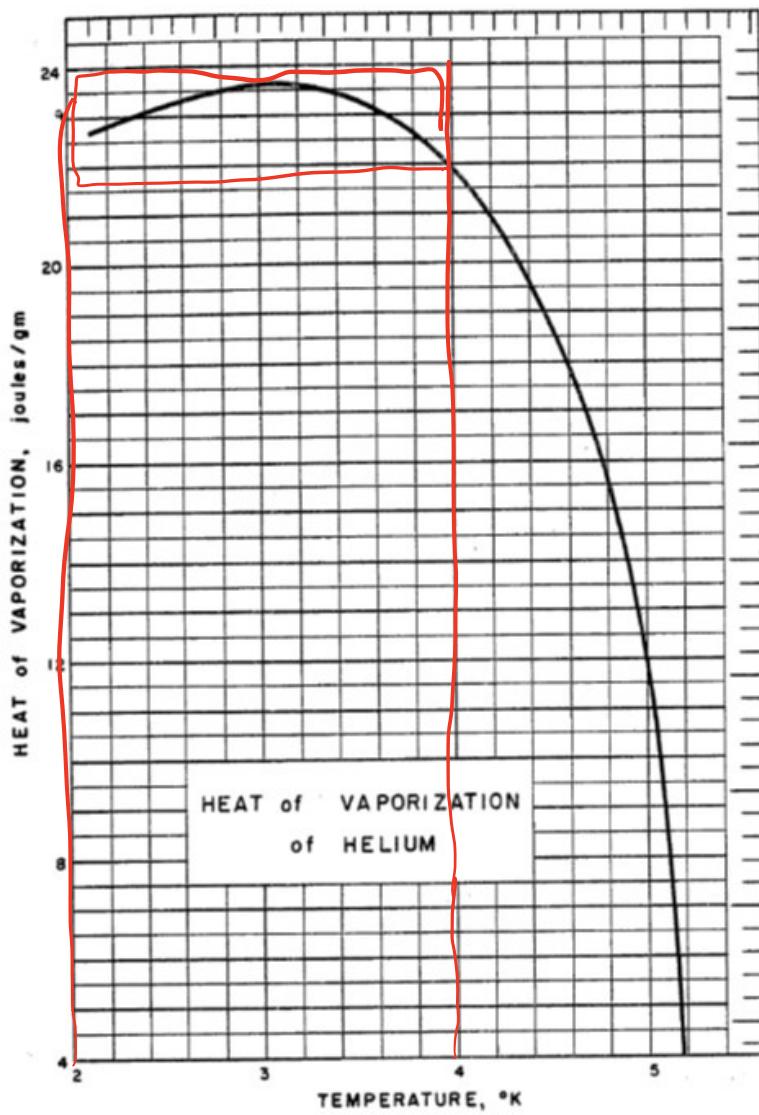
Treat the vapour as an ideal gas:

$$V = \frac{Nk_B T}{P}$$

$$\frac{dP}{dT} = \frac{LP}{Nk_B T^2} \approx \frac{dP}{P} \approx \frac{L}{Nk_B T^2} dT \quad \approx \text{const.}$$

In general,  $L$  can be temp dependent.

However, for liquid  ${}^4\text{He}$ ,  $L$  doesn't change much between  $1\text{ K}$  &  $4\text{ K}$ .



| Temp.<br>°K | $H_v$<br>Joules<br>gm | Temp.<br>°K | $H_v$<br>Joules<br>gm |
|-------------|-----------------------|-------------|-----------------------|
| 2.20        | 22.8                  | 4.00        | 21.9                  |
| 2.40        | 23.1                  | 4.20        | 20.9                  |
| 2.60        | 23.3                  | 4.40        | 19.7                  |
| 2.80        | 23.5                  | 4.60        | 18.0                  |
| 3.00        | 23.7                  | 4.80        | 15.6                  |
| 3.20        | 23.6                  | 5.00        | 12.0                  |
| 3.40        | 23.5                  | 5.10        | 8.99                  |
| 3.60        | 23.2                  | 5.15        | 6.70                  |
| 3.80        | 22.7                  | 5.18        | 4.00                  |

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$$\int \frac{dP}{P} = \frac{L}{Nk_B} \int \frac{dT}{T^2}$$

