

## Notes for today

- Reading: Ch. 3 and continuing to Ch. 4.
- Reminder about lecture recording, I can send a recording link if you have to miss.
- Still looking for volunteer for problems 3 & 6

van der Waals gas

where we left off last time:

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \quad \text{Or,} \quad \overset{\text{per-particle}}{P + \frac{a}{v^2} = \frac{kT}{v - b}}$$

Can we find entropy?

$$ds = \left[\frac{1}{T}(u, v)\right] du + \left[\frac{P}{T}(u, v)\right] dv$$

Alternative, assume:  $u = \frac{3}{2}kT - a/v$  Recall work done in expanding at const.  $T$

$$\frac{1}{T} = \frac{\frac{3}{2}k}{u + a/v} \quad \frac{P}{T} = \frac{k}{v - b} - \frac{\frac{3}{2}k \frac{a}{v^2}}{u + a/v}$$

Solution  $S = Nk \ln \left[ (v - b)(u + a/v)^{\frac{3}{2}} \right] + Ns_0$

$\frac{3}{2} \Rightarrow c$   
general case (text)

Note this is one possible solution of vdW eqn, but assuming a constant  $C_V$  specifies this result.

# van der Waals gas

$$S = Nk \ln \left[ (v - b)(u + a/v)^{\frac{3}{2}} \right] + Ns_0 \quad u = \frac{3}{2}kT - a/v$$

Specific heat:

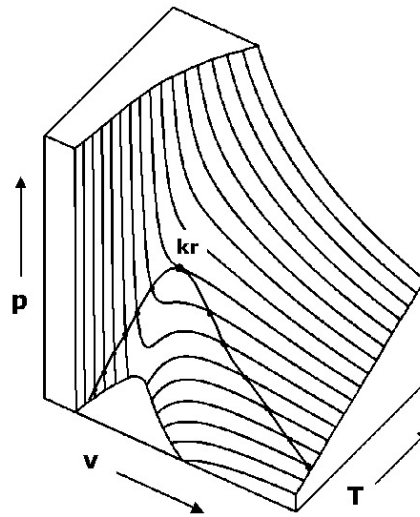
$$C_V = T \left. \frac{\partial S}{\partial T} \right]_{VN} = \frac{3}{2} Nk_B$$

Independent of volume &  $T$   
(not generally valid: breaks down near liquid condensation temperature)

TABLE 3.1  
Van der Waals Constants and Molar Heat Capacities of Common Gases<sup>a</sup>

Gas	$a$ (Pa·m <sup>6</sup> )	$b$ (10 <sup>-6</sup> m <sup>3</sup> )	$c$
He	0.00346	23.7	1.5
Ne	0.0215	17.1	1.5
H <sub>2</sub>	0.0248	26.6	2.5
A	0.132	30.2	1.5
N <sub>2</sub>	0.136	38.5	2.5
O <sub>2</sub>	0.138	32.6	2.5
CO	0.151	39.9	2.5
CO <sub>2</sub>	0.401	42.7	3.5
N <sub>2</sub> O	0.384	44.2	3.5
H <sub>2</sub> O	0.544	30.5	3.1
Cl <sub>2</sub>	0.659	56.3	2.8
SO <sub>2</sub>	0.680	56.4	3.5

<sup>a</sup> Adapted from Paul S. Epstein, *Textbook of Thermodynamics*, Wiley, New York, 1937.



3.1. The constants  $a$  and  $b$  are obtained by empirical curve fitting to the van der Waals isotherms in the vicinity of 273 K; they represent more distant isotherms less satisfactorily. The values of  $c$  are based on the molar heat capacities at room temperatures.

$C_V$

## Differentials:

$$dU = TdS - PdV \equiv \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV \quad \text{example of exact differential}$$

### Useful general mathematical properties:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{order of differentiation}$$

e.g.  $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = -1/\left(\frac{\partial S}{\partial P}\right)_V$  a Maxwell relation

Sometimes can't measure  $S$  directly, could measure adiabatic temperature change.

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z \quad \text{reciprocal}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial t}\right)_z = \left(\frac{\partial x}{\partial t}\right)_z \quad \text{chain rule; same as: } \left(\frac{\partial x}{\partial y}\right)_z = \frac{\left(\frac{\partial x}{\partial t}\right)_z}{\left(\frac{\partial y}{\partial t}\right)_z}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1 \quad \text{cyclical}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial t}\right)_y \left(\frac{\partial t}{\partial y}\right)_z + \left(\frac{\partial x}{\partial y}\right)_t \quad \text{converting partials}$$

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Specific heat:

$$C_P = T \left. \frac{\partial S}{\partial T} \right|_{PN} = T \left. \frac{\partial S}{\partial T} \right|_{VN} + T \left. \frac{\partial S}{\partial V} \right|_{TN} \left. \frac{\partial V}{\partial T} \right|_{PN}$$

$C_V$

$$\left. \frac{\partial S}{\partial V} \right|_{TN} = \frac{k}{v - b} \quad \left. \frac{\partial V}{\partial T} \right|_{PN} = \frac{Nk}{P - a/v^2 + 2ab/v^3}$$

$TV\alpha^2 / N\kappa_T$   
 can show (Maxwell relations)  
 More general result.

