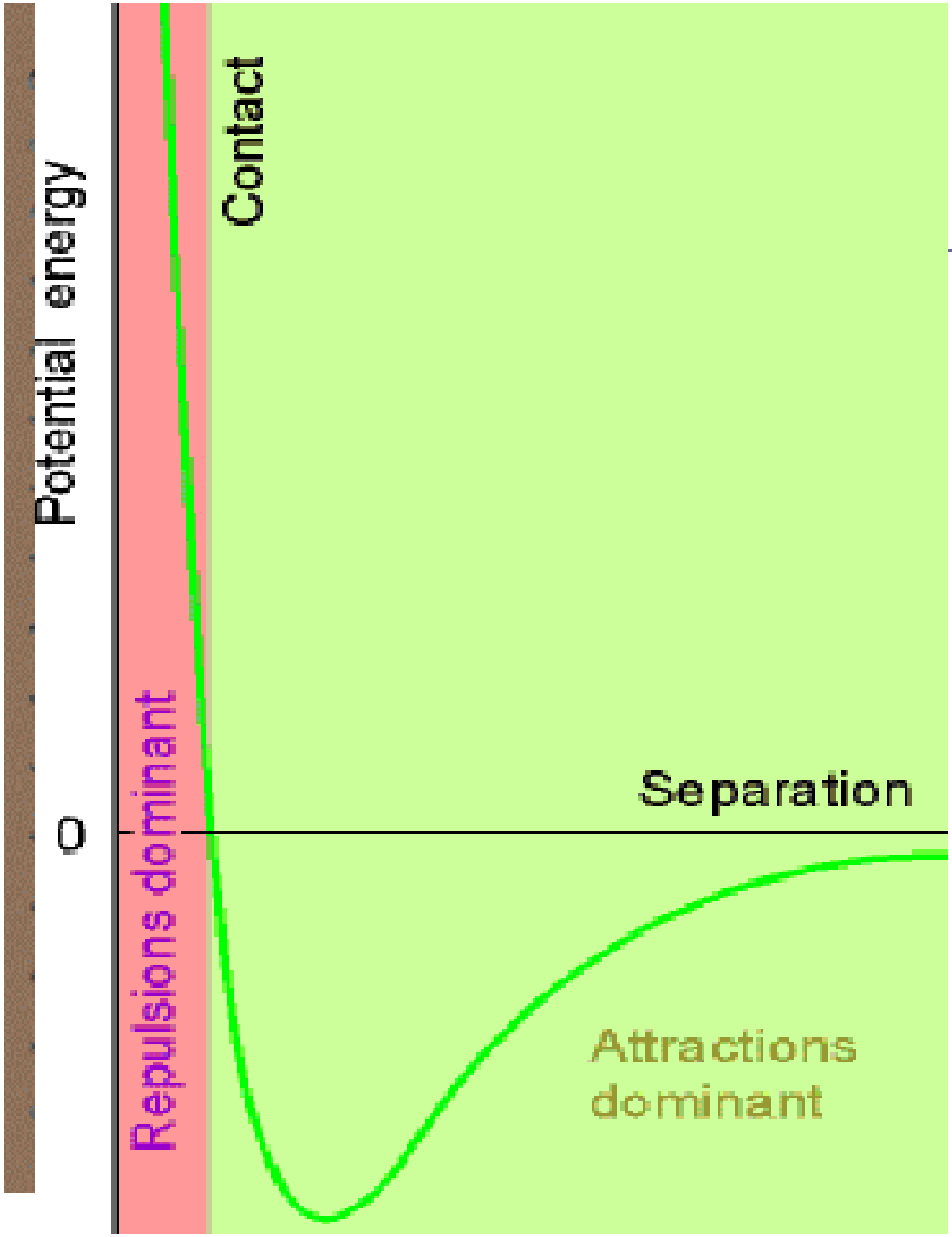
Real Gases

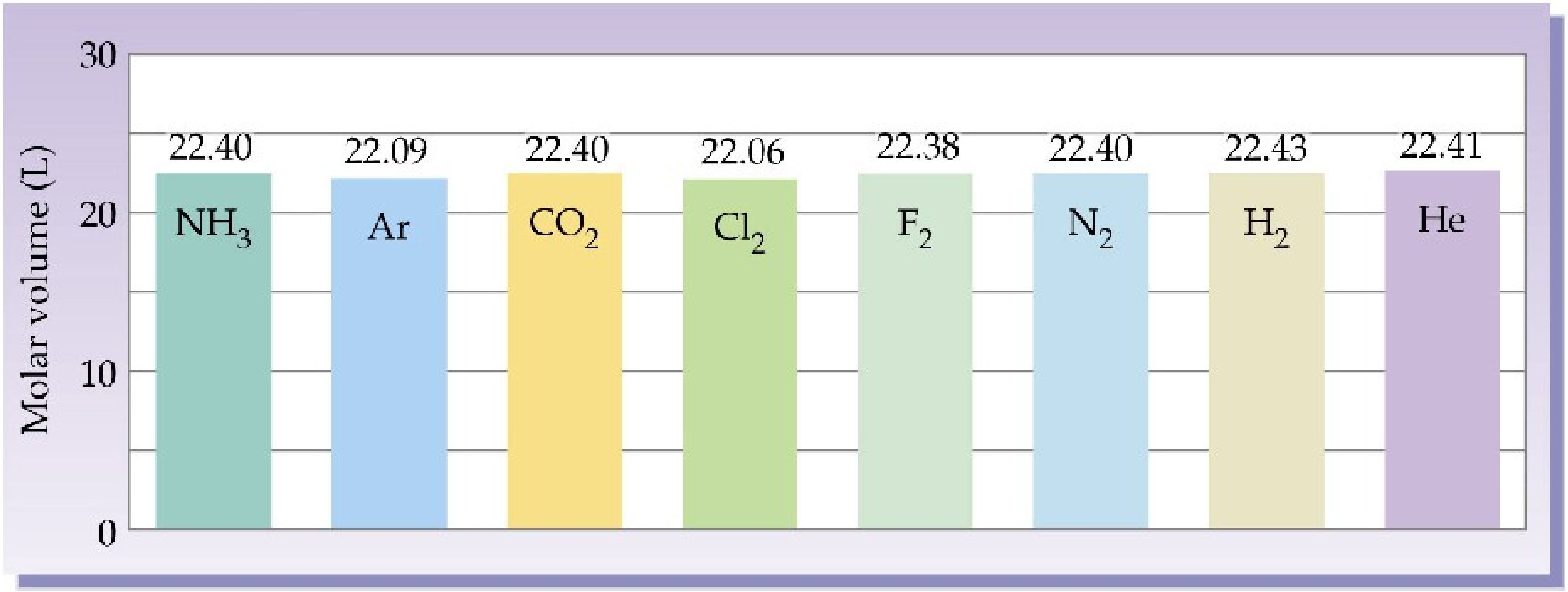
- ✓ Real gases differ from perfect gases in two ways.
- ✓ The molecules DO attract each other when not in contact.
- ✓ The molecules DO occupy some volume (region where repulsions dominate)
  - Repulsions dominate in this region because when molecules get close enough to "touch" they push each other away.

