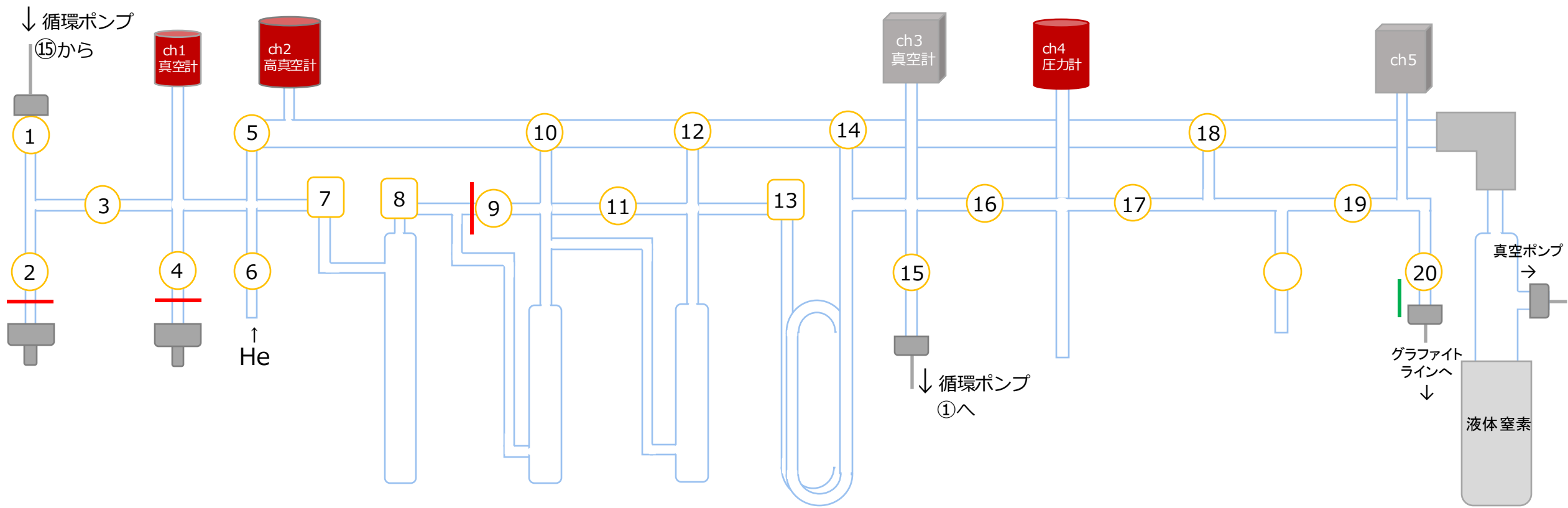


^{14}C Measurement Seawater Sample Pretreatment

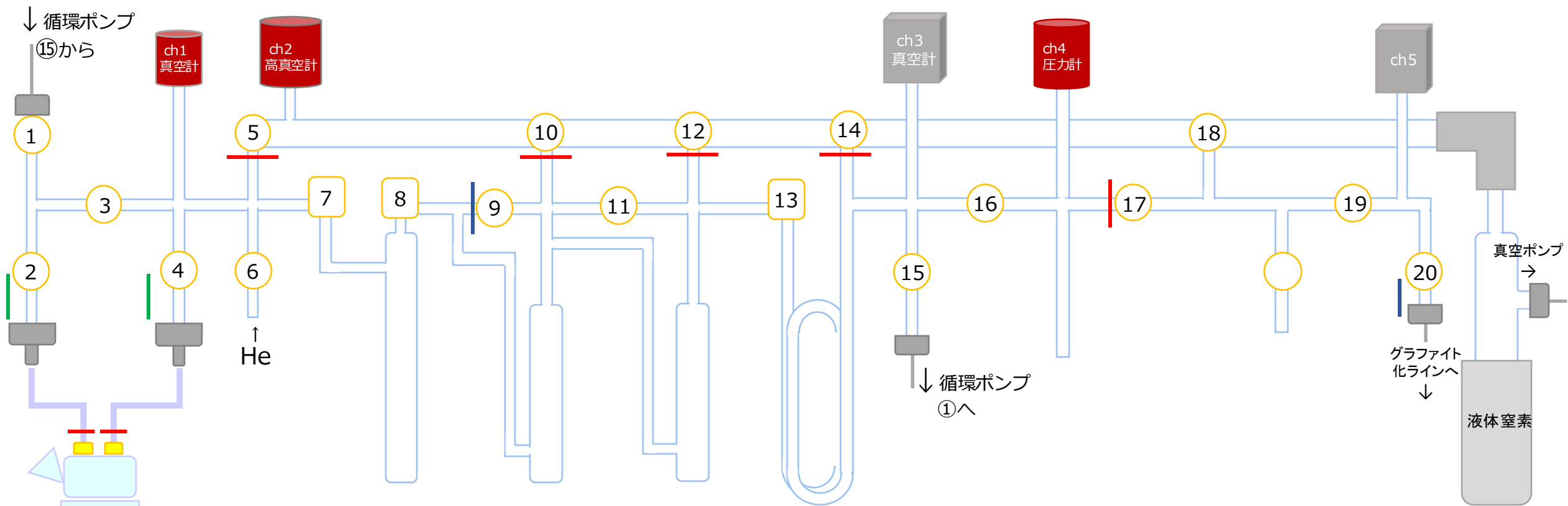
2024.9.24

Translated & Edited by
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Based on the manual by Yukiko HIGUCHI & Yosuke MIYAIRI



1. Confirm that valves 2, 4, and 9 are closed, and the others are open.
2. Before beginning, check if ch2 pressure at E^{-5} (highest $5 \times E^{-3}$ if not the 1st sample)
3. Install the cold trap (liquid nitrogen).
 - Water trap in front of the rightmost vacuum pump.
 - The amount of liquid nitrogen should be just under half



4. Connect the sample.

Place the phosphoric acid on the left side.

