

PREVIOUSLY ON

...*Thermodynamics*

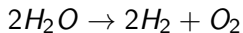
- Analytic Relations in Thermodynamics.
- Maxwell and Cyclic Relations.
- Equation of state, can relate thermodynamic measurables.
- Heat capacity, thermal expansion, compressibility/bulk modulus.
- Specify what is held constant: C_p and C_v ; K_S and K_T
- Force may not be the derivative of energy.
- Availability: work from equilibration.

Fukushima Disaster I: the explosion

Minimise Gibbs Free Energy

$$G=U - TS + PV$$

Favours high entropy at high temperature



Entropy is counting things...

$$3 > 2$$

High temperature created H_2 .
Hydrogen explosion.



The earthquake and tsunami killed over 15,000 people.

About 50 people died due to the evacuation.

There were no known casualties caused by radiation exposure.

Free Expansion and Joule Coefficient

Reanalyse Irreversible Free Expansion (see lecture 4)

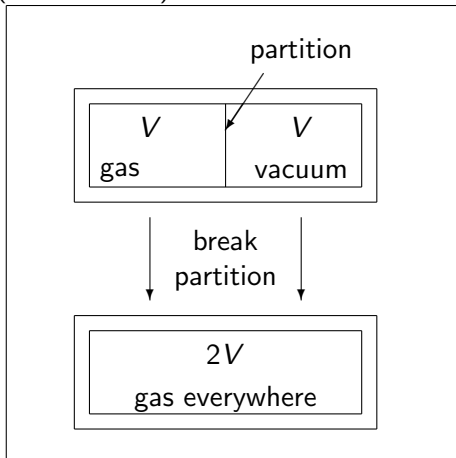
Surroundings “rigid adiabatic”
means $dS_0 = 0$; $dV_0 = 0$.

Choose thermodynamic potential U :

$$dU = dQ + dW = 0 + 0 = 0$$

System: How does change in V
affect T ?

Want $(\frac{\partial T}{\partial V})_U$



The Joule coefficient for a free expansion

Want $\left(\frac{\partial T}{\partial V}\right)_U$, so use $dT = \left(\frac{\partial T}{\partial V}\right)_U dV + \left(\frac{\partial T}{\partial U}\right)_V dU$

Consider an equivalent reversible process e.g. choosing $U = \text{constant}$; $dU = 0$

$$\Delta T = \int_{V_i}^{V_f} \left(\frac{\partial T}{\partial V}\right)_U dV = \int_{V_i}^{V_f} \mu_J dV$$

Eliminate “unmeasurable” U, S

Use cyclical rule, defⁿ of C_V central equation, & Maxwell relation

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = - \left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{C_V} \times \left(\frac{\partial U}{\partial V}\right)_T$$

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

$$\mu_J = \frac{1}{C_V} \left(P - T \left(\frac{\partial P}{\partial T}\right)_V \right)$$

Thus μ_J can be calculated from the Equation of State $U(P, T)$.

Examples: $\mu_J = \frac{1}{c_V} \left(P - T \left(\frac{\partial P}{\partial T} \right)_V \right)$

Ideal gas : $\mu_J = 0$ (as before)

The van der Waals equation: for one mole $\left(P + \frac{a}{v^2} \right) (v - b) = RT$,
can be written as a *virial expansion*: Equation of state in powers of density.

$$\begin{aligned} P v &= RT \left(1 + \left(b - \frac{a}{RT} \right) \left(\frac{1}{v} \right) + b^2 \left(\frac{1}{v} \right)^2 + \dots \right) \\ &= RT (1 + B_2/v + B_3/v^2 + \dots) \end{aligned}$$

$B_2, B_3 \dots$ are temperature dependent ($B_1 = 1$ gives ideal gas limit).
To estimate ΔT , need (μ_J) for that gas and the **increase** Δv in volume.
Estimate μ_J using the first virial coefficient:

$$\mu_J = -\frac{1}{c_V} \times \frac{RT^2}{v^2} \times \frac{dB_2}{dT}$$

For argon, $dB_2/dT = 0.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$. Doubling its volume gives
 $\Delta T \approx -0.6 \text{ K}$.

"The name of our corporate character, because of the way it's written, has been regarded as inappropriate, or has been misunderstood among English-speaking people"
Fridge manufacturer Fukushima Industries