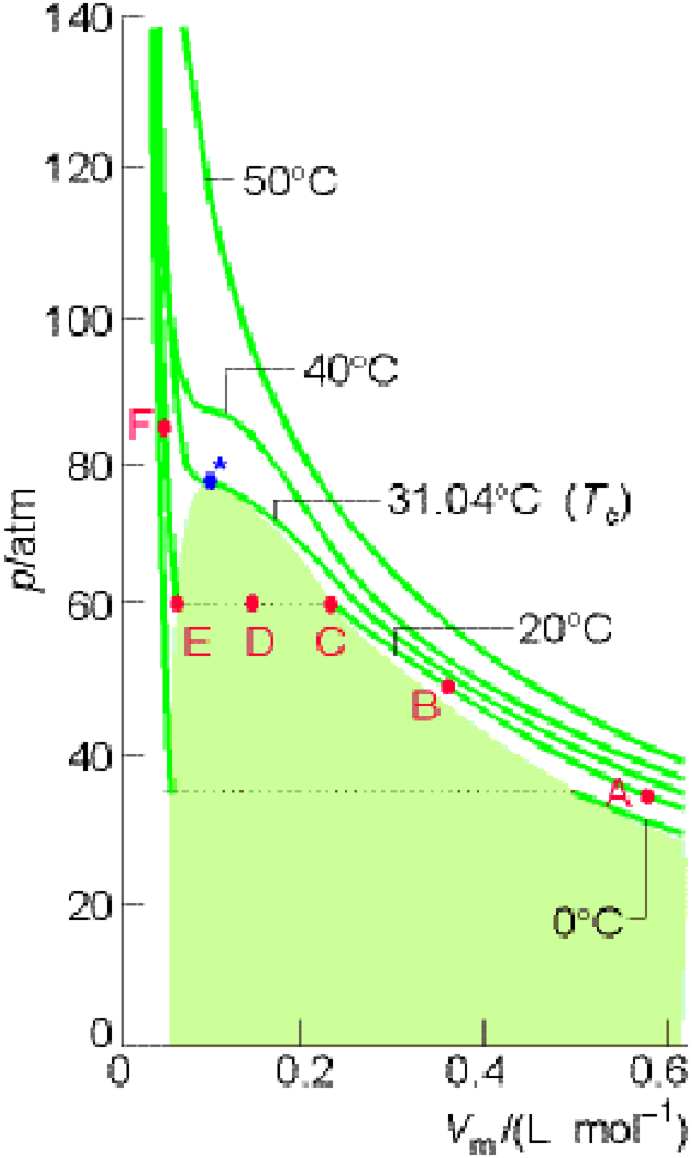


Real Gases

- ✓ Intermolecular attractions give rise to a potential energy.
- ✓ Attractions correspond to a lowering of total energy; repulsions to a raising of energy.
- ✓ At very large separations there is almost no attraction or repulsion.

TABLE 9.4 Molar Volumes of Some Real Gases at STP





Real Gas p-V Isotherms

- At high temperatures the isotherms resemble those of a perfect gas (Boyle's law).
  - The same is true at low pressure.
- Different substance have different p-V behaviors.
  - CO_2 is shown at right.
- In the colored region there are two phases present -- gas and liquid.

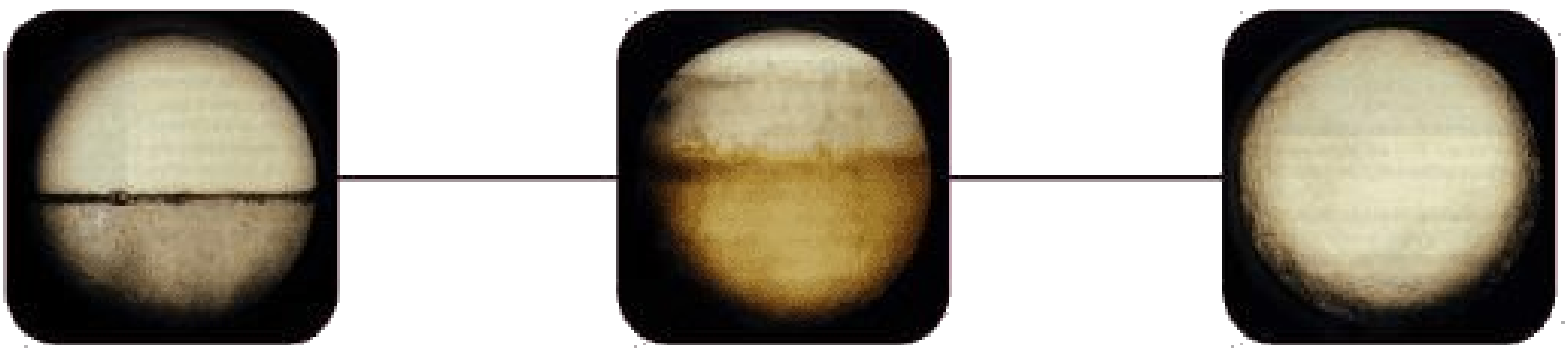
p-V Behavior at Various T's

- Note the 20 ºC isotherm in the previous slide.
  - As pressure is increased from point A there is a rising curve, ABC, followed by a horizontal portion CDE, and a very steeply rising portion EF.
  - Along ABC, CO_2 is a gas; along EF it is a liquid; along CDE both phases are present.
- Note the 31.04 ºC isotherm.
  - The horizontal portion has shrunk to a point.
  - Above this temperature there is no two-phase region.
  - 31.04 ºC is the **critical temperature** of CO_2.