2 - Center

4 - Right side

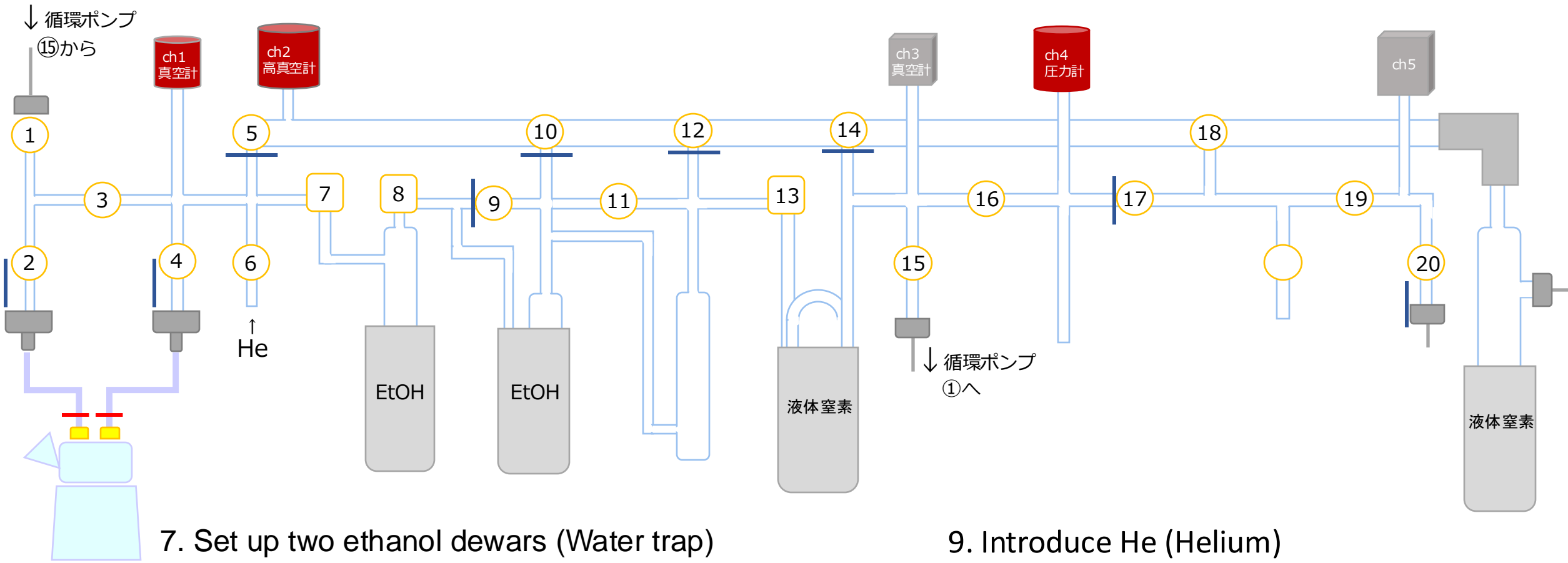
5. Open valves 2 and 4.

- Vacuum the metal pipe section until Ch2 reaches 10^{-5} to 10^{-4} .

6. Close valves 5, 10, 12, 14, and 17.

- Ensure that the gas circulation section is closed against the high-vacuum pump.

In the meantime, prepare 2 water traps (LN₂ + Ethanol) & 1 CO₂ trap (LN₂)



7. Set up two ethanol dewars (Water trap)

- Cool the ethanol to about **-90°C** with liquid nitrogen
- Fill the dewar with to about 70% of its capacity
- At the 7-8 and 9-10 positions

8. Set up the liquid nitrogen dewar (CO₂ trap)

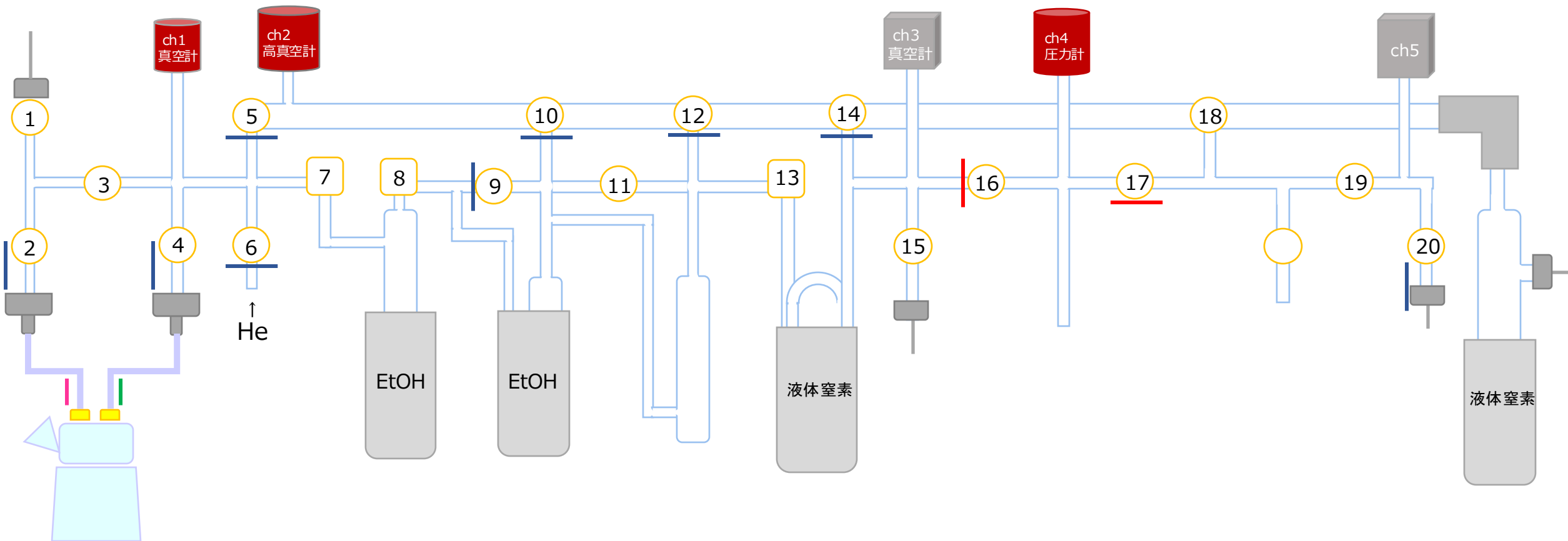
- Fill the dewar with liquid nitrogen to about 50% of its capacity
- At the 13-14 position

9. Introduce He (Helium)

- Until the pressure of ch4 reaches 700 mbar
- If too much:
close 16 → (2) open 17 to release some He → (3) open 16 to check ch4 → (4) repeat (1)-(3) till ch4 goes back to 700 mbar