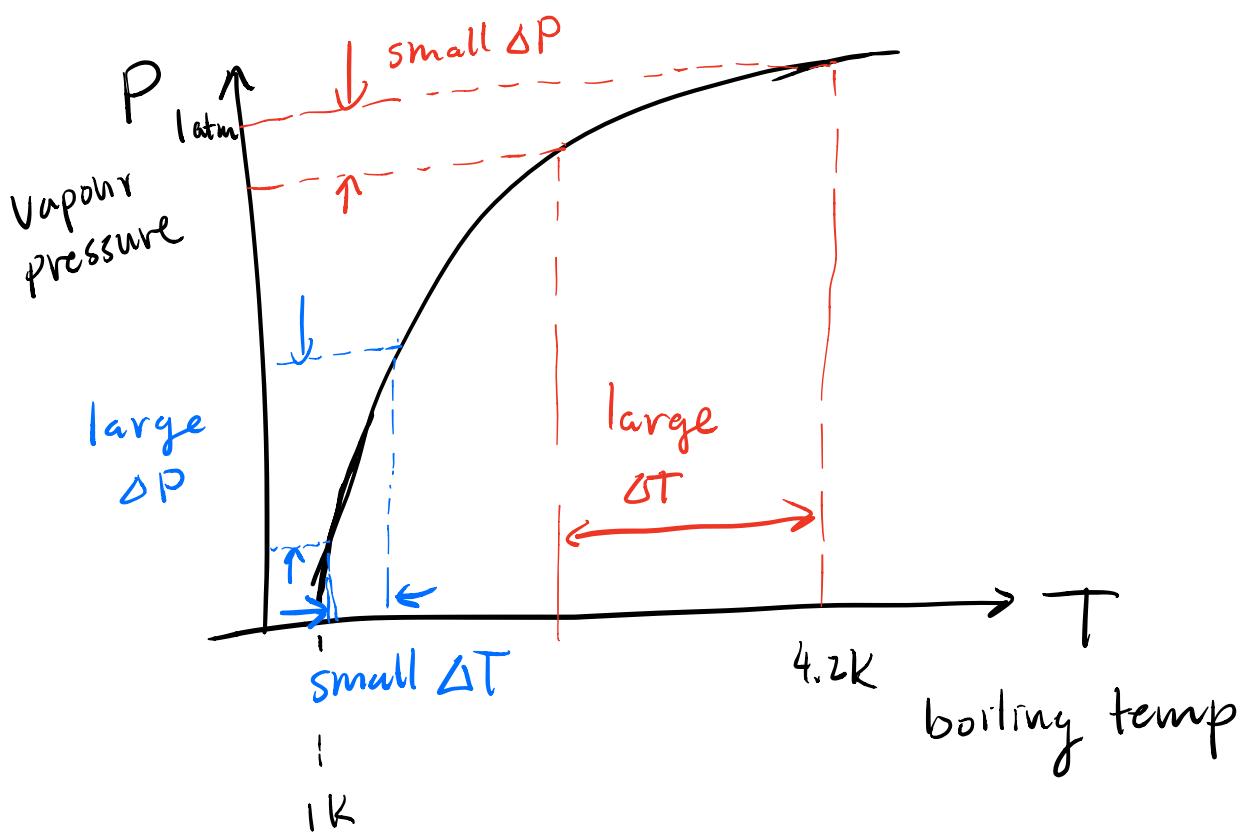
$$\ln P \approx -\frac{L}{Nk_B} \frac{1}{T} + B'$$

Integration  
const.