The Critical Temperature

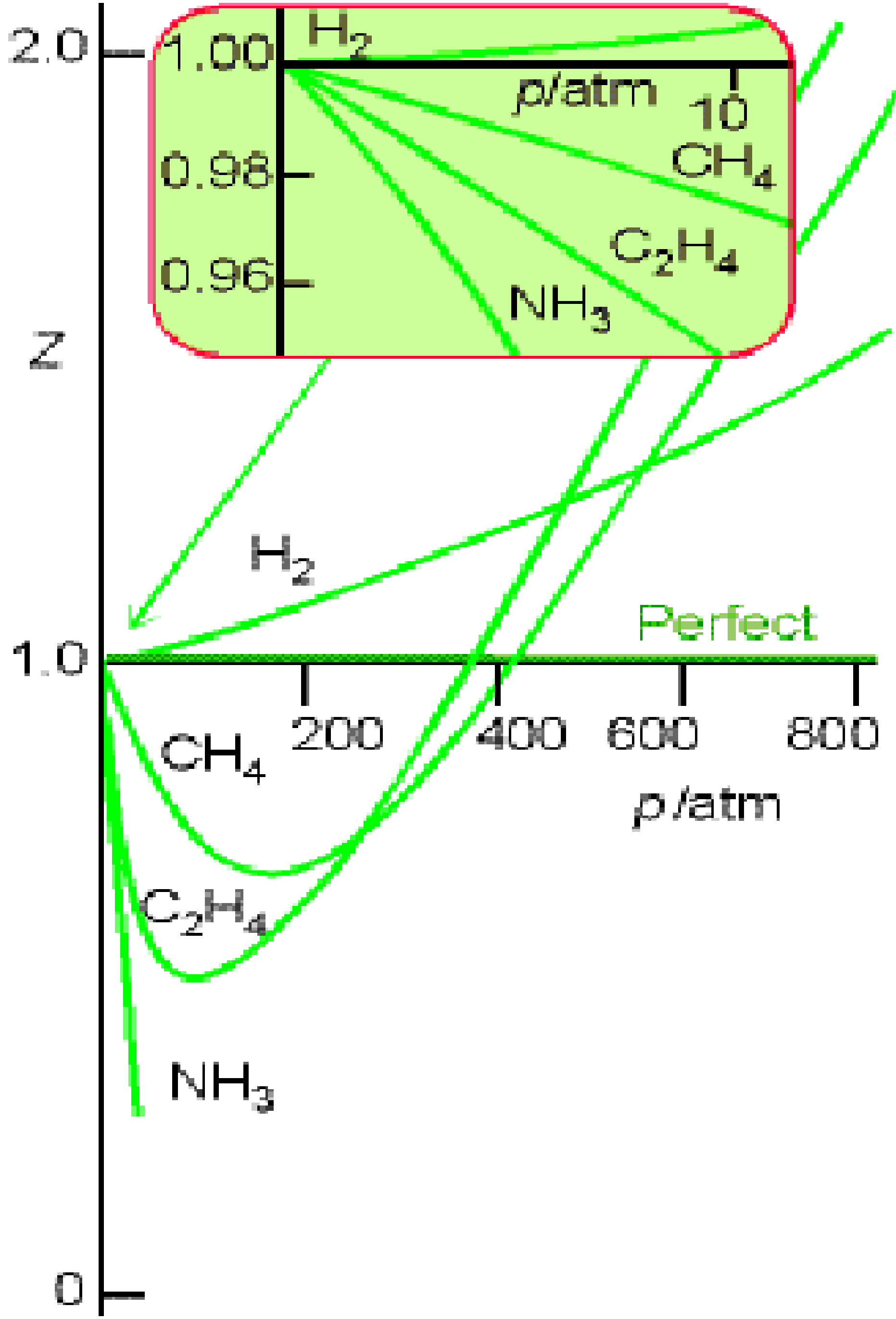
- The **critical temperature** (T_c) is the temperature above which a gas cannot be liquified, no matter what the pressure.
  - The pressure required for liquefaction at that temperature is the **critical pressure** (p_c).
    - Can you estimate the critical pressure for CO_2?
- As pressure is increased isothermally . . .
  - below the critical pressure a sharp boundary is formed when the two-phase region is entered.
    - This boundary becomes less easy to see at temperatures closer to T_c.
  - at T_c no boundary every exists -- the system changes smoothly from all gas to all liquid.

The figure below shows three photos of the same system. From left to right, the temperature is increasing. In the left photo, there are two phases present, liquid and gas, and the distinction between them is obvious. The center photo is near the critical temperature, so the separation of the two phases is becoming obscured. In the photo on the right, there is no phase distinction, so this is above the critical temperature and is a supercritical fluid.