10. Close valve 6 (He inlet)

- Record the He pressure



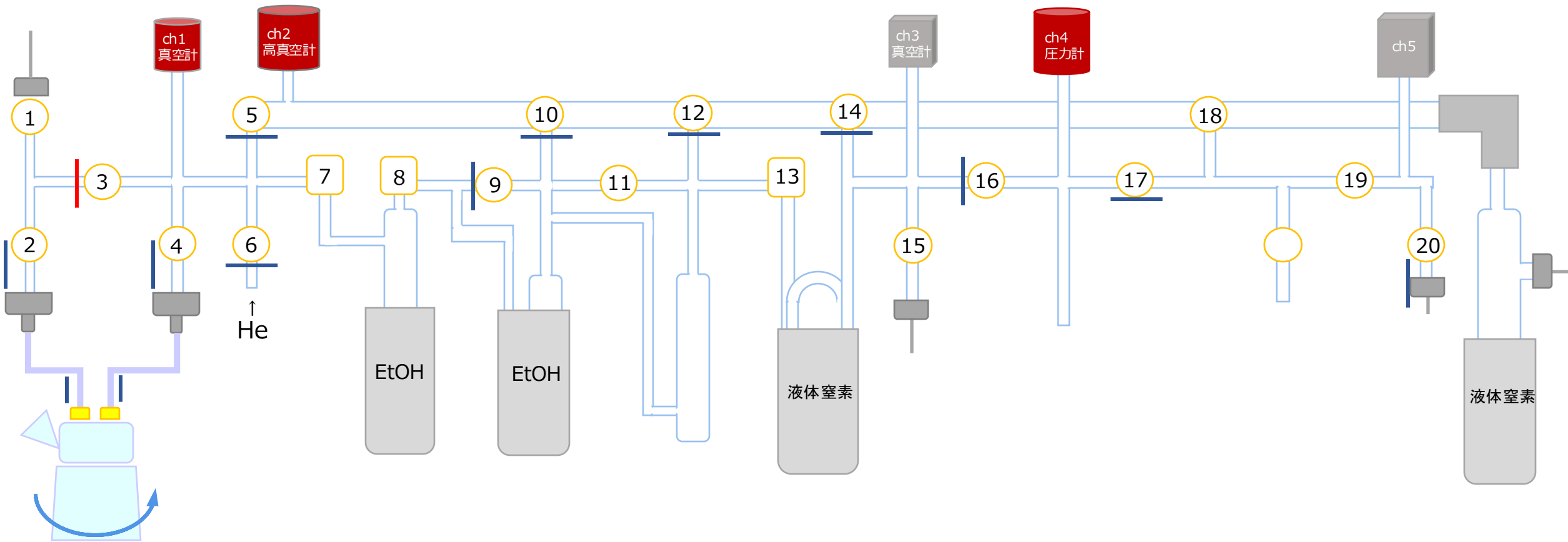
11. Open the **right valve** (gas outlet) of the bubbling device.
- Confirm that the pressure of CH₄ reaches 800 mbar
 - Record the pressure of 4ch

12. Open the **central valve** (gas inlet).

13. Close valve 16, take a breath, then open valve 17.
4ch should reach 0 mbar.

14. Rotate the phosphoric acid container and add the phosphoric acid to the sample.

Be careful not to open the central valve first, as seawater might be sucked into the line!

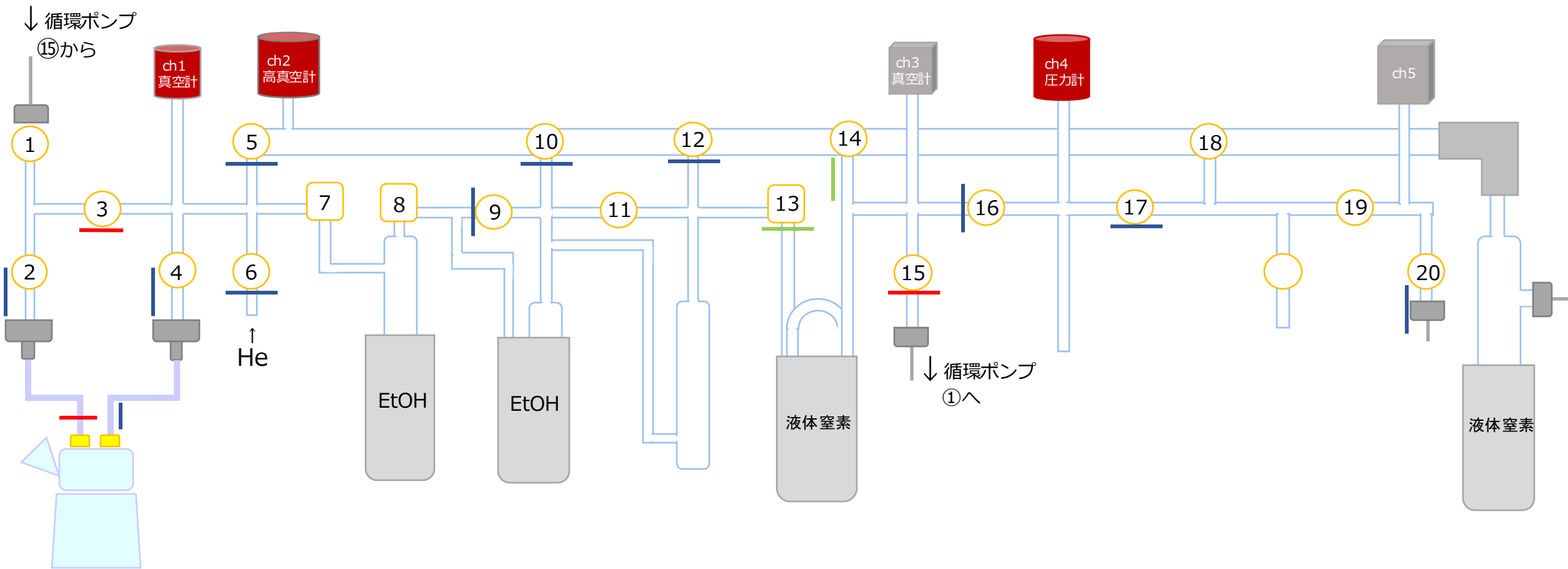


15. Close valve 3.

16. Turn on the circulation pump (left side of the device).

Let the seawater bubble for about 15 minutes.

*The seawater sample will bubble as the gas circulates.



17. Turn off the circulation pump and close the center of the bubbling device (gas inlet).

Be careful, as seawater will backflow during exhaust if you forget!