Fukushima disaster II



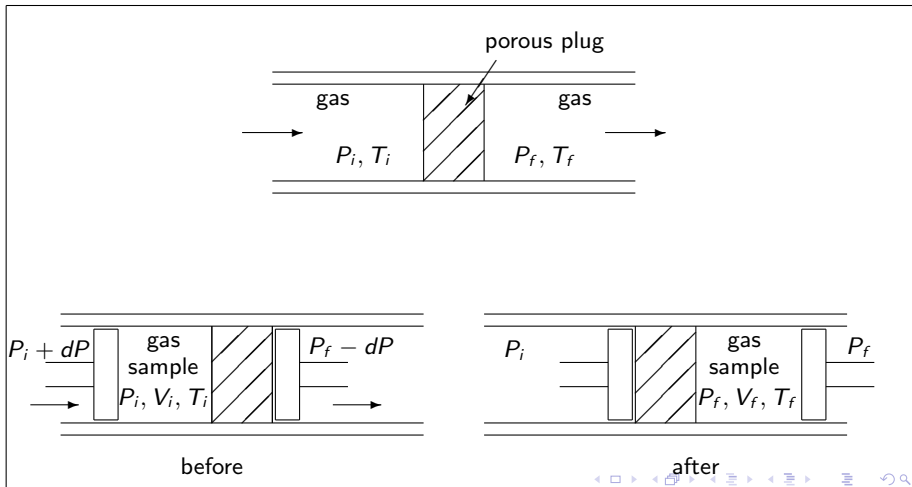
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Don't pick on the Japanese ...



The Joule-Kelvin coefficient for a throttling process

Real refrigeration requires cycling of the working fluid, i.e. flow.
Joule-Kelvin Expansion is a forced expansion (throttling process) e.g.
gas forced adiabatically through porous plug: **work** done, **no heat** transfer.



Joule-Kelvin Expansion and Coefficient

For a Joule-Kelvin expansion the *surroundings*,

- have no entropy change $\Delta S = 0$, no heat flow.
- exert constant external pressure. $\Delta P = 0$ (both sides)

For a Joule-Kelvin expansion the *system*,

- $\Delta Q = 0 = TdS$ (Equivalent reversible process)
- Work $PdV = P_i V_i - P_f V_f$; Energy $\int_i^f dU$
- First Law $U_f - U_i = P_i V_i - P_f V_f$
- $H_f = H_i$ consider a reversible *isenthalpic* process.

Rest of cycle: Pressure difference is maintained by pump (work), hot reservoir is a heat exchanger to the atmosphere.

Joule-Kelvin Expansion and Coefficient

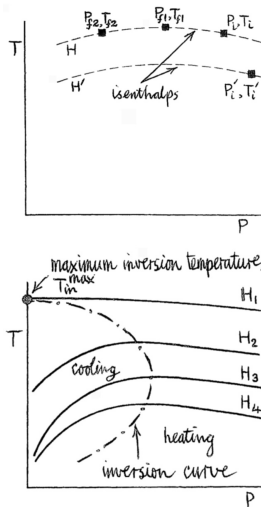
The most appropriate indicator diagram shows (T, P) .

The states visited (P_i, T_i) , (P_{f1}, T_{f1}) , (P_{f2}, T_{f2}) , etc. form an isenthalp.

Isenthalps typically have a maximum temperature.

The curve through the maxima of the isenthalps is called the inversion curve.

$$\begin{aligned} \text{Cooling: } (\partial T / \partial P)_H &> 0 \\ \text{Warming: } (\partial T / \partial P)_H &< 0. \end{aligned}$$



Change P , conserve H , so consider $T = T(P, H)$

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP + \left(\frac{\partial T}{\partial H}\right)_P dH = \left(\frac{\partial T}{\partial P}\right)_H dP = \int_{P_i}^{P_f} \mu_{JK} dP$$

Relate $\mu_{JK} = (\partial T / \partial P)_H$ to measurable material properties. Eliminate “unmeasurable” H , S using triple product and Maxwell.

$$\mu_{JK} = \left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P} \times \left(\frac{\partial H}{\partial P}\right)_T$$

Using $dH = TdS + VdP \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V$ we get...

$$\mu_{JK} = \frac{1}{C_P} \left(T \left(\frac{\partial V}{\partial T}\right)_P - V \right)$$

using a Maxwell relation in the final step to eliminate the unmeasurable S , leaving a differential of the equation of state.

Approximately, $\Delta T = \mu_{JK} \Delta P$,

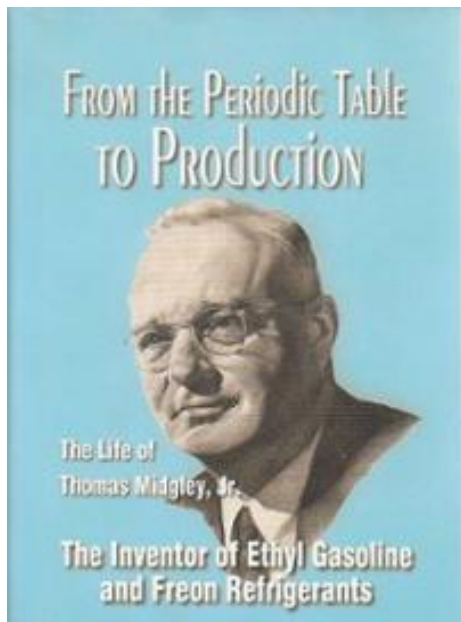
- 1 ideal gas: $(T (\frac{\partial V}{\partial T})_P = V)$, so $\mu_{JK} = 0$.
- 2 For a real gas ΔT may be negative **or positive** depending on conditions.
- 3 Inversion temperature is obtained from the condition $\mu_{JK} = 0$
- 4 Maximum inversion temperature by then setting $P = 0$.