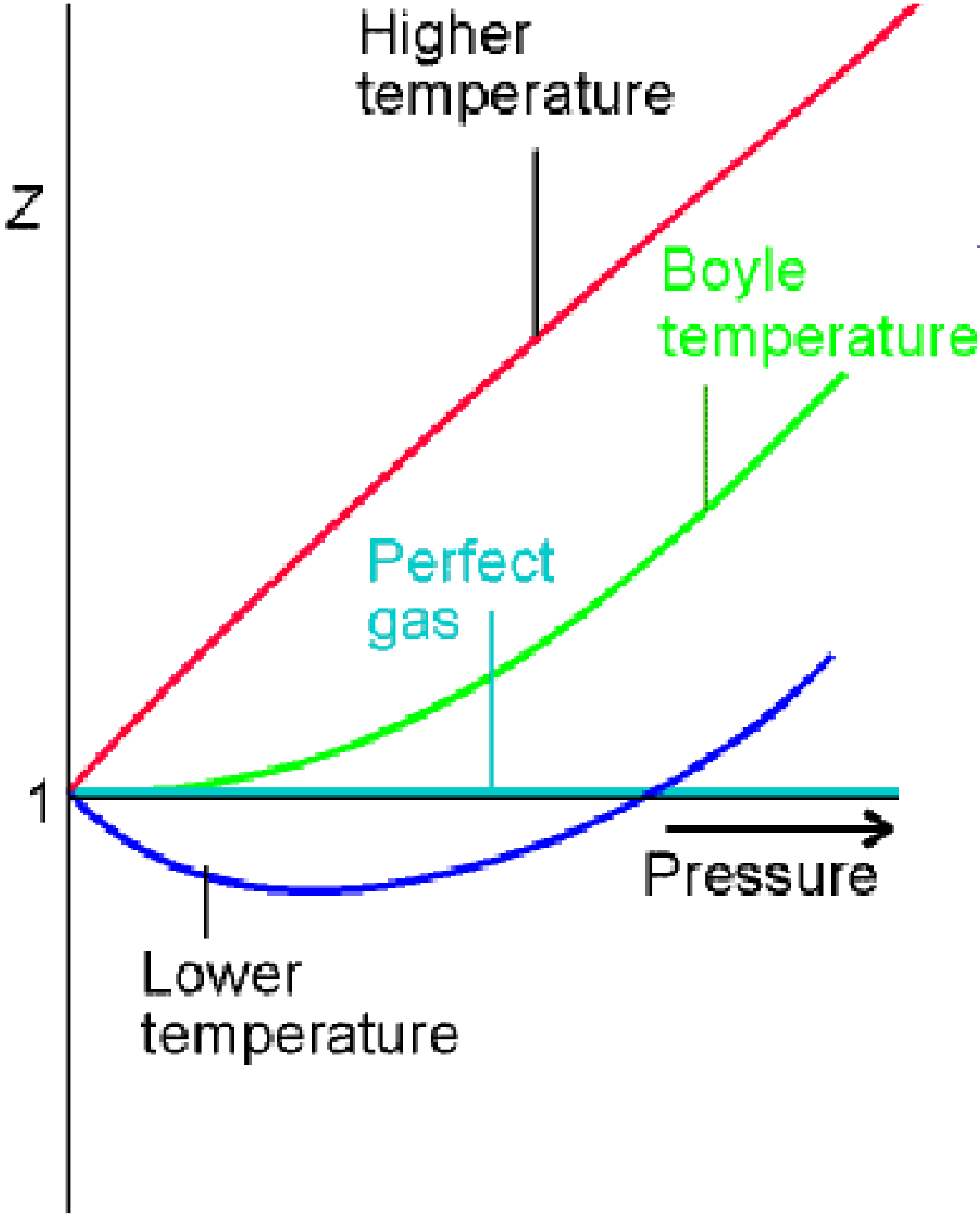
Z

- For a perfect gas, $pV/nRT = 1 = pV_m/RT$
- The ratio pV_m/RT is called the **compressibility factor**, Z.
- For real gases, Z can be either greater or less than 1.
- Z is greater than 1 when the volume is greater than that of a perfect gas at the same T and p.
  - This indicates less compressibility.
  - It also indicates that repulsion factors dominate.



Real Gas Behavior

- For all gases, Z approaches one as the pressure approaches zero.
- For all gases at a low enough temperature, Z starts out decreasing from 1 as the pressure is increased.
  - The figure at left is for 0 °C.
- For all gases at a high enough temperature Z never gets less than 1.
- What happens at high *p*?