18. Open valve 3 and close valve 15.

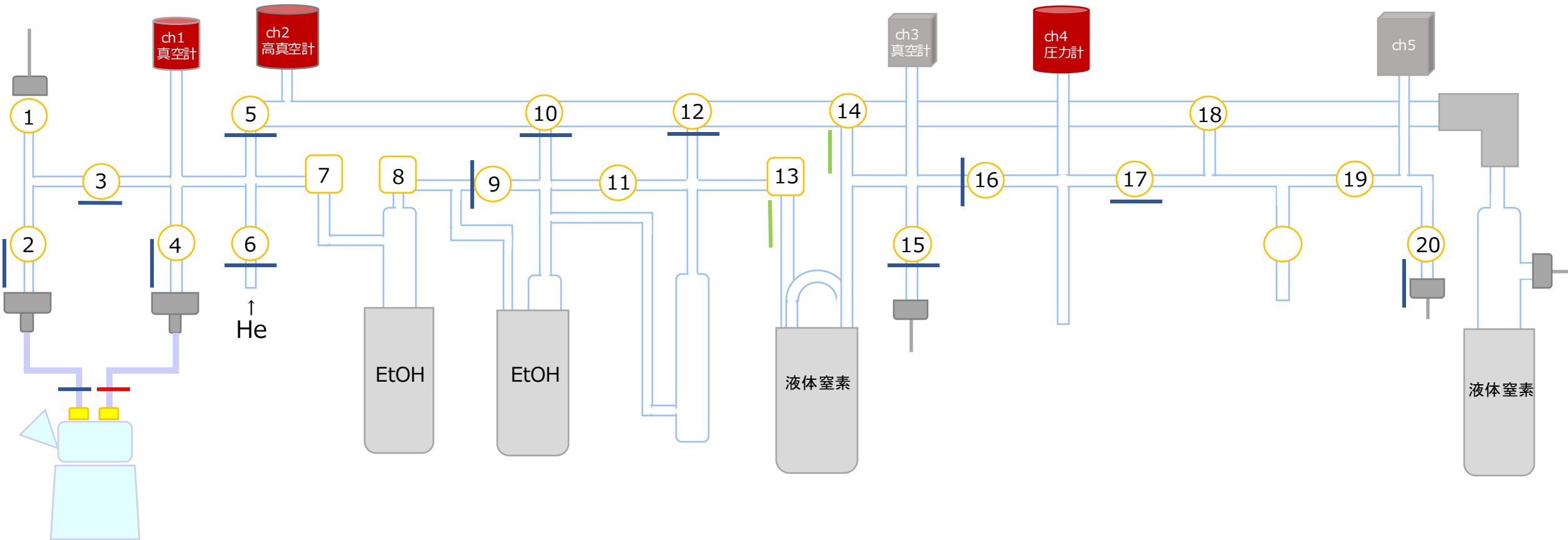
19. Degas the gas in the circulation part.

✘ Since quickly venting will put a heavy load on the pump, do it gradually!

【Procedure】

- Close 13 → Open 14 → Open 13 and repeat 2-3 times

Since you want to pass through the CO₂ trap (liquid nitrogen), vent from 14.



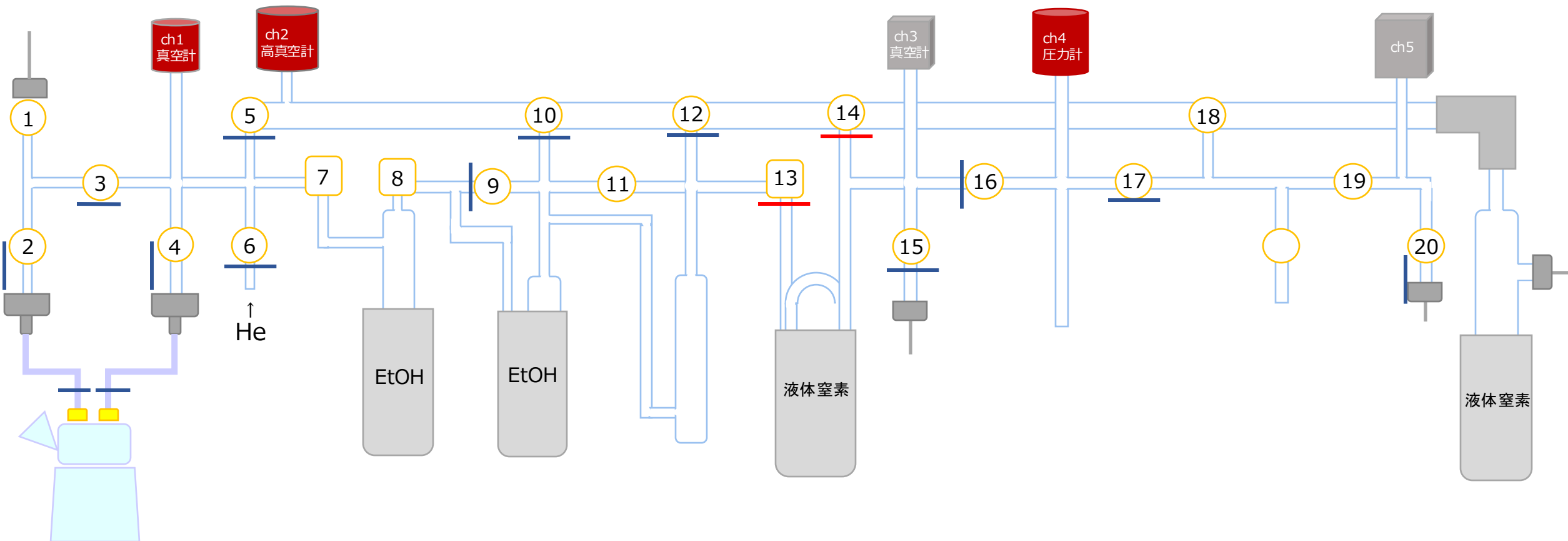
20. With valve 13 open, open 14 for 1-2 seconds and then close it immediately.

- When the vacuum level in the bubbling device decreases, seawater will boil vigorously, so monitor the seawater while performing this operation.
- Repeat this process 2-3 times.