$$\text{or } P = B e^{-L/(Nk_B T)}$$

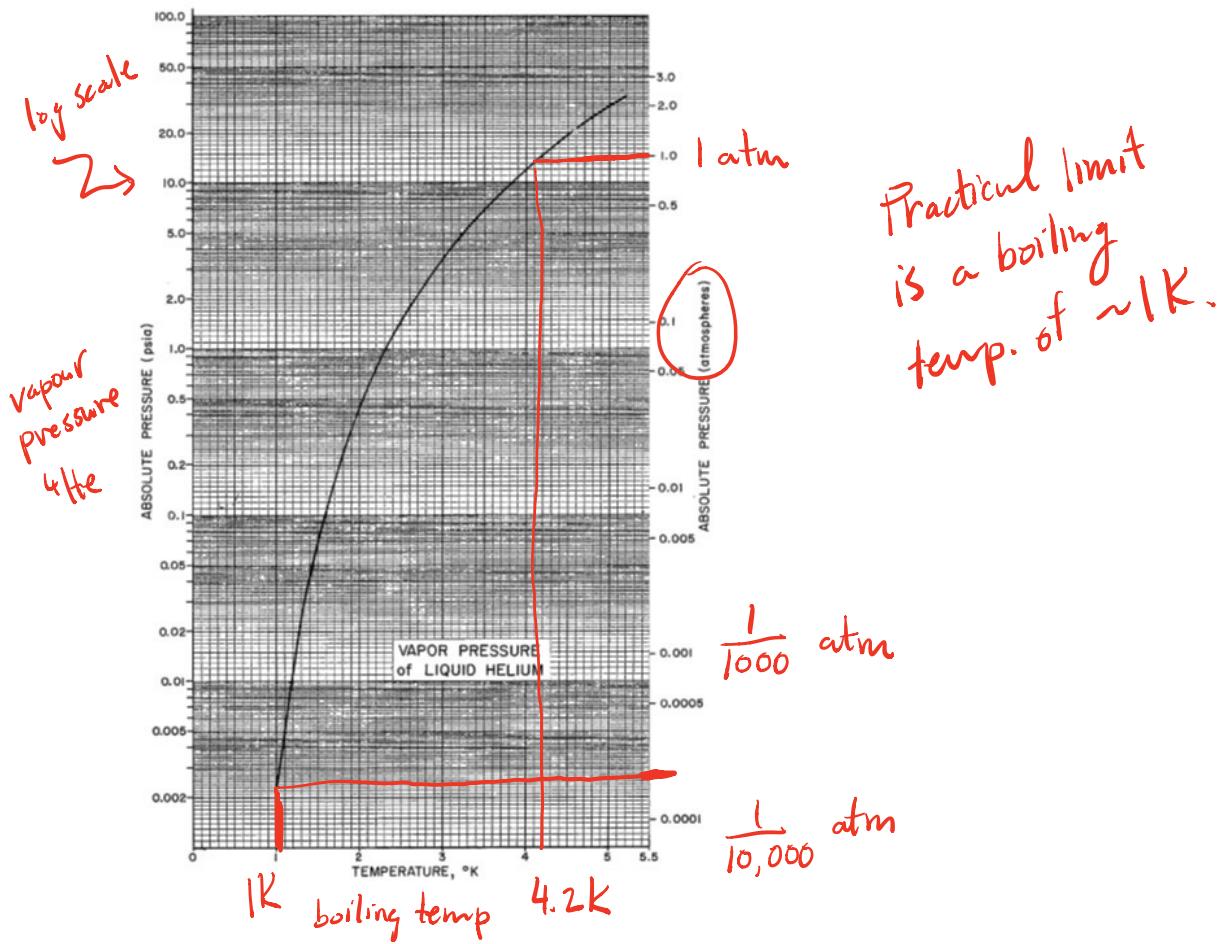
$$P \propto \exp\left[\frac{-L}{Nk_B T}\right]$$

vapour pressure



Initially, at high pressure, can lower boiling temp of liquid by using a pump to lower vapour pressure.

Eventually, pressure gets low & the temp. changes associated w/ further reductions in press. become small.



| Temp. |      | Pressure |                    | Temp. |      | Pressure |                    |
|-------|------|----------|--------------------|-------|------|----------|--------------------|
| °K    | °R   | mm Hg    | lb/in <sup>2</sup> | °K    | °R   | mm Hg    | lb/in <sup>2</sup> |
| 1     | 1.8  | 0.12     | 0.00231            | 3.2   | 5.76 | 243      | 4.68               |
| 1.2   | 2.16 | 0.62     | 0.0119             | 3.4   | 6.12 | 316      | 6.09               |
| 1.4   | 2.52 | 2.1      | 0.0404             | 3.6   | 6.48 | 402      | 7.74               |
| 1.6   | 2.88 | 5.7      | 0.101              | 3.8   | 6.74 | 503      | 9.68               |
| 1.8   | 3.24 | 12.5     | 0.241              | 4.0   | 7.2  | 619      | 11.9               |
| 2.0   | 3.6  | 23.8     | 0.456              | 4.2   | 7.56 | 753      | 14.5               |
| 2.2   | 3.96 | 41.      | 0.790              | 4.4   | 7.82 | 900      | 17.3               |
| 2.4   | 4.32 | 64.      | 1.23               | 4.6   | 8.28 | 1080     | 20.8               |
| 2.6   | 4.68 | 94.      | 1.81               | 4.8   | 8.64 | 1270     | 24.5               |
| 2.8   | 5.04 | 134      | 2.58               | 5.0   | 9.00 | 1490     | 28.7               |
| 3.0   | 5.40 | 183      | 3.53               | 5.2   | 9.36 | 1720     | 33.1               |

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