Close-up of Z vs. *p*

- Z always exceeds 1 at a high enough pressure
  - for all gases
  - at all temp's
- At the **Boyle temperature** Z starts out with zero slope.

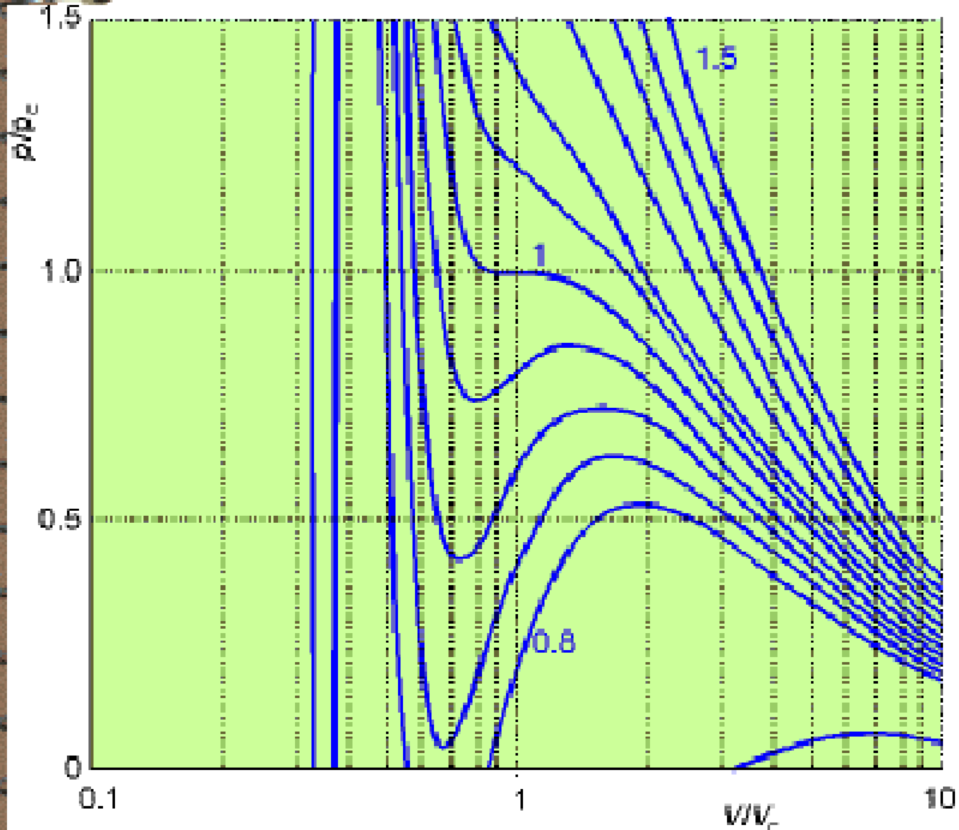
Real Gas Equations of State

- ✓ $pV = ZnRT$ is true, but not very useful.
  - Z has different values for each gas at each temperature and each pressure.
- ✓ OK to look up a couple of constants per gas if these constants hold for a range of temperatures or pressures.
- ✓ The **virial equation** uses a couple of constants per gas
  - $pV_m / RT = 1 + B / V_m + C / V_m^2 + \ldots$
  - is at least good for a range of pressures.