21. Close the right side of the bubbling device (gas discharge port).

22. With the gas discharge port of the bubbling device closed, degas the circulation line for a while.

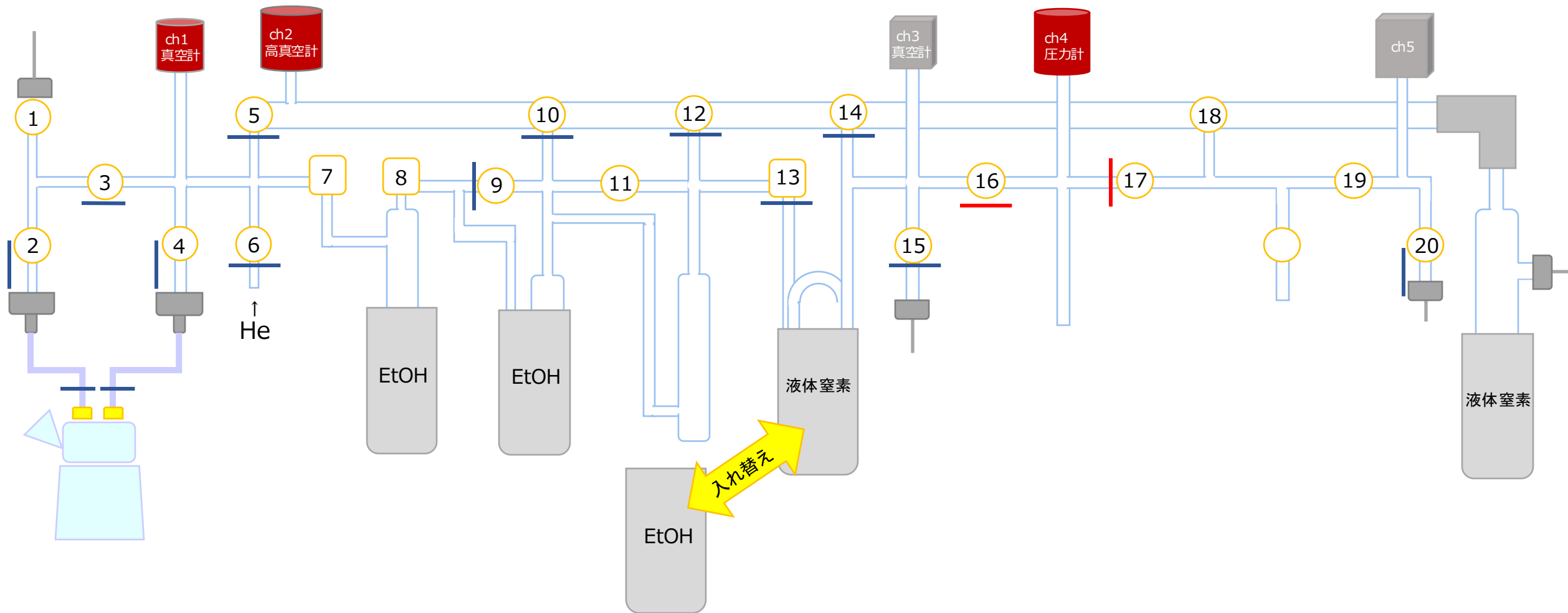
- Open 13 and 14
- Continue until Ch1 stabilizes



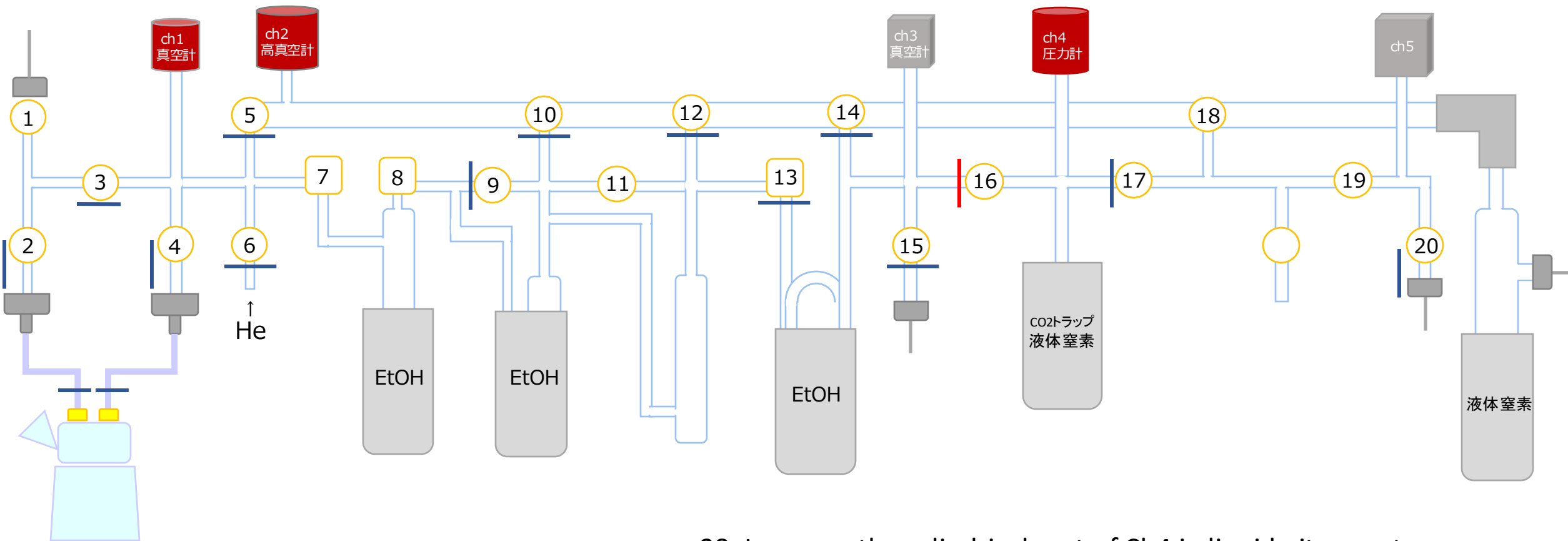
Memo

For this sample only, you can use the water trap used in steps 7-8 and 9-10 for operation 26. If you continue with the next sample, do not remove it, as it takes time for the water to drain.

- 23. Close valve 13.
- 24. Prepare the water trap (for 13-14).
Fill the EtOH + liquid nitrogen dewar completely. (At least more than the volume of liquid nitrogen in the CO₂ trap.)
- 25. Close valve 14.
Confirm that 13, 14, 15, and 16 are closed!



26. Replace the liquid nitrogen with ethanol. Do this quickly!
 Soak in EtOH for **about 5 minutes** until the CO₂ dissolves.
 (Replace the water trap to remove the water mixed with CO₂ in the CO₂ trap.)
27. Close valve 17 → Open valve 16.
 Confirm that it is dissolving in 4ch. (Pressure will increase.)

