

## Supplemental Information

### DMSO phase-change valve characterization

We investigated the effects of DMSO slug length and capillary diameter on the performance of the DMSO valves. In each case, the PTFE capillary was affixed in a straight configuration to the cooler with preloaded DMSO slug of the desired length. One end of the capillary was connected to a pressure regulator (max. output ~450 psig) connected to a nitrogen cylinder. At the other end of the capillary, downstream of the DMSO slug, another slug of DMSO colored by the Nile Red dye with length 10mm was loaded as a “monitoring slug” by syringe pump. The original position of this slug was marked on the tubing. After freezing the DMSO slug, the nitrogen pressure was increased until displacement of the monitoring slug was observed, indicating gas leakage through the DMSO valve. This pressure was recorded as the leakage pressure of the valve. The range of DMSO slug lengths tested was from 0.5 to 4.4 cm; two capillary inner diameters (0.012” and 0.020”) were tested. In each study described here, 3-5 experiments were performed for each data point.

**Figure S1** summarizes the leakage pressure as a function of DMSO slug length and capillary diameter. The figure shows that the leakage pressure increases linearly with slug length. This makes intuitive sense as the contact surface area of the DMSO with the capillary wall also increases linearly with slug length. For the same length of DMSO slugs in capillaries of two different inner diameters, the DMSO slug in the narrower capillary has a higher leakage pressure and its increase with slug length is steeper. This can be explained by the fact that the total force exerted by the nitrogen gas on the end of the frozen DMSO slug increases as the square of the capillary diameter, but the contact surface area increases only linearly with diameter of the capillary. For reference, in our demonstration batch reaction, a 0.012” ID capillary was used with a DMSO slug length of 4.4cm.

We also examined the influence of the curvature of the capillary “turns”. For a DMSO slug with the length of 2cm, we investigated bend radius from 0.8cm to  $\infty$  (i.e. straight) and found negligible effect on the leakage pressure (data not shown).

In addition to the geometric variables above, we investigated the effect of the adjacent heating on the DMSO slug stability. We used the 0.012” ID capillary with 1cm long DMSO slug, and the same setup configuration with the heater and cooler positioned 1.5 cm apart. In these experiments, after DMSO was frozen, the heaters were activated and the monitoring slug was found to move, presumably due to expansion of the air between the valve slug and monitoring slug. After the monitoring slug stabilized, its position was marked, and nitrogen was applied to the opposite side of the frozen DMSO valve. The pressure was increased until the valve leaked and caused the monitoring slug to move. It was found that the leakage pressures were almost the same when the heaters were off ( $110 \pm 25$  psig) or activated to 180°C ( $115 \pm 21$  psig), suggesting that the effect of heat conduction from adjacent heaters on DMSO valve is negligible (at least up to 180°C).

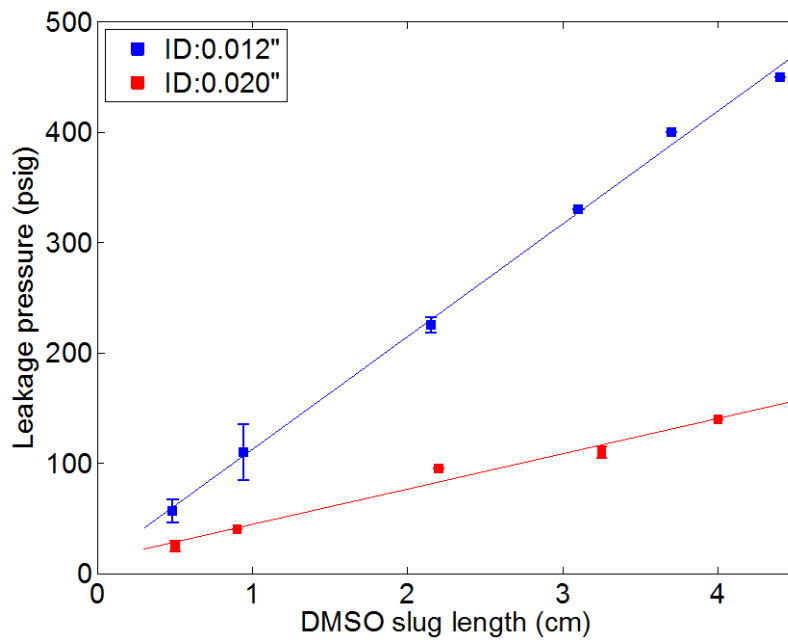


Figure S1: Influence of capillary diameter and DMSO slug length on valve performance.