Van der Waals Equation

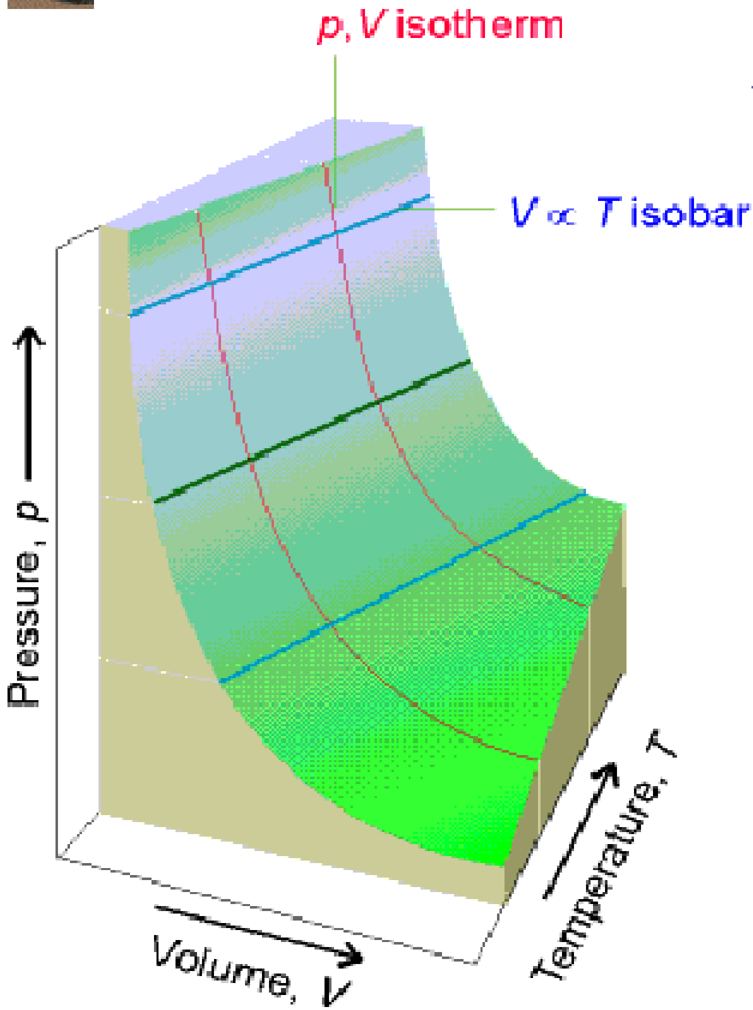
- The van der Waals equation is based on addressing the two ways that real gases differ from ideal gases.
  - Real gases molecules are not point particles. The volume occupied by a real gas must be reduced to match the "ideal" volume.
  - Real gas molecules exert (usually) attractive forces on each other, which reduces the pressure. The pressure exerted by a real gas must be increased to match the "ideal" pressure.
- vdW got: $(p + n^2a/V^2)(V - nb) = nRT$