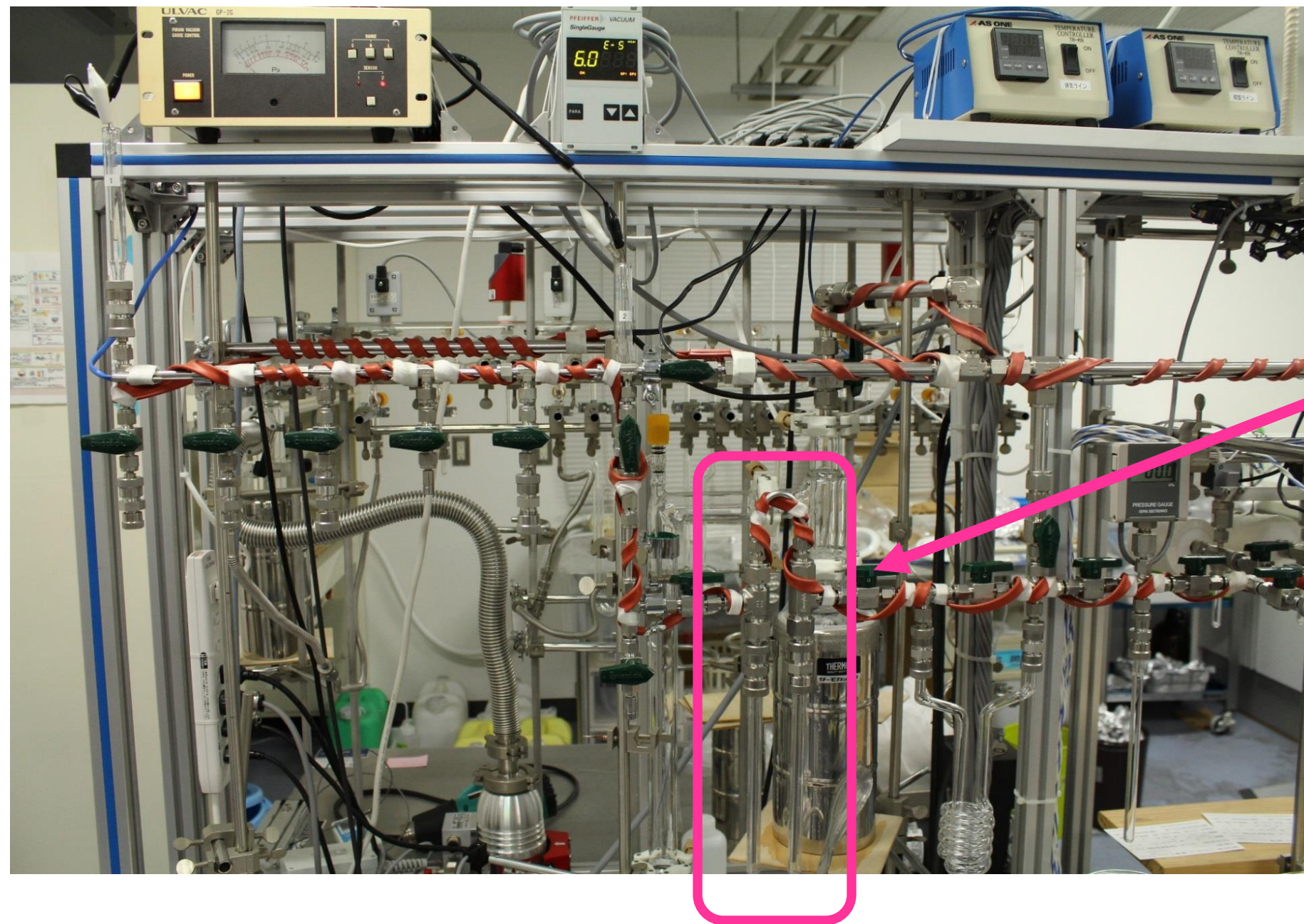


28. Immerse the cylindrical part of Ch4 in liquid nitrogen to collect CO₂.

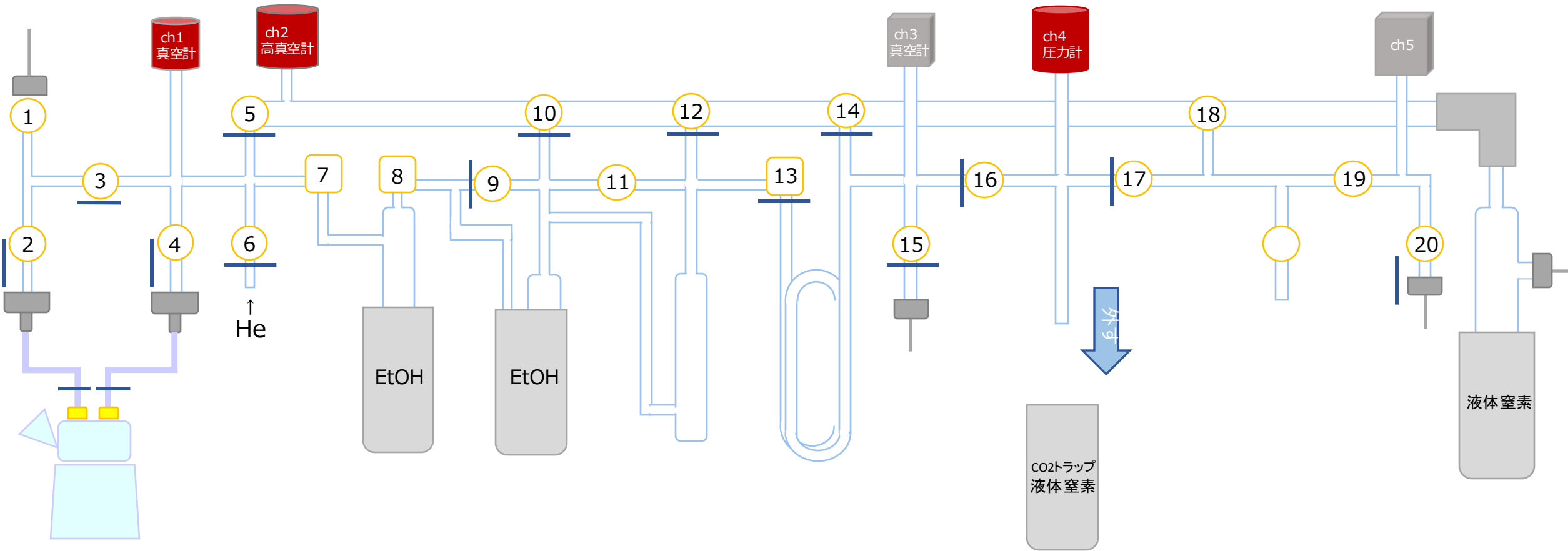
- Wait until the pressure in Ch4 reaches 0.

29. Close valve 16.

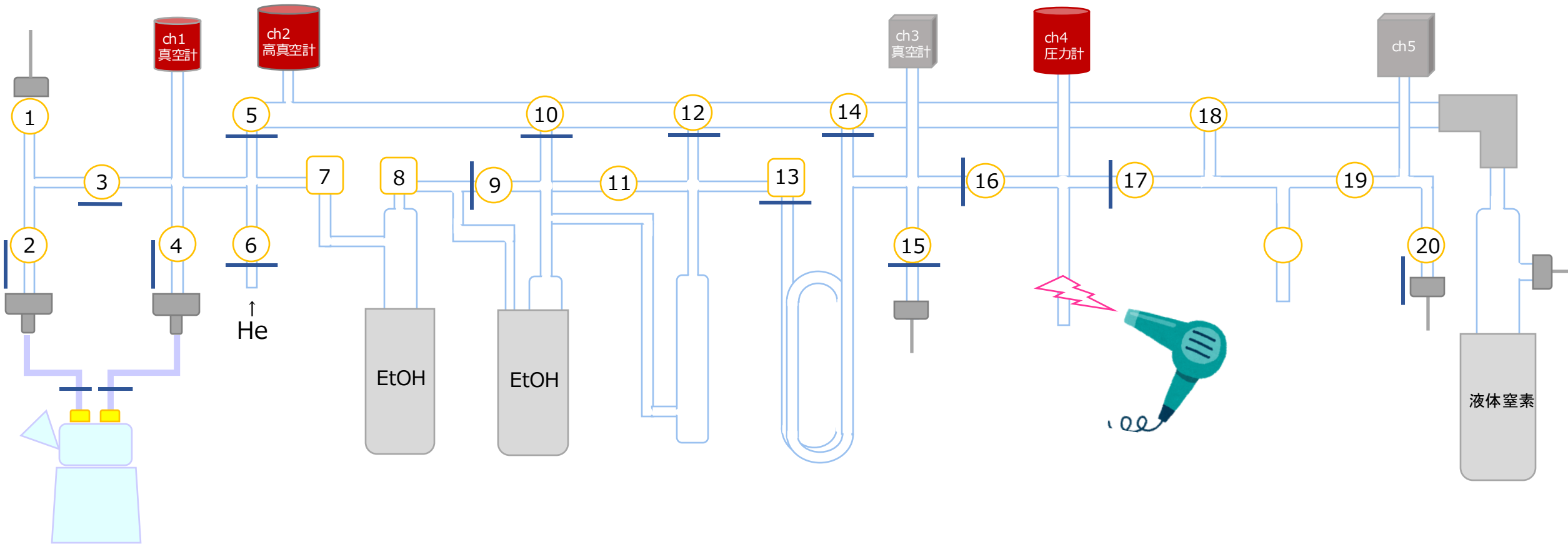
30. Remove the water trap from 13-14 and take it to the graphite line.