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More general result.

- Ideal gas,  $C_P = C_V + Nk_B$  ( $\Delta C = R$  per mole)
- Dilute Van der Waals gas, can see  $\Delta C > R$  per mole (difference is small)

### Irreversible & Reversible processes:

- Fundamental condition: spontaneous processes with change of entropy cannot occur in reverse; entropy sets the “arrow of time”. Any process in which number of accessible microstates ( $\Omega$ ) increases must be irreversible.

Irreversible process:  $\Delta S > 0$

Reversible process:  $\Delta S = 0$

- Further consideration: reversibility necessitates infinitely slow process, or one in which the system changes much more slowly than the internal relaxation times. Notation: Quasistatic processes.

$$dU = TdS - PdV + \mu dN + Bdl$$

mechanical
“chemical work”
magnetic

Heat flow, always changes entropy
All classified as work
 $I = MV$  bulk magnetization

$$\sum P_j dX_j$$

Notes:

- “Quasistatic”: work done in controlled process, system relaxed to equilibrium at all points along the way.
- Also no dissipation (e.g. absence of moving friction)



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Adiabatic

- Heat flow across  $\Delta T \neq 0$ : always generates entropy; Isothermal process can be reversed.
- However for quasistatic behavior, requires infinite time!

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- Can we combine both and still be reversible?

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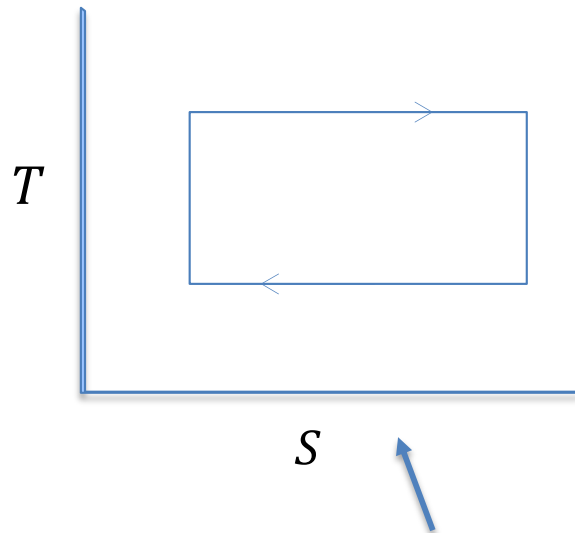
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- Can we combine both and still be reversible?  
Yes generally, but requires a series of thermal reservoirs.

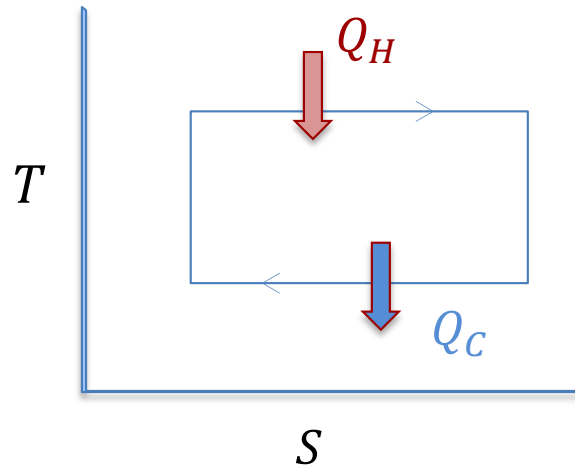
## Cycles:



This process:

- Individual processes involved?
- Net entropy change for one cycle?
- $Q$  and  $W$  per one time around cycle?

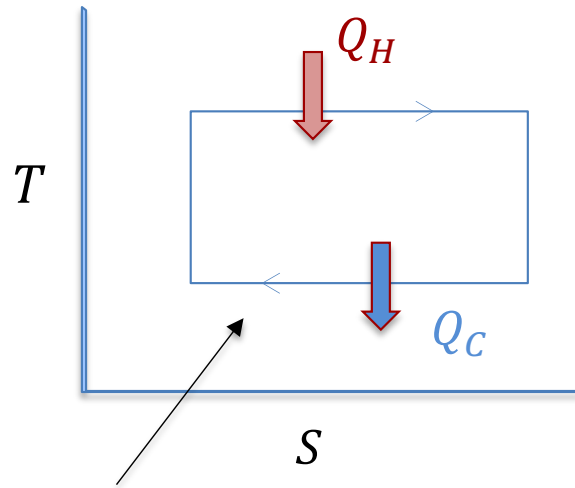
## Heat and Work processes:



Carnot cycle – **does not need to be ideal gas.**

- Reversible;  $\Delta S = 0$  heat engine or refrigerator.
- P-V diagram depends on working gas or fluid.
- Carnot cycle most efficient for same  $T_H$  &  $T_C$

## Heat and Work processes:



Work = T-S area inside  
Done by the gas.

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$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

$$e = 1 - \frac{T_C}{T_H}$$

- Heat flow: From & into “heat baths”:  
external reservoir (power plant heat exchanger);  
combustion of fuel; source of thermal photons, etc.
- **Carnot limit:** not 100% efficient (can't have  $Q_C = 0$ ).
- **Carnot-cycle power output is essentially zero!**