Table of values of maximum inversion temperature, T_{in}^{max} , for various gases

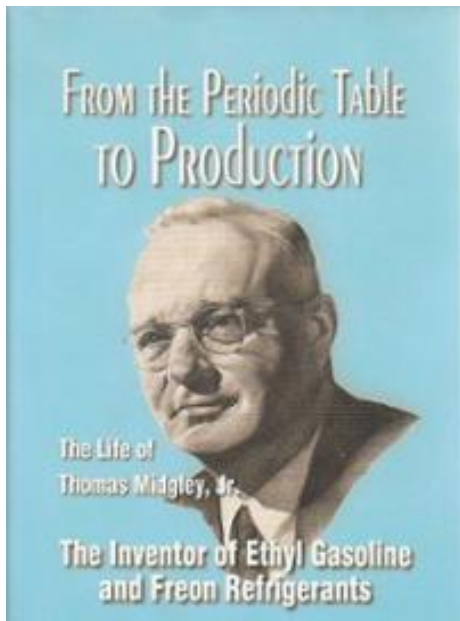
gas	max inversion temp (T_{in}^{max})	
argon	723 K	= 450°C
nitrogen	621 K	= 348°C
hydrogen	205 K	= -68°C
helium	51 K	= -222°C

Unluckiest scientist ever ?

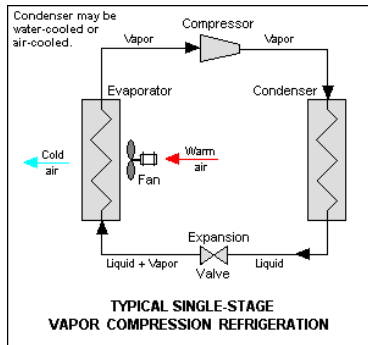
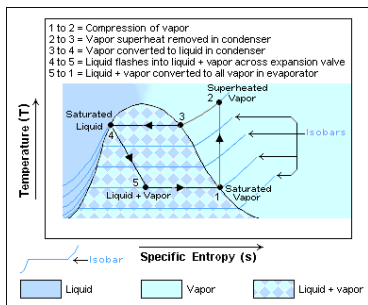
- Discovered and promoted the most effective refrigeration gas Dichlorodiuoromethane (Freon-12) and other CFCs
- Invented tetraethyllead additive to petrol to make it burn more evenly: “antiknocking” .
- Crippled by polio he invented a device to turn him over in bed.



- *CFCs destroyed the ozone layer and are about 10,000 times more efficient greenhouse gases than CO₂.*
- *Leaded petrol poisoned and killed millions of people*
- *In 1944 Midgley was strangled to death by his own device*



Vapour compression cycle



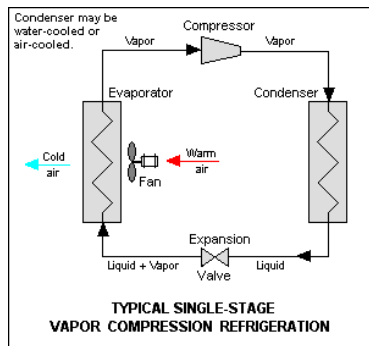
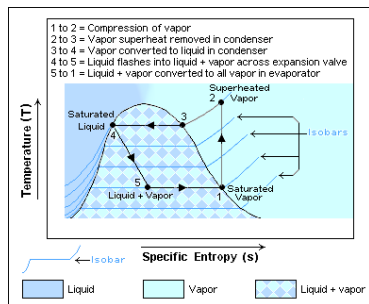
A massive $\left(\frac{\partial V}{\partial T}\right)_P$ occurs on boiling.

Exploit this to get an efficient fridge.

Dichlorodifluoromethane (Freon-12) ideal working fluid

Boiling point (1atm) : -29.8°C

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Dichlorodifluoromethane (Freon-12) ideal working fluid

Boiling point (1atm) : -29.8°C

Banned in 1996

(ozone layer, supergreenhouse gas)

Liquefying gases: Air and helium

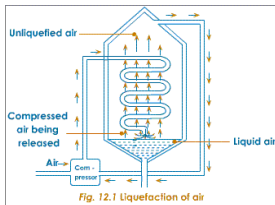


Fig. 12.1 Liquefaction of air

- Joule-Kelvin expansion used because fewer moving parts
- Pre-cooling is needed to give $T_i <$ the maximum inversion temperature (e.g. 51K in He)
- Pre-cooling by controlled adiabatic expansions above vapour-to-liquid phase transition.
- High pressure, gas throttled - some liquefies the rest helps pre-cool incoming gas, via a heat exchanger.