31. Install the ethanol dewar on the graphite line.



32. Remove the liquid nitrogen.



Memo

If there is a lot of CO₂ (>1100 mbar), adjust the gas amount by separating the gas as needed before transferring to the graphite port.

[Procedure] Close 18 and 19, then open 17 to diffuse the CO₂, etc.

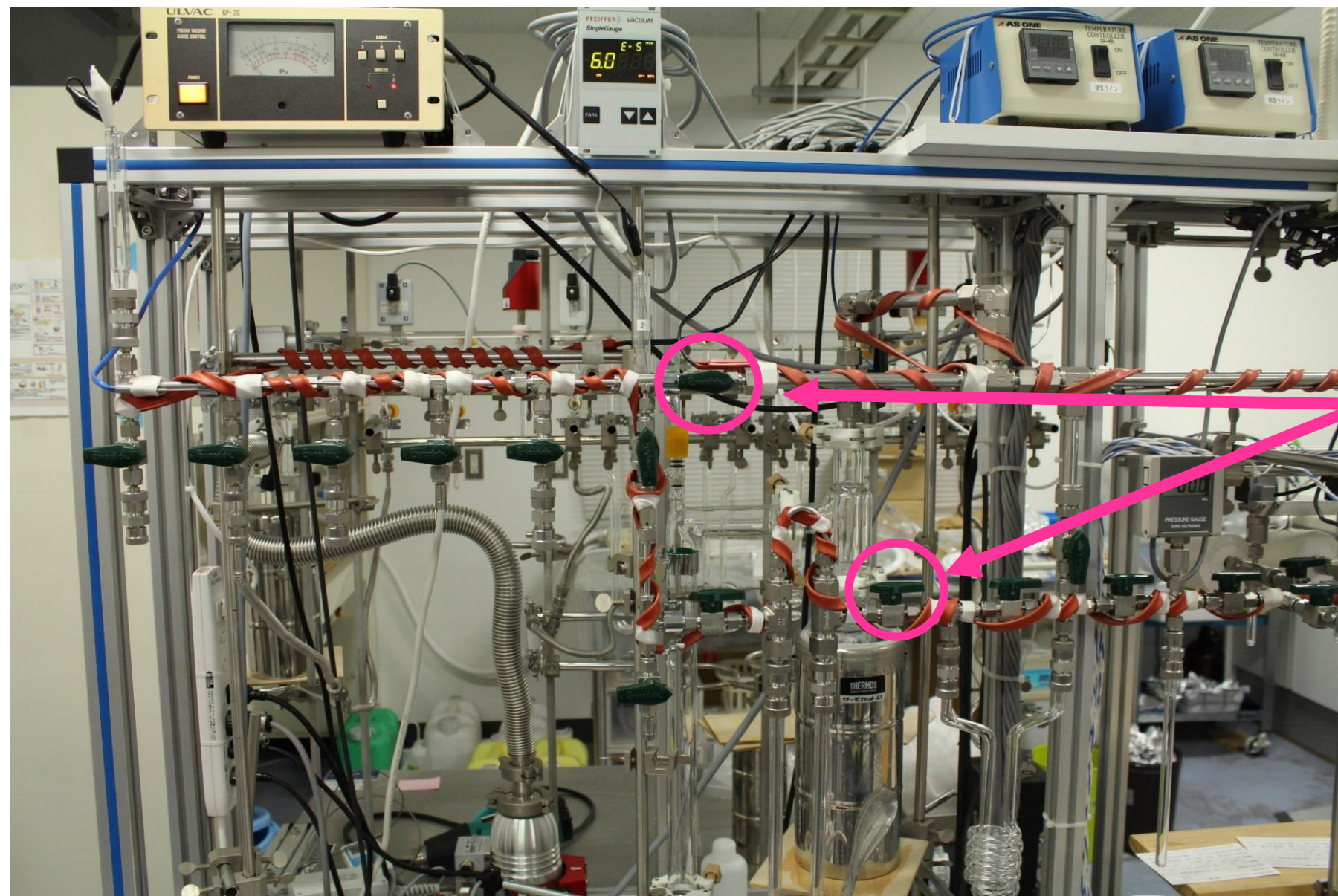
33. Melt the collected CO₂ with a dryer.

- Record the gas recovery amount for 4ch.