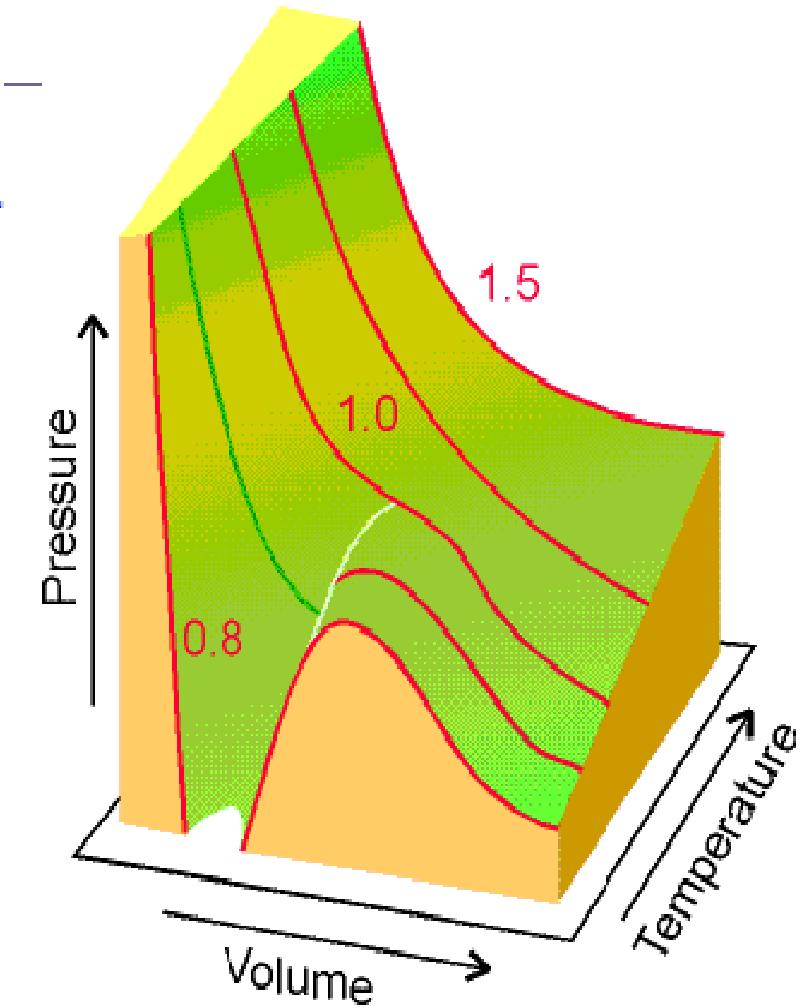
Plotting the van der Waals Equation

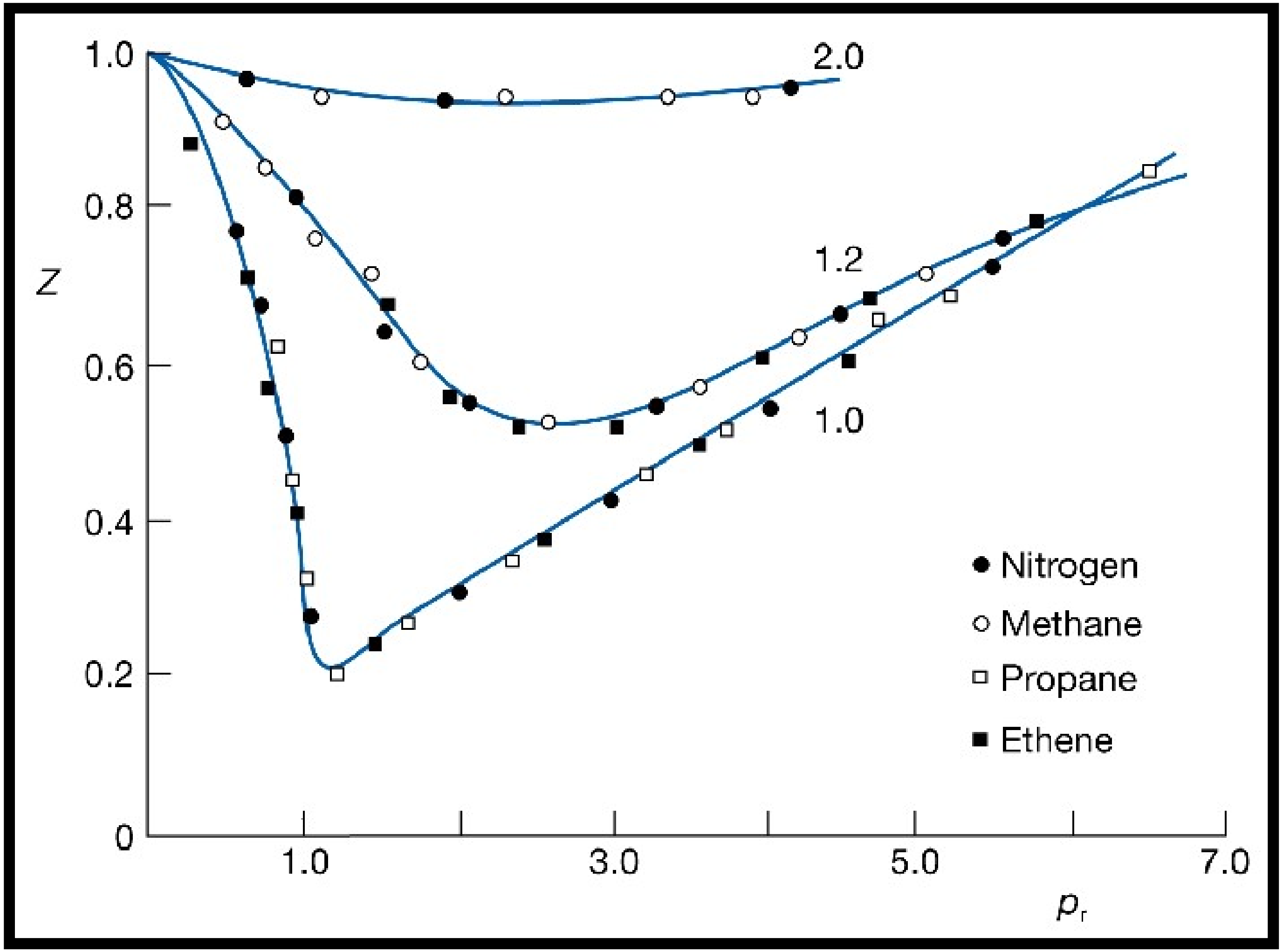


- If the vdW equation is expanded, it is cubic in V.
- Cubic equations have three roots.
- Physically, however, gases have only one volume at a given T, *p*.
- See also Figs. 1.21 and 1.22.

Ideal vs. Real Gases







Fator de compressibilidade de vários gases em função de coordenadas reduzidas

Referências

University of West Georgia

http://www.westga.edu/~chem/courses/chem410

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NASA

http://www.grc.nasa.gov/WWW/K-12/airplane/short.html