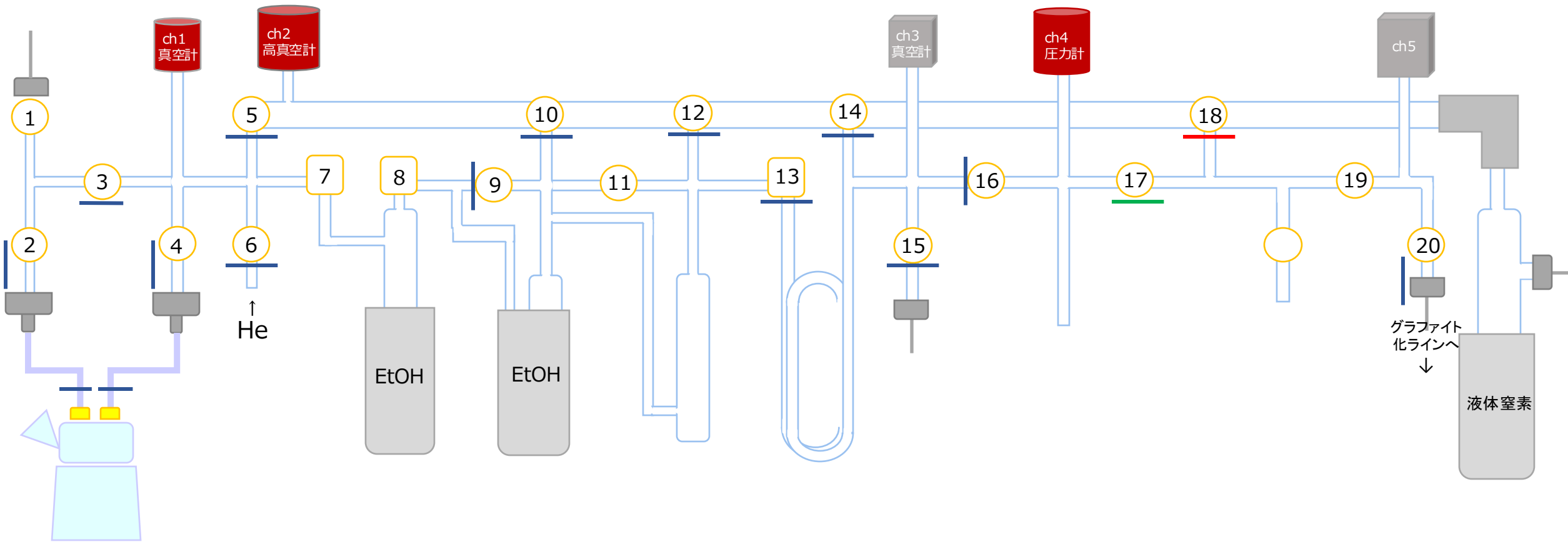
If 4ch is around 800, it's OK.

If it reaches 0, you have likely forgotten to close something.

※ The pressure gauge's display limit is 1100 mbar.
The pressure that won't damage 4ch is 3000 mbar.



34. When the pressure stabilizes around 10^{-3} to 10^{-4} , close the two valves on the graphite line to create a closed space for the high-vacuum pump.



35. Close valve 18.

36. Open valve 17.

Diffuse the carbon dioxide into the graphite line.

37. Proceed to the gas purification process (refer to a separate manual).

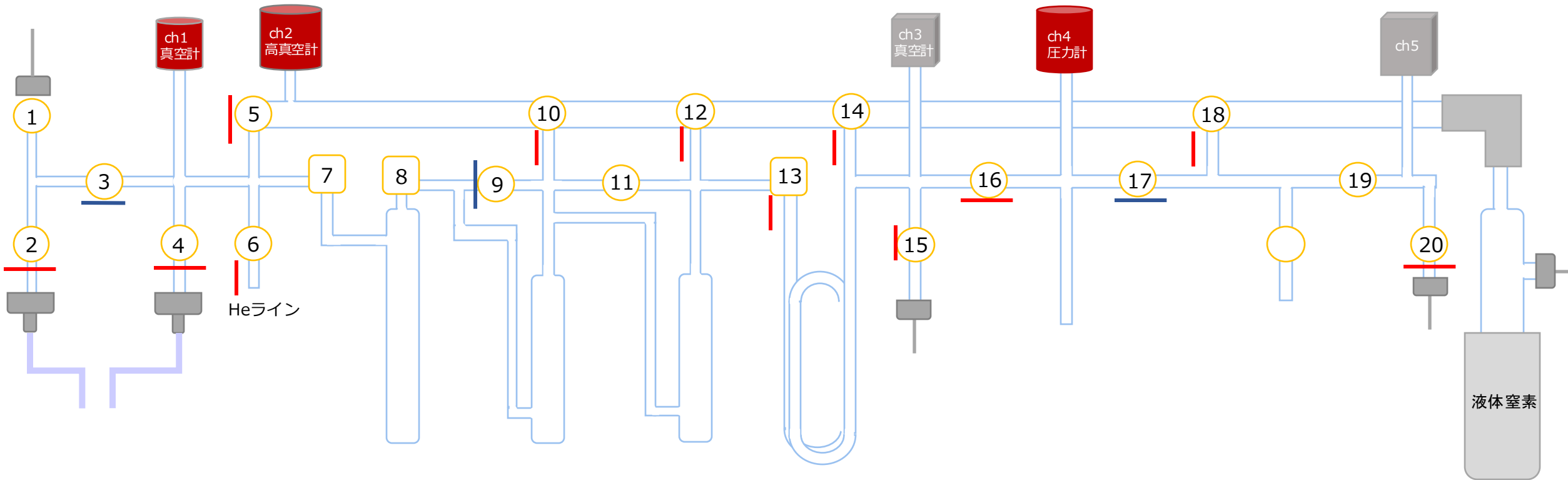
Graphitization – adding 250 hPa CO₂

1. Close VA11 & VA6
2. Put CO₂ trap (half LN₂ in small dewar) between VA5 & VA6
3. Open VA3 slowly
4. Add LN₂ (the one between VA5 & VA6) till full
5. Record “Pirani Residual Gas Pressure”
6. Open VA11 and wait till pressure drops to ~E⁻³
7. Close VA5
8. Remove CO₂ trap between VA5 & VA6
9. Heatgun tube between VA5 & VA6
 - Watch G11 → record “Monometer G11”
10. Aim at putting 250 hPa (1 mgC) ±50 of CO₂ in each sample port (VB1-VB10)
 - E.g. use magnet to open valve of sample valve → close VA6, VA10 and/or VA7 → put LN₂ under sample valve → open VA6 → wait till G11 and sample port drops to 0 hPa → remove LN₂ → heatgun to check total CO₂ amount → adjust the gas till you get 200-300 hPa of sample gas
11. Record CO₂ pressure
12. Open VA10, 7, 6, 5, 13 etc. to throw away leftover gas
13. Close the valve that connect the water line and the graphitization line
14. Next sample!

Graphitization – adding H₂

-----after finishing all samples of the day-----

1. Put LN₂ below all sample ports (do 5 ports x 2 times if you have 10 samples) and make sure the pressure drops to 0
2. Open sample valve (VB1-10) to vacuum
3. Open VA8 to vacuum
4. Wait till the pressure meter on the top left drops to below $5 \times E^{-3}$ or E^{-4}
5. Close VA6 and VA10
6. Add hydrogen gas (2 times of sample) from the one with the smallest amount
7. Close sample valve (VB1-10)



38. After use, open valves 3, 5, 6, 10, 12, 13, 14, 15, 16, 17, 18, 19 and 20 to evacuate the entire line.

***7 & 8 always open, but NEVER take off water trap**

Otherwise too much water vapor gets into the line and the vacuum might stop

***Open valves from right to left**

39. Close valves 2, 4, and 9 (always closed).

40. Remove the sample bottle.